PREVALENCE AND SIGNIFICANCE OF ORGANIC CONTAMINANTS AND METALS IN AQUATIC ECOSYSTEMS IN THE ETHEKWINI AREA OF KWAZULU-NATAL

Report to the
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by

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EXECUTIVE SUMMARY

BACKGROUND

Organic chemicals, including polycyclic aromatic hydrocarbons, pesticides, and polychlorinated biphenyls are routinely analysed in water, sediment and biological tissue for ecological and human health risk assessment purposes in many regions of the world. This is because these chemicals pose significant risks to ecological and human receptors when present at elevated concentrations. Many of these chemicals have a high bioaccumulation potential and, unlike metals (some organic forms excluded), also a high biomagnification potential. An important pathway of exposure to these chemicals for humans is dietary, with the consumption of fish and shellfish one of the most significant of the dietary pathways. Many organic chemicals, such as polychlorinated biphenyls, are also persistent in the environment, meaning that they retain their chemical form and have long half-lives. Because of their persistence and their toxicity the production and use of some organic chemicals has been banned or restricted under conditions of the Stockholm Convention on Persistent Organic Pollutants, to which South Africa is a signatory. Despite their banning, because of their persistence many of these chemicals continue to pose ecological and human health risks. For example, the production and use of polychlorinated biphenyls was banned in the late 1970s, yet in many parts of the world these chemicals remain a major ecological and human health concern.

In recent years there has been a significant increase in research on the prevalence and potential ecological and human health risks posed by organic chemicals in South African aquatic ecosystems. The level of attention is nevertheless far lower than in many parts of the world. For example, there are no local or national aquatic monitoring programmes that consistently monitor for chemicals such as polychlorinated biphenyls. There appear to be a number of reasons for this low level of attention in South Africa, including significant technical and human capacity constraints for organic chemical analysis and the high cost of analyses that is often considered prohibitive by public funding organisations. Also, many government agencies appear not to appreciate the significant risks that these chemicals pose to ecological and human receptors and consequently rarely stipulate the need for their monitoring. The majority of attention on organic chemicals in South Africa was historically and still is focussed on freshwater ecosystems.

South African coastal ecosystems have received comparatively little attention. There was a very strong focus on coastal pollution in the 1970s and 1980s, albeit that the focus was predominantly on metals in sediment. However, funding constraints in the late 1980s and early 1990s led to the virtual collapse of coastal pollution research and in particular research on organic chemicals. It should come as no surprise that our understanding on whether organic chemicals are widespread and significant contaminants of water, sediment and biological tissue in coastal ecosystems and whether they are cause for ecological and human health concern is virtually non-existent. Although there has been a significant increase in research on these chemicals in coastal ecosystems in the last 5-10 years, our understanding of their significance as contaminants of water, sediment and biological tissue in coastal ecosystems remains poor. This lack of understanding has important implications since coastal ecosystems, especially sheltered estuaries and embayments, are ecologically highly productive and provide numerous ecological goods and services to the benefit of the South African population. Sheltered estuaries and embayments are, however, well-known depositional zones susceptible to contaminant accumulation. Because of their use by humans for various purposes, including as a source of food (*e.g.* fish) and for recreation, exposure to contaminants accumulating in these systems represents a potentially significant source of risk to the health of human users.

OBJECTIVES AND AIMS

The overarching objective of this study was to improve our understanding on whether organic chemicals are widespread and significant contaminants of aquatic ecosystems in the eThekwini area of KwaZulu-Natal in South Africa, and, if so, to determine whether they are cause for concern from an ecological and human health risk perspective. The eThekwini area was identified as a case study for other coastal cities in South Africa, under the assumption that contamination trends evident in this city may be replicated in other coastal cities. Thus, the findings and recommendations arising from this study may be applicable to other coastal cities in South Africa. Several aims were identified to address the overarching objective.

AIM 1

Develop an understanding on whether organic chemicals are widespread and significant contaminants of sediment in aquatic ecosystems in the eThekwini area of KwaZulu-Natal, and if so determine whether they are cause for concern from an ecological risk perspective.

AIM 2

Develop an understanding on whether estuaries provide a faithful record of organic chemical inputs into the freshwater reaches of catchments, and identify at a basic level whether organic chemical concentrations in aquatic ecosystems are linked to land-use in the catchment.

AIM 3

Determine whether organic chemicals in fish and mussels in the eThekwini area of KwaZulu-Natal pose potential chronic and carcinogenic health risks to human consumers.

METHODOLOGY

Year 1

Sediment was collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2011. The systems spanned the range from highly urbanised and industrialised catchments to lightly urbanised and rural catchments. The sediment was analysed for a wide suite of physical and chemical parameters.

Year 2

Sediment was collected in three catchments wherein the sediment analysed in year 1 was identified as being the most contaminated by organic chemicals and metals, namely Durban Bay and the uMngeni and Isipingo River estuaries. The sediment was analysed for a wide suite of physical and chemical parameters.

Year 3

Fish and mussels were caught and collected in Durban Bay and the uMngeni and Isipingo River estuaries and analysed for a wide suite of physical and chemical parameters. The chemical concentrations were used for the purposes of a screening level human health risk assessment.

RESULTS AND DISCUSSION

Year 1

- Polycyclic aromatic hydrocarbons, DDX, polychlorinated biphenyls, and certain metals were frequent and in some cases significant contaminants of sediment sampled in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in September 2011.
- Polycyclic aromatic hydrocarbons were ubiquitous in sediment. The highest total polycyclic aromatic hydrocarbon concentrations were detected in sediment in rivers, estuaries and canals in the greater Durban area, that is, in catchments where the major land-use is urban and industrial. This suggests a

major proportion of the total polycyclic aromatic hydrocarbon concentration had an anthropogenic source. At the system specific level the highest total polycyclic aromatic hydrocarbon concentrations were detected in sediment in Durban Bay, the Amanzimnyama River and Island View Canal, although concentrations were relatively high at a single station in the uMngeni River estuary and a tributary of the estuary, in the Isipingo River, and below the confluence of the Umbilo and Umhlatuzana Rivers immediately prior to where these rivers discharge into Durban Bay. The Amanzimnyama River and Island View Canal discharge riverine and surface runoff into Durban Bay.

- Based on the ratio between various isomers, polycyclic aromatic hydrocarbons in sediment in the rivers, estuaries and canals sampled were diagnosed as being derived predominantly from combustion (pyrogenic) sources. Only at a few stations was there evidence for a strong petroleum or oil (petrogenic) contribution, albeit at no stations was there a dominant petrogenic source signal.
- Based on the comparison of polycyclic aromatic hydrocarbon concentrations to sediment quality guidelines derived to be protective of sediment-dwelling organisms in North American freshwater and coastal ecosystems there seems a likelihood that concentrations in sediment at some stations were posing an acute toxic risk to sediment-dwelling organisms. The greatest risk was for sediment in Durban Bay and Island View Canal, parts of the uMngeni River estuary and a tributary of the estuary, and parts of the Amanzimnyama, Umbilo/Umhlatuzana, Isipingo and Mbokodweni Rivers. The catchments of these systems are urbanised and/or industrialised. Polycyclic aromatic carbon concentrations in sediment in estuaries with lightly urbanised or rural catchments were too low to pose a risk to sediment-dwelling organisms.
- Only two organochlorine pesticides and one organophosphate pesticide were detected in sediment. DDT and its metabolites were widespread and in some cases significant contaminants of sediment in rivers, estuaries and canals. The source of the DDT is uncertain, but may include long-range atmospheric transport from malaria control areas in northern KwaZulu-Natal, where this pesticide is still used to control mosquitoes. However, this does not explain the high DDX concentrations in sediment in some systems and it is likely there are local sources of DDT to aquatic ecosystems in the eThekwini area. Chlordane was detected at a single station while chlorpyrifos was detected at four stations, three of which were situated in close proximity to one another in the uMngeni River estuary.
- Based on a comparison of pesticide concentrations to sediment quality guidelines derived to be protective of sediment-dwelling organisms in North American freshwater and coastal ecosystems there seems a likelihood that DDX in sediment at some stations was posing an acute toxic risk to sediment-dwelling organisms. The highest risk was for sediment in the uMngeni River estuary and tributaries of the estuary, and at single stations in Durban Bay and the Umhlatuzana River.
- Polychlorinated biphenyls were widespread and in some cases significant contaminants of sediment in rivers, estuaries and canals in the greater Durban area, that is, in catchments where the major land-use is urban and industrial. The highest concentrations were detected in sediment in Durban Bay, the Amanzimnyama River, and Isipingo River and its estuary. Polychlorinated biphenyls were not detected in sediment in estuaries with lightly urbanised or rural catchments.
- Based on a comparison of polychlorinated biphenyl concentrations to sediment quality guidelines derived to be protective of sediment-dwelling organisms in North American freshwater and coastal ecosystems there seems a likelihood that concentrations in sediment at some stations were posing an acute toxic risk to sediment-dwelling organisms. The highest risk was for sediment in parts of Durban Bay and the Amanzimnyama and Isipingo Rivers.
- Sediment in Island View Canal, the Amanzimnyama River and Durban Bay was most frequently and severely metal contaminated. Based on a comparison of metal concentrations to sediment quality guidelines used to regulate the disposal of dredged material in South African coastal waters there seems a likelihood that concentrations in sediment in parts of the latter systems and at isolated locations in other systems were posing an acute toxic risk to sediment-dwelling organisms.
- The mean sediment quality guideline quotient approach to estimating the potential toxicological

significance of multiple chemicals in sediment suggested that the greatest likelihood for adverse effects posed by organic chemicals to sediment-dwelling organisms was for sediment in parts of Durban Bay, Island View Canal, Bayhead Canal and the Amanzimnyama River.

- Although the comparison of chemical concentrations to sediment quality guidelines suggests the likelihood that polycyclic aromatic hydrocarbons, DDX, polychlorinated biphenyls and metals in sediment at some stations in rivers, estuaries and canals were likely posing an acute toxic risk to sediment-dwelling organisms, the magnitude and probability of the risk differed depending on which the sediment quality guidelines used to interpret the data. This creates uncertainty on whether toxic effects were likely manifesting and identifies the need for the toxicity testing or some other form of biological assessment to resolve this uncertainty.
- The most frequent and severe organic chemical and metal contamination of sediment was in rivers, estuaries and canals with densely urbanised and industrialised catchments. Sediment in rivers and estuaries with lightly urbanised or rural catchments was not contaminated. This agrees with the scientific literature and highlights the impact of catchment development on aquatic ecosystem contamination and health.

Year 2

- Polycyclic aromatic hydrocarbons, some organochlorine pesticides, polychlorinated biphenyls, and certain metals were frequent and in some cases significant contaminants of sediment sampled in Durban Bay, the uMngeni River, its estuary and tributaries of the estuary, and in the Isipingo River and its estuary in May 2012. Organophosphorous pesticides were not detected at concentrations exceeding the method detection limit.
- As was the case for the study discussed in Chapter 1, polycyclic aromatic hydrocarbons were ubiquitous in sediment. It is likely that polycyclic aromatic hydrocarbons in sediment at the majority of stations had a predominantly anthropogenic source considering that the major land-use in the catchments of each system studied is urban and industrial (albeit to varying degrees). The highest total polycyclic aromatic hydrocarbon concentrations were generally detected in sediment in Durban Bay and in rivers and canals that discharge surface runoff into the Bay, namely Island View Canal, Bayhead Canal and the Amanzimnyama River. Total polycyclic aromatic hydrocarbon concentrations in the uMngeni River catchment, and especially in the Umbilo and Umhlatuzana Rivers in the Durban Bay catchment were generally low. This said, one of the highest total polycyclic aromatic hydrocarbon concentrations was detected at a station situated in a tributary of the uMngeni River estuary, adjacent to an industrial park.
- Based on the ratio between various isomers, polycyclic aromatic hydrocarbons in sediment in the rivers, estuaries and canals sampled were diagnosed as being derived predominantly from combustion (pyrogenic) sources. Only at a few stations was there evidence for a strong or dominant petroleum or oil (petrogenic) contribution.
- Based on the comparison of polycyclic aromatic hydrocarbon concentrations to sediment quality guidelines derived to be protective of sediment-dwelling organisms in North American freshwater and coastal ecosystems there seems a likelihood that concentrations in sediment at some stations were posing an acute toxic risk to sediment-dwelling organisms. The greatest risk was for sediment in Durban Bay, Island View Canal and Bayhead Canal.
- Seventeen organochlorine pesticides and/or metabolites were detected in sediment at concentrations exceeding the method detection limit. Toxaphene was the most frequently detected pesticide, at 13 of the 54 stations sampled. However, the majority of stations where this pesticide was detected were situated in Durban Bay, alluding to a source in or near the Bay.
- Chlordane and DDX concentrations at numerous stations exceeded sediment quality guidelines derived to be protective of sediment-dwelling organisms in North American freshwater and coastal ecosystems, with the highest potential risk for DDX at two stations in the Amanzimnyama River.

- Polychlorinated biphenyls were detected in sediment collected at 24 of the 54 stations sampled. Polychlorinated biphenyls were detected in all sediment samples collected in Durban Bay and in all or the majority of samples collected in the Amanzimnyama River, Island View Canal and Bayhead Canal. The highest total polychlorinated biphenyl concentration was detected at a station in Durban Bay, situated off a stormwater outfall, closely followed by the concentration at another station in Durban Bay situated near vessel maintenance and construction facilities. Polychlorinated biphenyls were sporadically detected at low concentrations in the uMngeni River, its estuary and tributaries of the estuary, and in the Umhlatuzana and Umbilo Rivers.
- Based on the comparison of total polychlorinated biphenyl concentrations to sediment quality guidelines derived to be protective of sediment-dwelling organisms in North American freshwater and coastal ecosystems there seems a likelihood that concentrations in sediment at some stations were posing an acute toxic risk to sediment-dwelling organisms. The highest potential risk was for sediment in Durban Bay, particularly at the stations mentioned above, and in some parts of the Isipingo River.
- The most frequent and severe metal contamination of sediment was in Island View Canal, at numerous stations in Durban Bay, at one station in the Amanzimnyama River, and at two stations in a tributary of the uMngeni River estuary. Based on a comparison of metal concentrations to sediment quality guidelines used to regulate the disposal of dredged material in South African coastal waters there seems a likelihood that concentrations in sediment in parts of the latter systems and at isolated locations in other systems were posing an acute toxic risk to sediment-dwelling organisms.
- The mean sediment quality guideline quotient approach to estimating the potential toxicological significance of multiple chemicals in sediment suggested that the greatest likelihood for adverse effects posed by organic chemicals to sediment-dwelling organisms was for sediment in some parts of Durban Bay, Island View Canal, Bayhead Canal and the Amanzimnyama River.
- As mentioned previously, polycyclic aromatic hydrocarbons were ubiquitous in sediment in both surveys, although the concentrations differed slightly between surveys. The trend in polychlorinated biphenyl contamination of sediment was also comparable between surveys. Although DDT and its metabolites were widespread and significant contaminants of sediment in both surveys, there was a relatively large difference in the frequency of detection between surveys and, importantly, the contribution of technical DDT to the DDX concentration differed. Chlordane was more frequently detected in the survey performed in 2012. The general consistency of trends in contamination of sediment by these chemicals implies it is not necessary to monitor for these chemicals in sediment annually, but surveys could be performed every three to four years to determine whether there is any change in the magnitude and frequency of contamination.
- Polycyclic aromatic hydrocarbon concentrations in sediment collected in rivers, estuaries and canals in the eThekwini area in 2011 and 2012 were generally higher compared to concentrations reported for other areas of South Africa. DDX concentrations in sediment were generally comparable to concentrations reported for other areas of South Africa, with the exception of very high concentrations in sediment collected at two stations in the Amanzimnyama River. Total polychlorinated biphenyl concentrations in sediment were generally comparable to concentrations reported for other areas of South Africa. However, more congeners were analysed than in comparator studies, making direct comparison of the data difficult.
- A relatively small proportion of polycyclic aromatic hydrocarbon concentrations in sediment collected in rivers, estuaries and canals in the eThekwini area in 2011 and 2012 were 'high' by international standards. However, a large proportion of the concentrations exceeded the median concentration reported in international studies.
- Although chlordanes were sporadically detected in sediment collected in rivers, estuaries and canals in the eThekwini area in 2011 and 2012, the concentrations were high compared to concentrations reported for many studies in other parts of the world, with many of the concentrations falling within the 90th percentile of the concentration distribution. Numerous DDX concentrations fall in the upper part of

the range reported for studies in reported in international studies, with the concentrations in sediment at two stations in the Amanzimnyama River being the 7th and 8th highest. Although endosulfans were only detected in sediment at one station in the 2012 survey, the concentration was the second highest reported for any comparative international study. Toxaphene concentrations at four stations far exceed the highest concentration reported for comparative international studies, while concentrations at several other stations fall near the upper part of the range for comparator studies.

- Polychlorinated biphenyl concentrations in some sediment samples collected in rivers, estuaries and canals in the eThekwini area in 2011 and 2012 were 'high' by international standards, albeit that these are well below the extremely high concentrations reported in some comparator studies.
- Although the comparison of chemical concentrations to sediment quality guidelines suggests the likelihood that polycyclic aromatic hydrocarbons, DDX, chlordanes, polychlorinated biphenyls and metals in sediment at some stations in rivers, estuaries and canals were likely posing an acute toxic risk to sediment-dwelling organisms, the magnitude and probability of the risk differed depending on which the sediment quality guidelines used to interpret the data. This creates uncertainty on whether toxic effects were likely manifesting and identifies the need for the toxicity testing or some other form of biological assessment to resolve this uncertainty.
- Toxicity testing of sediment using the H4IIE cell bioassay suggested that polycyclic aromatic hydrocarbon and polychlorinated biphenyl concentrations in sediment at numerous stations sampled in rivers, estuaries and canals in the eThekwini area were high enough to suspect they were posing a toxicological risk to sediment-dwelling organisms. An important finding was that toxicity testing and estimates of risk posed by contaminants in sediment using sediment quality guidelines were weakly correlated.

Year 3

- Fish caught and mussels collected in Durban Bay and in the uMngeni and Isipingo River estuaries in 2013 had accumulated polycyclic aromatic hydrocarbons, DDX and polychlorinated biphenyls in their tissue, while one fish species in Durban Bay had also accumulated a very low concentration of dieldrin in its tissue.
- The suite of organic chemicals detected in the tissue of fish and mussels generally reflected the suite of chemicals detected in sediment within the catchment of each system studied. A notable exception was chlordane, which was detected in sediment at one station in 2011 and relatively frequently in 2012, but was never detected in the tissue of fish and mussels. As stated above, dieldrin was detected in the tissue of a single fish species but was never detected in sediment. The fish and mussels sampled were thus suitable sentinels for organic contaminant monitoring in the catchments of Durban Bay and uMngeni and Isipingo River estuaries.
- Copper, chromium, manganese, mercury, lead and zinc were accumulated to above background concentrations by mussels at most or all collection locations in Durban Bay. Each of these metals apart from manganese are widespread and in some cases significant contaminants of sediment in Durban Bay. However, cadmium and nickel are also widespread and/or significant contaminants of sediment in Durban Bay, yet there was no evidence that mussels in the Bay had accumulated these metals to higher than background concentrations. In fact, mussels in Durban Bay typically had lower cadmium and nickel concentrations in their tissue compared to mussels collected along the eThekwini shoreline.
- Metal concentrations in fish were, with some exceptions, broadly comparable between species and between fish in the different systems studied. The notable exceptions were *Sillago sihama*, which accumulated arsenic to far higher concentrations than other fish species, the ambassids *Ambassis gymnocephalus* and *Ambassis natalensis*, which had various metals present in their tissue at considerably higher concentrations compared to other fish, and for mercury, which was generally present at higher concentration in the tissue of fish in Durban Bay compared to the uMngeni and Isipingo River estuaries.

- The small, shoaling ambassids *Ambassis gymnocephalus* and *Ambassis natalensis* had accumulated higher concentrations of numerous chemicals in their tissue compared to other fish species and may prove to be useful sentinel species for identifying whether metals and organic chemicals are likely to be accumulating in sediment in estuaries and in the tissue of larger estuarine fish that are consumed by recreational and subsistence fishers. If so, this will considerably reduce monitoring costs as these fish are typically more abundant and far easier to catch compared to larger fish species, which are typically analysed for such studies.
- The concentrations of some chemicals in the tissue of fish and mussels caught or collected in Durban Bay and the uMngeni and Isipingo River estuaries were high by international standards, although direct comparison of data to international studies should be treated with caution because of different analytical methods used, different suites of chemicals analysed (*e.g.* number of polychlorinated biphenyl congeners), and different species and/or sizes of fish analysed.
- The finding that fish and mussels had accumulated contaminants in their tissue is important as it confirms that various metals, polycyclic aromatic hydrocarbons, polychlorinated biphenyls and DDX were in a bioavailable form in each of the systems studied and may thus be posing a toxic risk to other fauna, including sediment-dwelling organisms, organisms that are regularly in close contact with sediment, and piscivorous birds and otters amongst others.
- Recreational and subsistence fishers that consume fish and mussels caught or collected in Durban Bay and the uMngeni and Isipingo River estuaries face potential carcinogenic and non-carcinogenic health risks due to exposure to contaminants accumulated by these organisms. The most significant risks are for recreational and subsistence fishers that consume fish and mussels caught or collected in Durban Bay, which agrees with the more widespread and significant contamination of sediment in the Bay and in its catchment.
- Although there are limitations and uncertainties associated with the risk assessment component of this study, it is nevertheless recommended that recreational and subsistence fishers restrict the number of meals of fish and mussels they consume each month because of the potential risks associated with exposure to chemicals these organisms have accumulated in their tissue. Infants and children under 12 years age, and females that are pregnant, intending to become pregnant or are nursing, should restrict consumption of fish and mussels caught or collected in each of the systems studied to below the meal limits recommended in this study.
- There are numerous health benefits associated with the consumption of fish and shellfish. Thus, while recreational and subsistence consumers should be warned against eating certain fish caught and mussels collected in Durban Bay and the uMngeni and Isipingo River estuaries, they should not be advised to limit fish consumption altogether but to consume fish caught in other estuaries in the eThekwini area, or fish purchased in retail stores.

CONCLUSIONS

This overarching objective of this study was to improve the understanding on whether polycyclic aromatic hydrocarbons, polychlorinated biphenyls, and organochlorine and organophosphorous pesticides are widespread and significant contaminants of sediment and biological tissue in aquatic ecosystems in the eThekwini area of KwaZulu-Natal, and if so, to determine whether they are cause for concern from an ecological and human health risk perspective. The eThekwini area was used as a case study, under the assumption that contamination trends evident in this large coastal city may be replicated in other coastal cities. The findings and recommendations arising from this study may thus be applicable to other coastal cities in South Africa.

The findings showed that polycyclic aromatic hydrocarbons, polychlorinated biphenyls, and DDT and metabolites were widespread and at times significant contaminants of sediment in rivers, estuaries and canals in the eThekwini area. Chlordanes were less frequent, but often significant contaminants of

sediment in the survey performed in 2012. At numerous stations, specifically in catchments that are urbanised and industrialised, the magnitude of contamination was sufficient to suspect these chemicals were posing an acute toxic risk to sediment-dwelling organisms. This conclusion was through the comparison of contaminant concentrations to sediment quality guidelines. Although toxicity testing using the H4IIE cell bioassay confirmed toxicity in some sediment samples, there was often only a weak correlation between contaminant concentrations and toxicity. Confirmation of the potential toxic risk posed by the organic chemicals, but particularly polychlorinated biphenyl, was provided by the analysis of contaminant concentrations in the tissue of fish caught and mussels collected in Durban Bay and in the uMngeni and Isipingo River estuaries. This showed that contaminant concentrations in many fish species and in mussels were high enough to pose a potential chronic and carcinogenic health risk to human consumers (and by implication other organisms). This finding has important implications in that it calls for the more frequent monitoring of contaminant monitoring in fish and shellfish and the communication of the findings to recreational and subsistence fishers. Commissioning such monitoring and communicating the findings will largely be the responsibility of local municipalities and/or provincial government departments, and budgets need to be allocated for this purpose.

The findings of this study motivate for similar studies in other coastal cities. Of particular concern in the eThekwini area was the widespread and at times significant contamination of sediment by polychlorinated biphenyls and the accumulation of these chemicals in the tissue of fish and mussels. Polychlorinated biphenyls are highly toxic and pose significant ecological and human health risks. Based on this finding, in the eThekwini area at least there is need for the routine monitoring of these contaminants in aquatic monitoring programmes. Whether similar problems exist in coastal cities in South Africa is unknown.

Although not discussed in this report a collaborative study by the CSIR and Virginia Institute of Marine Sciences on sediment samples collected for the survey discussed in Chapter 1 identified significant and widespread brominated flame retardant contamination of sediment in the eThekwini area (La Guardia *et al*., 2013; see Appendix 1). In fact, brominated flame retardant concentrations in some systems rival those in the Pearl River Delta area of China, where a significant proportion of the world's demand for flame retardants is met, and exceed concentrations in parts of the United States of America (La Guardia *et al*., 2013). Brominated flame retardants are persistent, bioaccumulative and lipophilic, with the result that they may pose similar ecological and human risks to polychlorinated biphenyls. However, little is known on whether brominated flame retardants are widespread and significant contaminants of sediment and biological tissue in South African coastal ecosystems, a situation that warrants further attention.

This study has provided evidence for significant sources of organic and metal contaminants to aquatic ecosystems in the Durban Bay catchment. Inflows from the Amanzimnyama River, Island View Canal, Bayhead Canal, and numerous stormwater outfalls are important vectors for the introduction of contaminants to Durban Bay. There is also evidence that certain port activities are significant sources of contaminants to the Bay. The sources of contaminants need to be identified, controlled and reduced if there is to be any improvement in water and sediment quality in Durban Bay. This will reduce the uptake of contaminants by fish, shellfish and other biota, and thereby reduce potential health risks posed by contaminants in fish and shellfish to human consumers. An Estuarine Management Plan for Durban Bay has been formulated and is in the process of being updated. The plan recognises the need for a catchment scale approach to the sustainable management of the Bay. The findings of this study can be incorporated into the Estuarine Management Plan and used to identify and prioritise areas of the catchment where contaminant source identification, reduction and control procedures should be implemented.

RECOMMENDATIONS

- Based on the findings of this study, it is recommended that similar studies be performed in other cities along the South African coastline. This will inform whether the trends in metal and organic chemical contamination of sediment and the accumulation of organic chemicals by fish and shellfish in the eThekwini area is also relevant to these cities. These studies should be used to inform whether metals and organic chemicals should be routinely analysed in sediment, fish and shellfish as part of aquatic monitoring programmes. The ultimate purpose of these studies should be to inform whether and what management intervention is required to control and reduce the sources of contaminants to coastal aquatic ecosystems.
- Polycyclic aromatic hydrocarbons were ubiquitous in sediment in the eThekwini area, and in catchments where the predominant land-use is urban or industrial were likely to have been predominantly derived from anthropogenic sources. Based on the scientific literature it seems inevitable this ubiquity will apply to other cities along the South African coastline, and indeed also inland cities. It is recommended, therefore, that polycyclic aromatic hydrocarbons should routinely be analysed in sediment as part of aquatic monitoring programmes in urbanised and industrialised areas. Municipal authorities should make allowance in budgets for such monitoring. In this context, it is strongly recommended that both parent and alkylated polycyclic aromatic hydrocarbons should be analysed, to facilitate source tracking. However, analysing for alkylated polycyclic aromatic hydrocarbons has significant cost implications and the decision on whether to analyse for these hydrocarbons should be made on a case by case basis.
- There are significant sources of polychlorinated biphenyls in highly urbanised and industrialised catchments in the eThekwini area, as reflected in concentrations of these chemicals analysed in sediment for this study. A more comprehensive assessment of the spatial extent and magnitude of contamination of sediment by these chemicals should be performed, for the purpose of source identification, reduction and control. In this context, all 209 possible congeners should be analysed. However, recognising that analyses for all possible 209 congeners is expensive, particularly for routine monitoring, this study should concurrently evaluate the efficacy of using enzyme-linked immunosorbent assay (ELISA) tests as a rapid screening tool for polychlorinated biphenyls in South Africa. This is because ELISA testing is far cheaper than instrumental analysis.
- Although the use of sediment quality guidelines as a tool for assessing sediment quality has numerous limitations (see discussion this report), sediment quality guidelines provide a useful tool for screening contaminant concentrations in sediment so as to prioritise sites that require further attention (*e.g.* through biological assessment). There are sediment quality guidelines for organic chemicals in South African freshwater and coastal ecosystems, and the only metal guidelines are those used for determining whether sediment identified for dredging in South African ports is of a suitable quality for openwater disposal. Because of this lack of sediment quality guidelines there is no consistency in the use of international sediment quality guidelines by South African researchers. There is, therefore, a need to define sediment quality guidelines for freshwater and coastal ecosystems in South Africa. The guidelines should preferably be derived using co-occurring data on sediment contaminant concentrations, sediment toxicity, and benthic invertebrate community structure and composition. However, as no sediment toxicity testing procedures have been defined for South African freshwater and coastal ecosystems (see below), and generating such data will be both time consuming and expensive, as an interim measure it will be necessary to adopt international sediment quality guidelines for both metals and organic chemicals. However, it is likely that international sediment quality guidelines will not be appropriate to South African freshwater ecosystems, due to differences in the geology of sediment parent material. Sediment quality guidelines should thus only be defined after baseline concentrations for toxicologically significant metals in sediment have been defined for freshwater ecosystems in different areas of South Africa. There is, therefore, an urgent need to define baseline concentrations to toxicologically significant metals in South African freshwater ecosystems. It is

further recommended that the Water Research Commission, in partnership with relevant local and national government departments (*e.g.* the Department of Environmental Affairs) establish a working group that is mandated with identifying water and sediment quality guidelines for organic chemicals, and subsequently for metals once baseline concentrations for different areas of South Africa have been defined. This working group should also be mandated with identifying research priorities in this context.

- Although the chemical analysis of sediment can be used to identify whether sediment is contaminated, a significant limitation is that this does not provide an understanding on whether the contaminants are in a bioavailable form. This is important since contaminants can only exert a toxic effect if they are in a bioavailable form, that is, in a form that can cross biological membranes. In this study, although concentrations of several organic contaminants exceeded sediment quality guidelines and were thus identified as cause for concern, it is unknown whether these were actually exerting a toxic effect. It is also uncertain whether other potential contaminants that were not measured may have been causing toxicity. There is, therefore, a need for the development and validation of whole sediment toxicity testing procedures for freshwater and coastal ecosystems in South Africa, as a tool for determining whether contaminants in sediment are exerting a toxic effect on sediment-dwelling organisms.
- The concentrations of several chemicals in the tissue of fish caught and mussels collected in Durban Bay and the uMngeni and Isipingo River estuaries were high enough to pose a potential risk to the health of human consumers. The most notable were polychlorinated biphenyls and mercury. Since it was never the intent of this study to perform a comprehensive human health risk assessment, it is recommended that a comprehensive risk assessment be performed. This study should focus on the analysis of at least ten individuals of target species, which should include species that are commonly consumed by recreational and subsistence fishers in addition to ambassids (see below). Analysing ten individuals represents a compromise between a sufficient sample size to allow an estimate of variability in contaminant accumulation between individuals and the costs of sample analysis. However, because subsistence consumers are likely to retain fish of a range of sizes it is recommended that for the two to three most commonly consumed fish species the relationship between tissue contaminant concentrations and fish size be assessed. The suite of analytes targeted should include those recommended by the United States Environmental Protection Agency. However, such analyses will be extremely expensive and it may be worthwhile to restrict analyses at the outset to polychlorinated biphenyls, mercury and toxaphene. In this context, all possible 209 polychlorinated biphenyl congeners in addition to Aroclors should be analysed.
- A key unknown in the context of determining the potential human health risk posed by contaminants in fish and shellfish tissue are fish and shellfish consumption rates for South African recreational and subsistence fishers. Default consumption rates for the population of the United States of America were thus used. Although these probably encompass consumption rates for the South African population, this is unknown. It is thus recommended that a survey of fish and shellfish consumption rates for recreational and subsistence consumers in the eThekwini area of KwaZulu-Natal be performed. This study should also determine the how long recreational and subsistence have fished in Durban Bay, whether these fishers are aware of the risk posed by contaminants in fish and shellfish to their health, and whether their consumption patterns are likely to change knowing that contaminants in fish and shellfish in the Bay pose a potential risk to their health. This study is important since fish caught in local estuaries are evidently an important source of protein for economically marginalised sections of the population, yet there is a distrust that any advice against the eating of fish because they pose a health risk is to restrict the catching of fish by these fishers.
- Based on the findings of this study there is a possibility that recreational and subsistence consumers in other large coastal cities may also face potential health risks through the consumption of fish and shellfish caught and collected in estuaries and indeed also the freshwater reaches of catchments. It is, therefore, recommended that the potential risk of exposure to contaminants through a fish and shellfish consumption pathway be extended to other large coastal cities. In fact, a comprehensive assessment of

the risks posed by contaminants in fish and mussels in coastal cities should be performed annually, or at least every two years. The resultant information should be communicated to recreational and subsistence fishers, to enable them to make an informed decision on whether to continue catching and consuming fish in contaminated coastal ecosystems.

- This study has highlighted the potential use of small, forage fish (specifically ambassids) as sentinels for contaminant monitoring in South African estuaries, based on the fact that they accumulated numerous contaminants in their tissue to high concentrations. Also, these fish are abundant and far easier to catch compared to other fish, which will reduce the costs associated with fish collection. It is recommended that a study that compares concentrations of chemicals in the tissue of ambassids and larger fish between putatively contaminated and uncontaminated estuarine ecosystems in the eThekwini area of KwaZulu-Natal be performed, as a case study on the potential use of these fish as sentinels for contaminant monitoring. The study should aim to resolve whether ambassids naturally accumulate higher metal concentrations in their tissue compared to other fish, particularly fish that are frequently consumed. The relationship between chemical concentrations in the tissue of ambassids and larger commonly consumed fish should be explored to determine whether concentrations in ambassids can be used to predict likely concentrations in larger, commonly consumed fish. The study should also investigate the importance of small, forage fish as a vector for the transfer of contaminants through estuarine food webs, including to higher trophic level organisms such as birds.

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CHAPTER 1: GENERAL INTRODUCTION

Organic chemicals, including polycyclic aromatic hydrocarbons, pesticides and polychlorinated biphenyls, are routinely analysed in water, sediment and biological tissue for ecological and human health risk assessment purposes in many parts of the world. This is because these chemicals pose significant risks to ecological and human receptors when present at elevated concentrations (*e.g.* Jobling *et al*., 2002; Burreau *et al*., 2004; Alexander *et al*., 2007; Stahl *et al*., 2009; Blocksom *et al*., 2010). Many of these chemicals have a high bioaccumulation potential and, unlike metals (some organic forms excluded), also a high biomagnification potential. In other words, concentrations of these chemicals increase through the food web, usually reaching highest concentrations in (fatty tissue of) apex predators. An important pathway of exposure to these chemicals in humans is dietary, with the consumption of fish and shellfish being one of the most significant of the dietary pathways. Many organic chemicals, such as polychlorinated biphenyls, are also persistent in the environment, meaning they retain their chemical form and have long half-lives. Because of their persistence and their toxicity, the production and use of some organic chemicals has been banned or restricted under conditions of the Stockholm Convention on Persistent Organic Pollutants, to which South Africa is a signatory.

In recent years there has been a significant increase in research on the prevalence and potential ecological and human health risks posed by organic chemicals in South African aquatic ecosystems. The level of attention is nevertheless far lower than in many parts of the world. There appear to be a number of reasons for this low level of attention in South Africa, including significant technical and human capacity constraints for organic chemical analyses, and the high cost of analyses. Also, many government agencies appear not to appreciate the significant risk that these chemicals pose to ecological and human receptors and consequently rarely stipulate the need for their monitoring. The majority of attention on organic chemicals in South Africa was historically and still is focussed on freshwater ecosystems (*e.g.* Hassett *et al*., 1987; Weaver, 1993; Schulz *et al*., 2001; Awofolu and Fatoki, 2003; Dalvie *et al*., 2003; Sibali *et al*., 2008; Quinn *et al*., 2009; Nieuwoudt *et al*., 2009; Quinn *et al*., 2013). There are good reasons, including that agricultural practices are important sources of pesticides and the industrial and economic heartland of South Africa, where many of these chemicals had and still have application is situated far from the coast. Furthermore, research scientists that have played an important role in identifying the significance of these chemicals as contaminants of aquatic ecosystems and the ecological and human health risks they pose are based at institutions situated far from the coast (*e.g.* CSIR in Pretoria, North-West University, University of Johannesburg, University of Pretoria). Studies on freshwater ecosystems in South Africa have identified a wide range of organic chemicals that are contaminants of water, sediment and biological tissue, including human tissue, and have alluded to the ecological and human health risks they pose (*e.g.* Bouwman *et al*., 1990; Schulz *et al*., 2001; Bouwman *et al*., 2008; Polder et al., 2008; Sibali *et al*., 2008, Barnhoorn *et al*., 2009, 2010; Bornman *et al*., 2010; Bouwman *et al*., 2012; Wepener *et al*., 2012; Quinn *et al*., 2013).

South African coastal ecosystems have received comparatively little attention. There was a very strong focus on coastal pollution in the 1970s and 1980s, albeit that the focus was predominantly on metals in sediment. However, funding constraints in the late 1980s and early 1990s led to the virtual collapse of coastal pollution research and in particular research on organic chemicals. It should come as no surprise that our understanding on whether organic chemicals are widespread and significant contaminants of water, sediment and biological tissue in coastal ecosystems and whether they are cause for ecological and human health concern is virtually non-existent. Although there has been a significant increase in research on these chemicals in coastal ecosystems in the last 5-10 years (*e.g.* Schlenk *et al*., 2005; Vosloo and Bouwman, 2005; Bollmohr *et al*., 2007, 2008, 2009; Roos *et al*., 2011), our understanding of their significance as contaminants of water, sediment and biological tissue in these ecosystems remains poor. This lack of understanding has important implications since coastal ecosystems, especially sheltered estuaries and embayments, are ecologically highly productive and provide numerous ecological goods and

services to the benefit of the South African population. Sheltered estuaries and embayments are, however, well-known depositional zones susceptible to contaminant accumulation. Because of their use by humans for various purposes, including as a source of food (*e.g.* fish) and for recreation, exposure to contaminants accumulating in these systems represents a potentially significant source of risk to the health of human users.

The overarching objective of this study was to improve our understanding on whether organic chemicals are widespread and significant contaminants of aquatic ecosystems in the eThekwini area of KwaZulu-Natal in South Africa, and, if so, to determine whether they are cause for concern from an ecological and human health risk perspective. The eThekwini area was identified as a case study for other coastal cities in South Africa, under the assumption that contamination trends evident in this city may be replicated in other coastal cities. Thus, the findings and recommendations arising from this study may be applicable to other coastal cities in South Africa. Several aims were identified to address the overarching objective, including developing an understanding on whether estuaries provide a faithful record of organic contaminant inputs into the freshwater reaches of catchments, and the identification at a basic level on whether the extent and magnitude of sediment contamination is linked to land-use in catchments.

The first of these aims was identified for several reasons. First, sampling in the riverine reaches of catchments can be challenging, particularly in urbanised and industrialised areas since gaining waterside access is often difficult. Even if waterside access is possible it is often difficult to collect sediment in a river if it is not of a wadeable type, since access by vessel is difficult or hazardous. Second, the travel time between sampling points in an urban setting can be significant, even though the distance between sampling points may be relatively short. Thus, the cost implications of monitoring rivers in urban settings can be significant. Lastly, fine-grained sediment, which is the predominant sink for contaminants in aquatic ecosystems, may be patchily distributed and seasonally variable in rivers depending on the prevailing hydrology, potentially resulting in variable contaminant concentrations. If contaminant concentrations are temporally and spatially highly variable and sampling in rivers does not take into account of adequately capture this variability, then the findings may not highlight the need for contaminant source identification and control when this is in fact necessary. Although sampling in estuaries presents logistical challenges these generally pale in significance compared to sampling in rivers. Since sediment in estuaries is usually dominated by fine-grained material because of the depositional nature of this environment, the probability for contaminant accumulation in estuaries is high. Also, the behaviour of many chemicals changes between fresh and saline water. This leads to the so-called salting-out of contaminants and other materials in estuaries. It should theoretically, therefore, be possible to develop an understanding on whether certain classes of contaminants are being introduced into the riverine reach of a catchment and the relative importance of contaminant input by measuring their presence in the estuarine reach. If so, then the focus on the freshwater reach can be restricted to catchments identified as problematic based on the findings for the estuarine reach. The cost implications of this rationalised focus are self-evident. While this approach is theoretically sound, potential limitations are that estuaries are of a depositional nature and excessive deposition of sediment may smother and dilute traces of contaminants introduced into the freshwater reach. Also, there may be significant sources of contaminants directly to the estuarine and not freshwater reach of a catchment. An aim of this study was thus to identify whether there is congruence between organic contaminant profiles in the freshwater and estuarine reaches of catchments in the eThekwini area.

As stated previously, many organic chemicals pose significant ecological and human health risks. However, whether these chemicals are present in South African coastal ecosystems at concentrations that are of ecological and human health concern is uncertain, because of the previously mentioned lack of understanding on prevalence and concentrations of these chemicals in coastal ecosystems. A further aim of this study was thus to determine whether these chemicals are present in aquatic ecosystems in the eThekwini area of KwaZulu-Natal at concentrations that pose ecological and human health risks.

Although not a specific aim, this study demonstrates South Africa's commitment to one of the conditions of the Stockholm Convention on Persistent Organic Pollutants, by performing research in this field, and provides information on which to assess the significance of chemicals included in this convention from a South African perspective

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CHAPTER 2: POLYCYCLIC AROMATIC HYDROCARBON, PESTICIDE, POLYCHLORINATED BIPHENYL AND METAL CONTAMINATION OF SEDIMENT IN RIVERS, ESTUARIES AND CANALS IN THE ETHEKWINI AREA OF KWAZULU-NATAL

2.1 INTRODUCTION

At the outset of this study it was unknown whether polycyclic aromatic hydrocarbons, polychlorinated biphenyls and pesticides were widespread or significant contaminants of sediment in aquatic ecosystems in the eThekwini area of KwaZulu-Natal. The decision was thus made to first perform a screening study on the magnitude and extent of contamination of sediment by these chemicals in the study area. The rationale was this would provide the focus for a more comprehensive assessment of catchments where sediment was identified as most frequently and/or severely contaminated, to address certain study aims, and if contamination was not identified as widespread or significant to then decide whether a comprehensive assessment was in fact necessary. The primary aim for the study discussed in this chapter was therefore to perform a screening study on the spatial extent and magnitude of contamination of sediment in rivers, estuaries and canals in the eThekwini area by polycyclic aromatic hydrocarbons, polychlorinated biphenyls and pesticides. Although not target analytes, the sediment samples were also analysed for metals through a CSIR funded study and for brominated flame retardants through a study jointly funded by the CSIR and Virginia Institute of Marine Science. The findings of metal analyses of sediment are discussed in this report. The findings of brominated flame retardant analyses of sediment are provided in La Guardia *et al.* (2013) (see Appendix 1 for publication abstract).

The rationale for the focus on sediment is that polycyclic aromatic hydrocarbons, polychlorinated biphenyls and pesticides are typically hydrophobic and particle reactive and thus preferentially partition to and accumulate in sediment. The concentrations of these contaminants in sediment are thus usually substantially higher than concentrations in the overlying water column, and it is not uncommon for water quality to be classified good based on the comparison of contaminant concentrations to water quality guidelines but for sediment quality to be classified poor based on a similar comparison to sediment quality guidelines.

2.2 EXPERIMENTAL

2.2.1 Sampling design

Surface sediment (upper 5-10 cm) was the focus of attention since this is the biologically active zone and provides a record of the most recent chemical contamination, as opposed to deeper sediment that may represent historical contamination depending on the hydrological regime of the system of concern. The majority of sediment samples were collected from bridges spanning rivers, estuaries and canals and, with the exception of some estuaries where a vessel was used to collect samples, constrained this component of the sampling design to areas in catchments where bridges crossed rivers, estuaries and canals. The original intent was to collect sediment samples in August 2011, at the end of the dry season as this was expected to maximise the potential accumulation of contaminants in sediment. However, un-seasonally high rainfall resulted in flood-like conditions a few weeks prior to sampling and sampling was delayed for about one month. Thus, in September 2011 a total of 49 sediment samples were collected in 12 catchments with land-use patterns that spanned the range from rural to highly urbanised and industrialised (Figure 1.1). Sampling was, however, strongly biased to catchments in the greater Durban area, the majority of which are characterised by highly urbanised and/or industrial land-use. Single sediment samples were collected in the estuarine reaches of four catchments situated to the north and four catchments to south of the greater Durban area. Land-use within these catchments is rural or light urban. In other catchments sampling station

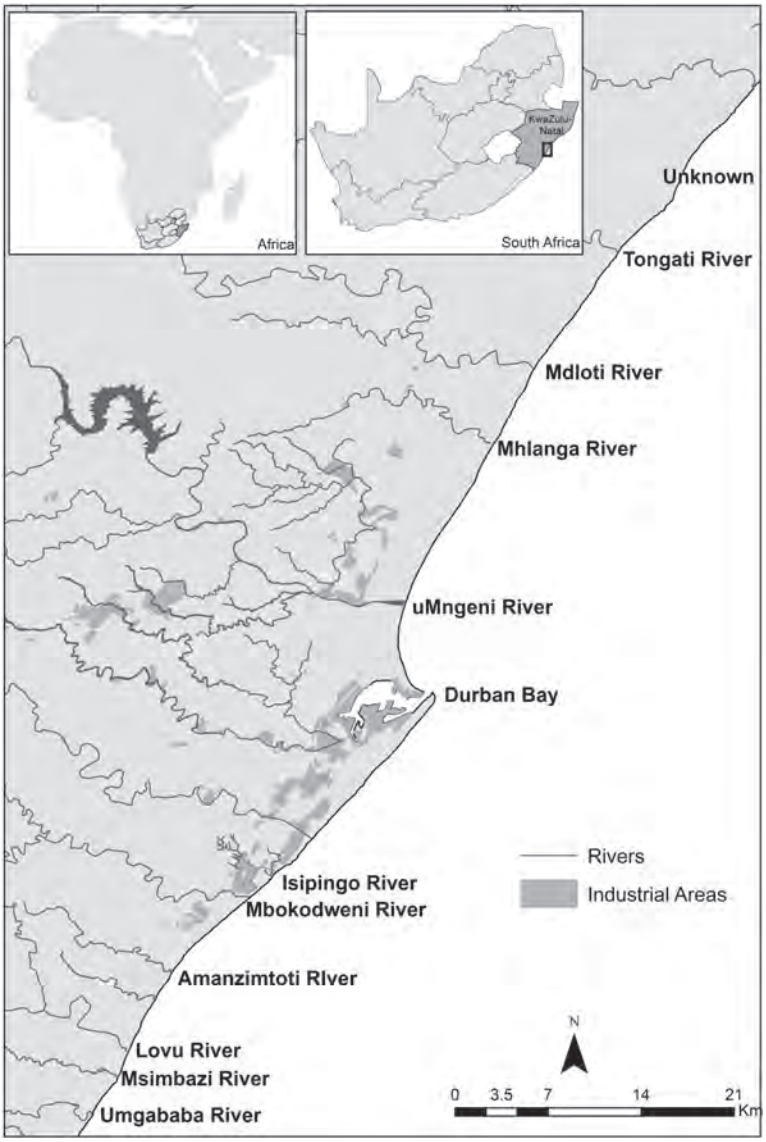

Figure 1.1. Map of the eThekwini area of KwaZulu-Natal showing the positions of catchments where sediment samples were collected in September 2011.

density was generally scaled to catchment size and/or the type and intensity of land-use within the catchment. Station positioning attempted to represent conditions in tributaries where possible, by sampling upstream and downstream of confluences. Sediment was absent or could not be collected at certain pre-identified sampling stations. In some cases the stations were substituted by a new station in close proximity, but this was not always possible. Pre-defined sampling station identifiers are retained in figures and graphs since measurements not reported here were also made at the stations and accounts for the sometimes irregular chronology of the station identifiers.

2.2.2 Brief description the study area

The eThekwini municipal area is situated in KwaZulu-Natal, on the northeast coast of South Africa. The city of Durban falls within the municipal area. As stated previously, sediment was collected in the riverine and/or estuarine reaches of 12 catchments, eight of which were situated beyond the greater Durban area. The name of one river could not be ascertained and is referred to as Unknown (station UNKN) in this report. The other systems were the Tongati, Mdloti and Mhlanga River estuaries to the north and the Amanzimtoti, Lovu, Umsimbazi and Umgababa River estuaries to the south. Land-use within catchments of these systems spans the range from predominantly rural (*e.g.* Umsimbazi River) to relatively lightly urbanised and industrialised (*e.g.* Amanzimtoti River, see Figures 1.2-1.4). Thus, none of these catchments

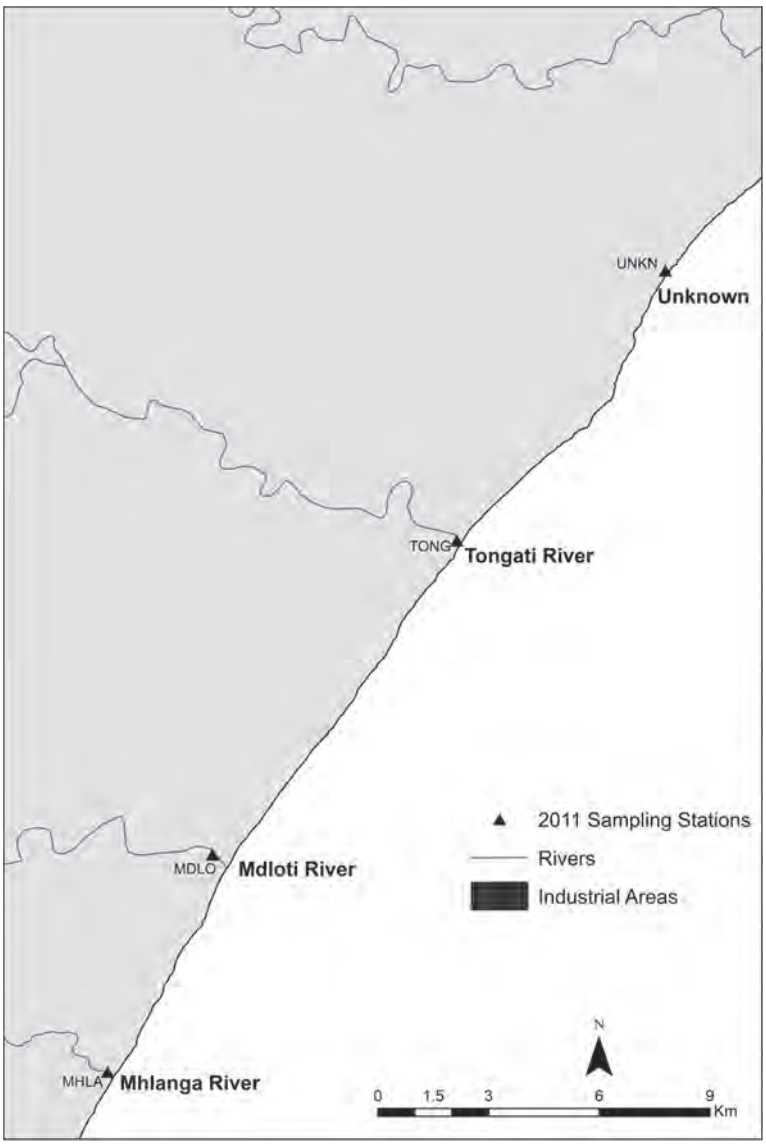

Figure 1.2. Map of the northern part of the study area showing the positions in catchments where sediment samples were collected in September 2011.

is 'free' of an anthropogenic influence. Land-use within the remaining catchments is urban and/or industrial. The uMngeni River has a large catchment that, in the Durban area at least, is highly urbanised and industrialised. Durban Bay is a large estuarine embayment situated in the 'heart' of Durban and is home to the Port of Durban, which is South Africa's busiest port in terms of vessel calls and containers handled. Three rivers discharge into Durban Bay, namely the Amanzimnyama, Umbilo and Umhlatuzana Rivers. The Umbilo and Umhlatuzana Rivers join a few hundred meters before discharging into the Bay and are consequently sometimes referred to in this report as the Umbilo/Umhlatuzana Rivers. Land-use in catchments of the Umbilo and Umhlatuzana Rivers is probably best described as urban to light industrial. Several wastewater treatment facilities discharge wastewater into these rivers, but most notably into the Umhlatuzana River. In contrast, land-use in the catchment of the Amanzimnyama River is predominantly industrial. This river is canalised for much of its length. Numerous stormwater outfalls and canals also discharge surface runoff from highly urbanised and industrialised areas into Durban Bay. The Isipingo River and its estuary are highly modified, to the extent that the riverine portion essentially comprises a network of canals draining a highly industrialised area. The catchment of the Mbokodweni River, which is situated a short distance from the Isipingo River and estuary, is also industrialised but not to the same degree as the Isipingo River.

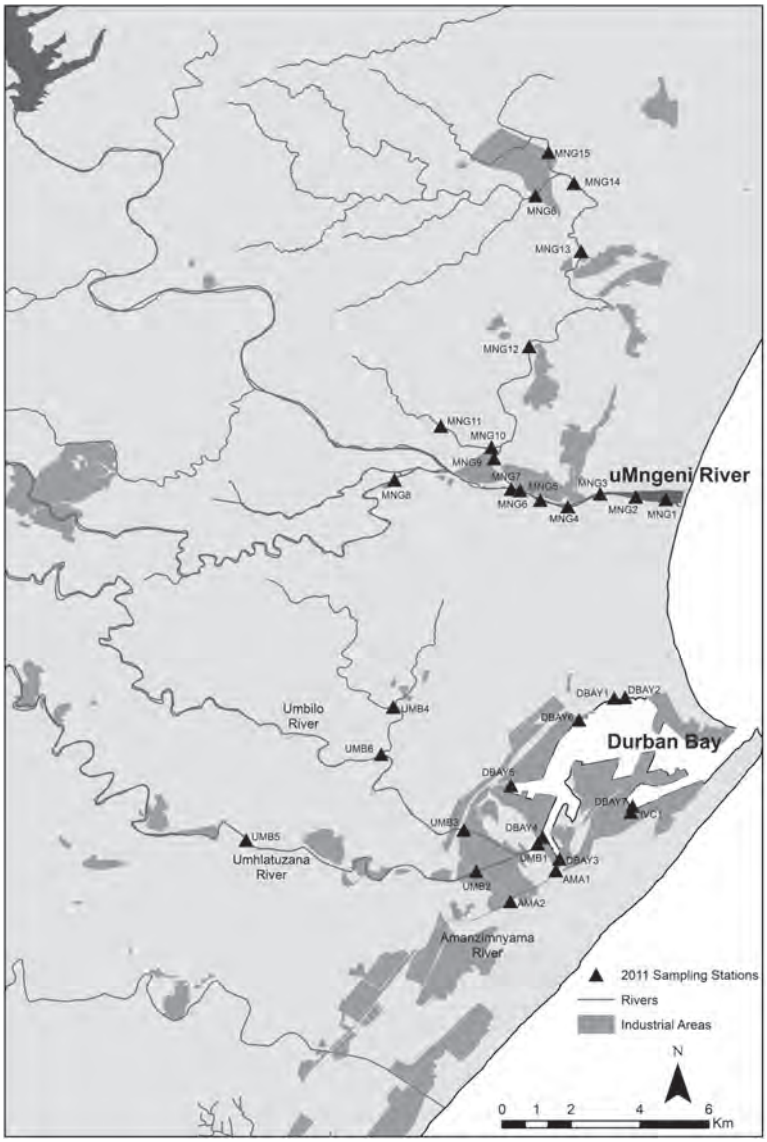

Figure 1.3. Map of the central part of the study area showing the positions in catchments and in Durban Bay where sediment samples were collected in September 2011.

2.2.3 Fieldwork

Before entering the field all sampling equipment, including grabs, bowls, scoops and cooler boxes were scrubbed with a hard brush, rinsed with tap water and allowed to dry in a clean room. Once dry the equipment was rinsed with deionised water followed by hexane (using a spray bottle where appropriate) and allowed to dry in a clean room. Where possible (*e.g.* bowls, spoons) equipment was sealed in Ziploc® bags when dry. Sediment sample storage jars (amber glass or high density polyethylene) were sequentially rinsed in tap water, hexane and deionised water. Aluminium foil liners for lids were treated similarly. Glass containers and aluminium foil liners were then placed in an oven at 100°C for 24 hrs. The jars were then stored individually in Ziploc® bags.

As stated previously, most sediment samples were collected from bridges. A vessel was used to collect sediment in the uMngeni River estuary and at five of the seven stations sampled in Durban Bay. Sediment was collected using a stainless steel van Veen grab. On retrieval excess water overlying sediment in the grab was drained through a bleeder hole, taking care not to lose fine-grained material. Three sediment samples were collected about 2-3 m apart at each station and composited in a glass bowl. The sediment was homogenised to a uniform consistency and colour using a stainless steel spoon. During homogenation fieldworkers (wearing powder free latex gloves) removed material not representative of the sediment

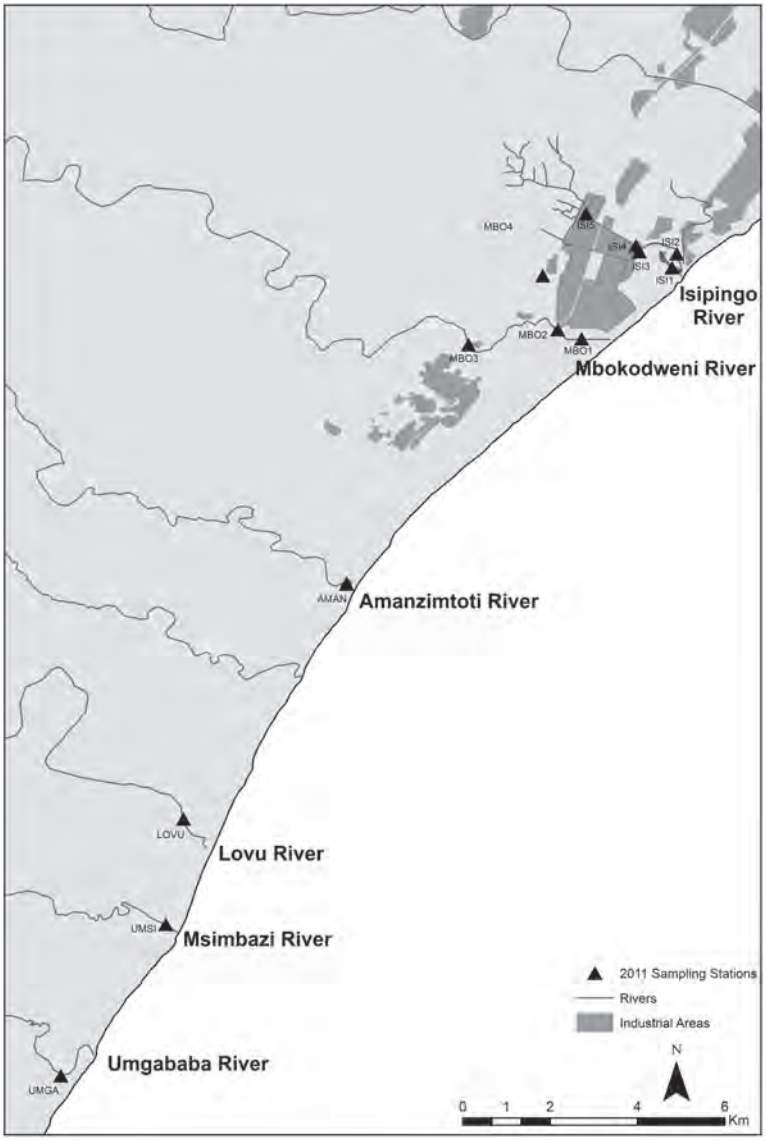

Figure 1.4. Map of the southern part of the study area showing the positions in catchments where sediment samples were collected in September 2011.

when detected, including small pebbles, twigs, leaves, and plastic material. After homogenation, aliquots of sediment were transferred to two high density polyethylene containers for metal and grain size analysis and an amber glass jar for organic chemical analysis. The apertures of glass jars were sealed with an aluminium foil liner before the lid was screwed on, taking care not to puncture the liner in the process. The glass jars were then wrapped in aluminium foil to limit photo-degradation of light sensitive chemicals. Samples were kept on ice in the field and immediately frozen on return to the laboratory.

To limit cross contamination of samples in the field the van Veen grab, compositing bowl, spoons and scoops were scrubbed with a hard brush, sprayed with hexane and rinsed with deionised water between sample collections.

2.2.4 Laboratory analyses

2.2.4.1 Sample preparation

Sediment destined for chemical and total organic carbon analysis was freeze dried and ball milled to a fine consistency. The milled sediment was transferred to new storage containers cleaned according to the same procedure described above.

2.2.4.2 Grain size composition

Sediment grain size composition was determined by wet and dry sieving the sediment into seven grain size classes, namely mud (<0.063 mm), very fine-grained sand (0.063-0.125 mm), fine-grained sand (0.125-0.250 mm), medium-grained sand (0.25-0.50 mm), coarse-grained sand (0.5-1.0 mm), very coarse-grained sand (1.0-2.0 mm) and gravel (>2.0 mm). The contribution of each grain size class is expressed as a fraction of bulk sediment dry weight.

2.2.4.3 Total organic content

About 1 mg of sediment was oven dried, weighed, and organic matter in the sediment then degraded using hydrogen peroxide. The sediment was then washed in distilled water, re-dried and re-weighed, and the difference in dry weight before and after organic matter degradation was used to determine the total organic content. The total organic content is expressed as a fraction of bulk sediment dry weight.

2.2.4.4 Total organic carbon

About 1-2 mg of dried sediment was weighed into silver boats. A small volume of hydrochloric acid (10%) was added to the sediment to degrade inorganic carbon. The addition of acid continued until foaming ceased. The sediment was then dried in an oven at 65^{o}C overnight. The boats were crimped and the total organic carbon measured using an Exeter CHN Model 440 CE analyser at 985^{o}C. Certified reference material BCCS-1 SRM was used to determine recovery. Blanks and the certified reference material were analysed with every batch of 10 samples. The method detection limit was 0.03%. Total organic carbon is expressed as a fraction of bulk sediment dry weight.

2.2.4.5 Organic chemicals

Organic chemical analysis of sediment was performed at the Virginia Institute of Marine Sciences (United States of America). A sodium sulphate blank travelled with each batch of samples through the preparation procedure. Before solvent extraction, dried sediment was spiked with a surrogate standard (PCB-30, PCB-65 and PCB-204) to monitor recovery of polychlorinated biphenyls and organochlorine pesticides. The sediment was also spiked with a deuterated standard mix (d8-naphthalene, d10-acenaphthene, d10-phenanthrene, d12-chrysene, d12-perylene) and 1,1-binaphthyl to monitor recovery of polycyclic aromatic hydrocarbons. Concentration-based method quantitation limits varied as a function of sediment density and analytical interferences in the samples. However, in general the quantitation limits were 0.1 ng.g^{-1}.

Sediment and sodium sulphate blanks were subjected to enhanced solvent extraction (Dionex ASE 200) using methylene chloride. Each extract was concentrated under nitrogen and purified by size exclusion liquid chromatography (Envirosep-ABC, 350 × 21.1 mm column) to remove biogenic co-extractives of large molecular size. The eluent was collected in vessels containing activated, elemental copper to remove co-extracted sulphur. The extracts were then reduced in volume and purified on 2 g silica gel solid-phase extraction columns to retain polar biogenic compounds. The first fraction was eluted from the silica column with 3.5 ml of hexane and discarded. The second fraction was obtained by elution with 6.5 ml of 60:40 hexane/dichloromethane and contained target analytes. The purified extracts were reduced to approximately 0.2 ml volume under nitrogen and decachlorodiphenyl ether and p-terphenyl added as internal quantitation standards.

Polychlorinated biphenyls, organochlorine pesticides and polycyclic aromatic hydrocarbons were detected using a Varian high resolution gas chromatograph using a split/splitless injector and a DB-5 column, (60 m, 0.32 mm id, 0.25 µm film) interfaced with a Varian ion trap mass spectrometer operated in the electron ionization mode. Five-point calibration curves of the desired analytes versus the internal standard (p-terphenyl for pesticides and polycyclic aromatic hydrocarbons; decachlorodiphenyl ether for polychlorinated biphenyls) were generated. Mass spectrometer quantitation was performed in the selected

ion storage mode using dominant m/z fragments. Recoveries of the surrogate standards were calculated. Quantitation of the target analytes, with and without surrogate recovery correction, was performed. PCB204 was used as a conservative recovery correction standard for polychlorinated biphenyls and organochlorine pesticides. PCB204 is less volatile than PCB30 and PCB65. Polycyclic aromatic hydrocarbons were corrected relative to the intermediate molecular weight surrogate 1,1-binaphthyl.

Method extraction efficiency was determined using three samples of National Institute of Standards and Technology Standard Reference Material (SRM) 1944. Extraction efficiencies (Table 1.1) generally fell within data quality objectives of 50-150% recovery and <50% relative percent difference. Laboratory blanks were found to contain no quantifiable concentrations of target analytes with the exception of polycyclic aromatic hydrocarbons, for which pyrene was detected in all three blanks at 10.0, 12.39 and 17.43 $ng.g^{-1}$ and benzo(e)pyrene in one blank at 10.24 $ng.g^{-1}$.

Table 1.1. Recoveries (%) of polychlorinated biphenyls, polycyclic aromatic hydrocarbons and pesticides from marine sediment reference standard NIST 1944 (National Institute of Standards and Testing).

Class	Compound	SRM 1	SRM 2	SRM 3	Average	Precision
Polychlorinated biphenyls	PCB8,5	87.1	109.8	91.5	96.13	12.52
	PCB18	96.2	114.4	93.6	101.40	11.18
	PCB28, 31	96.6	117.9	103.2	105.90	10.30
	PCB52	89.4	103.7	88.2	93.77	9.20
	PCB49	110.0	119.5	99.2	109.57	9.27
	PCB44	92.0	108.0	92.8	97.60	9.24
	PCB66,70,95	124.8	152.7	136.7	138.07	10.14
	PCB101,90	105.0	103.5	99.3	102.60	2.88
	PCB99	90.4	90.8	79.8	87.00	7.17
	PCB87,115	72.0	84.0	78.5	78.17	7.68
	PCB110	117.2	120.3	109.6	115.70	4.76
	PCB151	84.8	80.1	73.9	79.60	6.87
	PCB149	112.2	105.2	98.8	105.40	6.36
	PCB118	116.3	142.3	98.1	118.90	18.68
	PCB153,132	88.8	70.8	63.0	74.20	17.83
	PCB105	107.2	128.6	72.6	102.80	27.49
	PCB138,158	131.7	148.6	117.2	132.50	11.86
	PCB187	95.1	91.4	76.5	87.67	11.23
	PCB183	96.3	94.1	69.6	86.67	17.10
	PCB128	83.4	78.6	75.3	79.10	5.15
	PCB180,193	115.1	116.5	111.1	114.23	2.45
	PCB170,190	91.0	77.6	101.7	90.10	13.40
	PCB206	53.2	62.3	51.3	55.60	10.57
	PCB209	54.2	40.6	62.8	52.53	21.31
Polycyclic aromatic hydrocarbons	Phenanthrene	122.8	124.3	100.5	115.87	11.50
	Fluoranthene	137.7	149.5	139.8	142.33	4.42
	Pyrene	132.6	145.6	140.3	139.50	4.69
	Benz(a)anthracene	73.4	72.5	65.8	70.57	5.88
	Chrysene	72.9	69.6	67.0	69.83	4.23
	Benzo(b)fluoranthene	52.4	57.3	57.4	55.70	5.13
	Benzo(k)fluoranthene	92.1	97.0	82.1	90.40	8.40
	Benzo(e)pyrene	53.5	58.1	54.3	55.30	4.44
	Benzo(a)pyrene	50.9	56.1	51.3	52.77	5.48
	Indeno(1,2,3-cd)pyrene	60.1	63.5	53.9	59.17	8.23
	Dibenzo(a,h)anthracene	90.6	85.9	72.0	82.83	11.68
	Benzo(ghi)perylene	54.5	57.3	54.1	55.30	3.15
Pesticides	Hexachlorobenzene	66.4	67.4	63.2	65.67	3.34
	Cis-chlordane	89.8	80.3	80.8	83.63	6.39
	Trans-nonachlor	122.7	120.0	115.4	119.37	3.09

2.2.4.6 Metals

Metal analysis of sediment was performed at the Analytical Services Laboratory on the CSIR campus in Stellenbosch. Approximately 1 g of sediment was digested in HNO_3-HCl-H_2O_2 according to USEPA method 3050B. This is a 'near-total' digestion method that will dissolve most elements that could become 'environmentally available', but is not designed to dissolve metals bound in silicate structures (USEPA, 1996). Precision and recovery of the digestion and metal determination procedures were evaluated by analysing marine Standard Reference Material PACS-2 (National Research Council of Canada) with each batch of 10 sediment samples. Since the reference material is certified for total digestion the recovery of refractory metals (*e.g.* aluminium, chromium) was, as expected, somewhat below 100% (Table 1.2).

2.2.5 Data analysis

2.2.5.1 Basic procedures

Total polycyclic aromatic hydrocarbon and total polychlorinated biphenyl concentrations are the sum of all isomers or congeners analysed respectively unless otherwise stated. Isomers or congeners at concentrations below the method detection limit were assigned a value of zero for the purpose of total concentration calculation. DDX concentrations represent the sum of technical DDT and metabolites. Total chlordane concentrations represent the sum of cis- and trans-chlordane, cis- and trans-nonachlor, and oxychlordane. For pesticides concentrations below the method detection limit were also assigned a value of zero for purpose of total concentration calculation.

Correlation and linear regression analysis was used to examine the nature and strength of linear relationships between sediment parameters and/or chemical concentrations. Further details on data analysis procedures are provided in relevant sections of the text.

2.2.5.2 Estimation of potential toxicological risk posed by chemicals to sediment-dwelling organisms

Two approaches were followed to estimate the potential toxicological risk that chemicals in the sediment posed to sediment-dwelling organisms. In the first approach chemical concentrations were compared to numerical sediment quality guidelines derived to be protective of sediment-dwelling organisms. Sediment quality guidelines have not been derived for freshwater ecosystems in South Africa. Sediment quality guidelines were recently defined for the regulation of dredged material disposal in South African coastal waters, but there are only guidelines for metals. The lack of South African sediment quality guidelines for organic chemicals necessitated the use of international sediment quality guidelines for the freshwater and

Table 1.2. Recovery (%) of metals from marine sediment reference standard PACS-2 (National Research Council of Canada).

	Replicate										
Metal	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**Average**	**Minimum**	**Maximum**	**Precision**
Aluminium	45.3	44.4	44.6	43.8	44.8	46.2	45.8	45.11	43.79	46.18	2.09
Arsenic	86.3	80.4	82.8	83.1	85.7	94.4	79	86.93	78.98	95.62	7.11
Beryllium	100.8	114.6	117	83	111.3	91.8	90.1	95.40	74.74	117.04	15.79
Cadmium	100.7	96.9	95.7	95.9	90.3	96.9	94.2	94.36	90.25	96.87	2.28
Cobalt	85.3	80.6	84.4	79.2	81.1	87	85.6	84.28	79.18	87.70	3.68
Chromium	66.9	65.2	63.6	63.1	61	58.3	66.8	63.72	58.33	69.73	5.82
Copper	99.4	96	94.5	91.1	100.8	95.9	98.5	95.38	91.09	100.81	3.49
Iron	75.8	71.1	73.6	71.7	74	68.3	76.8	73.54	68.30	78.97	4.82
Manganese	62.2	56.8	67.8	60.5	64.3	57.7	56.8	61.14	56.77	67.81	6.96
Nickel	86.2	77.6	87	85.1	86	74.2	75.5	80.87	74.24	86.98	7.28
Lead	89.2	89.8	95.3	88.9	88.1	89.7	83.4	91.53	83.43	99.29	6.01
Vanadium	68.7	64.6	74	66.3	71.2	74	70.6	70.20	66.31	74.00	4.47
Zinc	93.9	95.3	101.8	93.5	93.7	92.2	88.2	93.77	88.19	101.78	4.96

saline reaches of catchments (Table 1.3). Two sets of sediment quality guidelines were used. The first was the consensus-based sediment quality guidelines derived for application in freshwater ecosystems in North America by MacDonald *et al*. (2000). The term consensus refers to the fact that the guidelines represent the geometric mean of several sets of sediment quality guidelines with a similar narrative intent. Two guidelines were derived, namely the Threshold Effect Concentration and the Probable Effect Concentration. The Threshold Effect Concentration represents the concentration below which adverse effects to sediment-dwelling organisms are unlikely to be observed while the Probable Effect Concentration represents the concentration above which adverse effects are likely to be observed. The range between the Threshold Effect Concentration and a Probable Effect Concentration is a grey area, with the probability of observing adverse effects increasing as the chemical concentration increases within this range.

The second set of sediment quality guidelines were derived for application in estuarine and marine ecosystems in North America by Long *et al*. (1995; sometimes referred to as the National Oceanic and Atmospheric Administration (NOAA) sediment quality guidelines). Two guidelines were derived, namely the Effects Range Low and Effects Range Median. As with the consensus-based sediment quality guidelines the Effects Range Low represents the concentration below which adverse effects to sediment-dwelling organisms are unlikely to be observed while the Effects Range Median represents the concentration above which adverse effects are likely to be observed. The range between the Effects Range Low and the Effects Range Median is also a grey area, with the probability of observing adverse effects increasing as the chemical concentration increases within this range.

The sediment quality guidelines used to regulate dredged material disposal in South African coastal waters

Table 1.3. Effects Range Low (ERL) and Effects Range Median (ERM) of the sediment quality guidelines derived by Long *et al*. (1995) and Threshold Effect Level (TEC) and Probable Effect Level (PEL) of the consensus-based sediment quality guidelines derived by MacDonald *et al*. (2000). All concentrations in $ng.g^{-1}$. PAH = polycyclic aromatic hydrocarbons, PCB = polychlorinated biphenyls, - = no guideline.

	Long *et al*. (1995)		MacDonald *et al*. (2000)	
Chemical	**ERL**	**ERM**	**TEC**	**PEC**
Acenaphthene	16	500	-	-
Acenaphthylene	44	640	-	-
Anthracene	85.3	1100	57.2	845
Fluorene	19	540	77.4	536
2-Methyl naphthalene	70	670	-	-
Naphthalene	160	2100	176	561
Phenanthrene	240	1500	204	1170
Sum low molecular weight PAH	552	3160	-	-
Benz(a)anthracene	261	1600	108	1050
Benzo(a)pyrene	430	1600	150	1450
Chrysene	384	2400	166	1290
Dibenzo(a,h)anthracene	63.4	260	33	NG
Fluoranthene	600	5100	423	2230
Pyrene	665	2600	195	1520
Sum high molecular weight PAH	1700	9600	-	-
Total PAH	4022	44793	1610	2280
Total PCB	22.7	180	59.8	676
Chlordane	-	-	3.24	17.6
Dieldrin	-	-	1.9	61.8
Sum DDE	2.2	27	4.88	28
Sum DDD	-	-	3.16	31.3
Sum DDT	-	-	4.16	62.9
DDX	1.58	46.1	5.28	572
Endrin	-	-	2.22	207
Heptachlor expoxide	-	-	2.47	16
Lindane (gamma BHC)	-	-	2.37	4.99

were used to estimate the potential toxicological risk posed by metals in the freshwater and saline reaches of catchments. The sediment quality guidelines were adopted from guidelines used in North America after consideration of baseline metal concentrations for sediment in South African coastal waters. Three guidelines were derived for metals, namely the Warning Level, Level I and Level II. The Level I and Level II are used for decision-making. The Warning Level is only used to provide a warning of incipient metal contamination. Sediment with metals at concentrations equivalent to or lower than the Level I is regarded as posing a low toxicological risk to sediment-dwelling organisms and is thus of a suitable quality for unconfined openwater disposal. Sediment with metals at concentrations between the Level I and Level II poses a potential toxicological risk to sediment-dwelling organisms, with the degree of risk increasing as the Level II is approached.

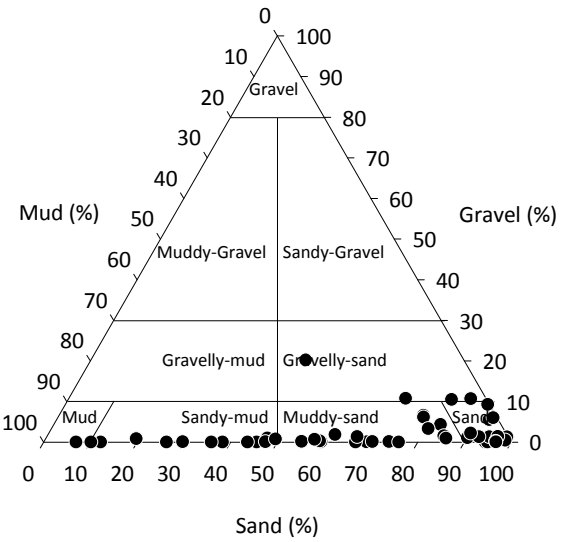

Figure 1.5. Ternary plot illustrating the proportional contribution of gravel, sand and mud to bulk sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2011.

The second approach followed to estimate the potential toxicological risk posed by chemicals in sediment to sediment-dwelling organisms was the mean sediment quality guideline quotient approach. Studies in North America have shown that the incidence and magnitude of sediment toxicity in laboratory toxicity tests and to sediment-dwelling organisms in the field increases incrementally with increasing mean sediment quality guideline quotient (*e.g.* Long *et al*., 2006). Mean sediment quality guideline quotients were calculated by dividing the concentration of each organic chemical by its respective Probable Effect Concentration or Effects Range Median provided there was a guideline for the chemical, summing the values, and then dividing the summed value by the number of chemicals for which guidelines were available.

2.3 RESULTS AND DISCUSSION[1]

2.3.1 Sediment grain size composition

Grain size is one of the most important variables that influence the accumulation of contaminants in sediment. This is because many contaminants are particle reactive and preferentially adsorb onto fine-grained material, because of the large surface area to volume ratio provided by the fine grains for adsorption and because the surface of silt and clay grains is electrically charged. Many contaminants also adsorb onto fine-grained material in suspension in the water column, including silt, clay and organic matter, and are ultimately deposited in sediment depositional zones (*i.e.* zones dominated by fine-grained sediment, and typically by mud). The small surface area to volume ratio provided by and absence of surface electric charges on sand grains mean that contaminant concentrations in sand-dominated sediment are usually (orders of magnitude) lower than in mud-dominated sediment. There may be exceptions to this general rule, such as coarse-grained sediment near vessel construction and maintenance facilities having high metal concentrations due to the introduction of metal flecks and metal-infused paint flakes.

An understanding of the grain size composition of sediment is particularly critical for interpreting metal concentrations in sediment since grain size is the single most important factor controlling natural metal

[1] Results of physical and chemical analyses of sediment are presented in Appendices 2-7.

concentrations in sediment in geologically homogenous areas (*e.g.* Horowitz and Elrick, 1987; Windom *et al*., 1989). This is because aluminosilicates, which predominate in clay, are the major natural metal-bearing phase of sediment. Naturally occurring metal concentrations are thus usually strongly positively correlated to the silt and clay (mud) fraction of sediment. Thus, mud dominated sediment has a naturally higher metal content than sand dominated sediment.

There is little point discussing in detail the grain size composition of sediment in the rivers, estuaries and canals sampled since these systems are naturally disparate in nature and the grain size composition can thus be expected to vary considerably between the systems. The primary purpose for analysing the grain size composition of sediment was to determine whether the mud fraction can account for the variability in organic chemical and metal concentrations in sediment. Nevertheless, a ternary plot revealed that the sediment sampled fell into five textural classes, namely sand, muddy-sand, sandy-mud, mud and gravelly sand (Figure 1.5). A large proportion of the samples were dominated by sand. This, in part, reflects the fact that many sediment samples were collected in the fast-flowing reaches of rivers, where fine-grained material is easily winnowed from the sediment by currents. Sediment in the estuarine reaches of catchments was often dominated by fine-grained material, but here too in many cases sand was the dominant textural class. The grain size composition of sediment sampled in the rivers, estuaries and canals spans a sufficient range to allow for the identification of unifying features in terms of organic chemical and metal association with fine-grained material, provided unifying features are evident.

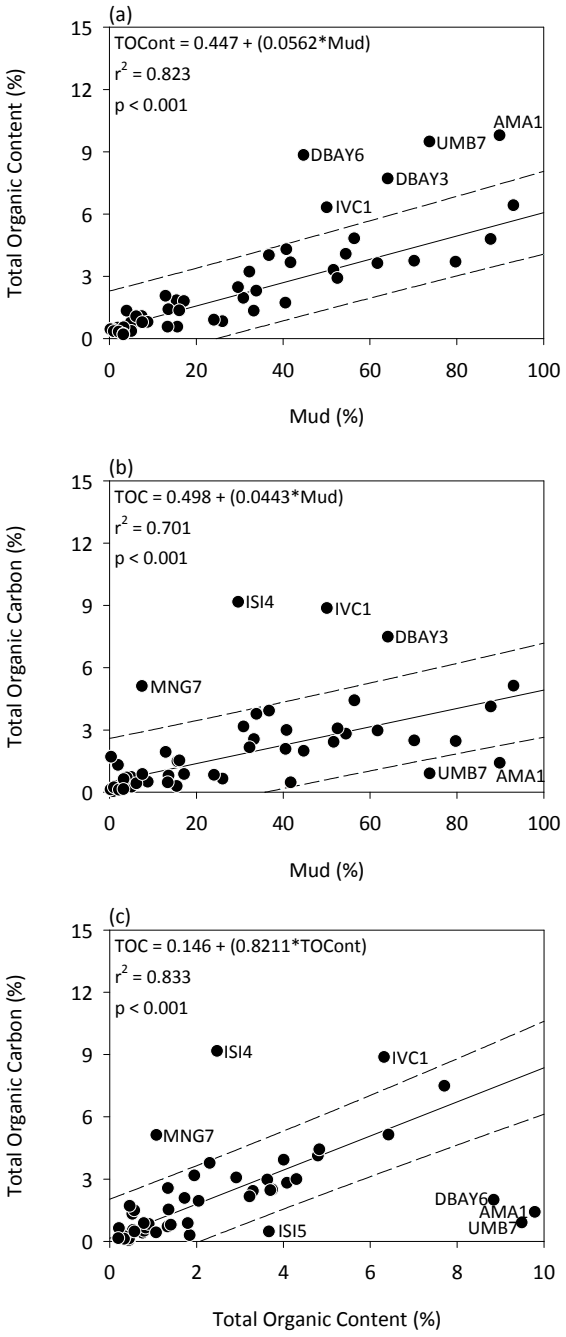

Figure 1.6. Relationship between mud and particulate organic matter indicator fractions in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2011. Linear regressions fitted to data trimmed of outliers (data points indicated by station identifiers) are given with 99% prediction limits, fitted parameters, coefficients of determination (r^2) and statistical significance (p).

2.3.2 Particulate organic matter

Particulate organic matter in sediment provides an additional site for the adsorption of particle reactive contaminants. Many organic contaminants are particularly partial to adsorption onto particulate organic matter (Wangersky, 1986; Stumm and Morgan, 1996). The primary reason for analysing the total organic content and total organic carbon fractions of sediment was thus to determine whether these indicators of particulate organic matter can account for the variability in organic chemical and (some) metal concentrations in sediment. Total organic carbon is often used to normalise organic contaminant concentrations in sediment under the premise that adsorption onto particulate organic matter controls the bioavailability of and hence ecological risk posed by these

contaminants. The purpose for analysing total organic content and total organic carbon was to determine which, if any, of these indicators provides the better understanding of particulate organic matter accumulation in sediment and is thus the more suitable normaliser of organic chemical concentrations. Also, the cost of total organic content analysis is far lower than the cost of total organic carbon analysis. If a strong relationship linear exists between these indicators and has a slope that approximates unity then total organic content can be used a surrogate for total organic carbon, with obvious cost saving implications.

Because of its fine size, particulate organic matter is deposited on and winnowed from sediment concurrently with mud depending on prevailing hydrodynamic conditions. Mud and particulate organic matter tend, therefore, to accumulate or be depleted in the same areas. There is thus often a strong positive linear relationship between the mud and particulate organic matter fractions in sediment in anthropogenically unimpacted rivers, estuaries and canals. Scatter plots of the mud versus total organic content and total organic carbon fractions of sediment revealed that while there was substantial scatter in the data a positive linear relationship was nevertheless evident for sediment at the majority of stations (Figure 1.6). This allowed the definition of mud-normalised baseline models for total organic content and total organic carbon. To define the baseline models, linear regressions and associated 99% prediction limits were fitted to the data. Data points falling outside the prediction limits were deemed outliers and sequentially trimmed, starting with the data point furthest from a prediction limit. Trimming continued until all data points fell between the prediction limits. Superimposing the data for all stations onto the baseline models identified sediment with a higher (enriched) or lower (depleted) than expected total organic content and total organic carbon (*i.e.* data points falling outside the baseline model prediction limits).

As indicated by the coefficients of determination (r^2), the relationship between mud and total organic content was stronger than the relationship between mud and total organic carbon (Figure 1.6a,b). The baseline model for total organic content identified the sediment at five stations as enriched with particulate organic matter while the model for total organic carbon identified the sediment at four stations as enriched with, and at two stations as depleted in particulate organic matter. Only two stations where the sediment was identified as enriched with particulate organic matter using the different baseline models were coincident, namely station DBAY3 in Durban Bay and station IVC1 in Island View Canal (Figure 1.6a,b). The cause of the mismatch was the large difference in the proportion of bulk sediment comprised by total organic content and total organic carbon in sediment at several stations (Figure 1.6c). Sediment at station AMA1 in the Amanzimnyama River, for example, was identified as amongst the most enriched with particulate organic matter by the baseline model for total organic content, but as highly depleted by the baseline model for total organic carbon. Since these indicators provide a measure of the contribution of particulate organic matter to sediment the relationship between them should theoretically be very strong. That this was not the case for some stations makes it difficult to determine which provides the most reliable indicator of particulate organic matter enrichment of sediment, and consequently which is the most suitable normaliser of organic chemical concentrations. Nevertheless, where organic chemical concentrations were normalised this followed the convention of using total organic carbon as the normaliser.

2.3.3 Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons are chemicals characterised by two or more fused benzene (aromatic) rings (Neff, 1979). There are two primary sources of polycyclic aromatic hydrocarbons to the environment, namely fossil fuels, including refined and unrefined crude oil, and the incomplete combustion of organic material such as wood, coal and oil (Boehm, 2006). Although there are natural sources of polycyclic aromatic hydrocarbons, including forest fires, oil seeps, coal and organic matter degradation (Neff, 1979;

Hites *et al.*, 1980; Stillman *et al.*, 1998; Baumard *et al*., 1999; Lima *et al.*, 2005), anthropogenic activities are recognised as the most significant source of polycyclic aromatic hydrocarbons released into the environment (Wakeham *et al*., 1980), with the incomplete combustion of wood, coal and oil the most significant anthropogenic sources (McCready *et al*., 2000; Mahler *et al*., 2005; Boehm, 2006; Mostert *et al*., 2010). Polycyclic aromatic hydrocarbons are generally hydrophobic and consequently preferentially partition to particulate material in the water column (*e.g.* suspended particulate material) and more commonly to bottom sediment (Karickhoff *et al*., 1979; Means *et al*., 1980; Douben, 2003). Sediment is the most important sink and reservoir for polycyclic aromatic hydrocarbons in the aquatic environment, with concentrations usually orders of magnitude higher than in the water column. Surface (stormwater) runoff is an important vector for the introduction of polycyclic aromatic hydrocarbons to aquatic ecosystems (Hoffman *et al*., 1984; Steur *et al*., 1997; Hwang and Foster, 2006; Stein *et al*., 2006). This is because polycyclic aromatic hydrocarbons released via vehicle exhaust and industrial emissions are deposited on impervious surfaces (*e.g.* roads, pavements) in urbanised and industrialised areas and are then mobilised by surface runoff to stormwater conveyance systems and ultimately to aquatic ecosystems. There is evidence that coal-tar-based sealants used to protect asphalt on roads and in parking lots are also significant sources of polycyclic aromatic hydrocarbons in stormwater and thus ultimately to aquatic ecosystems (Crane *et al*., 2010; Yang *et al*., 2010; Van Metre *et al*., 2010). A strong correlation between polycyclic aromatic hydrocarbon concentrations in sediment and the proportion of impervious cover in the catchment has been widely reported (*e.g.* Sanger *et al*., 1999; Holland *et al*., 2004; Garner *et al*., 2009).

Polycyclic aromatic hydrocarbons are of ecological and human health concern since some isomers are known or strongly suspected carcinogens and mutagens (IARC, 1991; USEPA, 1993; Luch, 2005). In general, low molecular weight (two and three ring) isomers display significant acute toxicity whilst high molecular weight (four to six ring) isomers display greater carcinogenicity. Due to toxicological concerns the United States Environmental Protection Agency has identified sixteen polycyclic aromatic hydrocarbons as priority pollutants (Keith and Telliard, 1979; see review by Xue and Washarsky, 2005). Polycyclic aromatic hydrocarbons generally do not bioaccumulate in the tissue of fish since they are extensively metabolised by vertebrates (Lemaire *et al*., 1990; Macdonald and Bewers, 1996; Meador, 2003), but may be accumulated to significant concentrations by bivalve shellfish. However, even in shellfish polycyclic aromatic hydrocarbons may be effectively metabolised. This does not mean polycyclic aromatic hydrocarbons do not cause deleterious effects to vertebrates; while metabolism serves as a pathway of detoxification for polycyclic aromatic hydrocarbons, some metabolites that are intermediates in this process possess carcinogenic, mutagenic and cytotoxic activity (Meador, 2003). Benthic invertebrates are more susceptible and many bioaccumulate polycyclic aromatic hydrocarbons and are in turn a source of exposure to higher level consumers, including humans (Varanasi *et al*., 1989, 1992; Meador *et al*., 1995; Meador, 2003).

Polycyclic aromatic hydrocarbons were detected at concentrations exceeding the method detection limit in sediment at all stations (Figure 1.7), although all isomers were not necessarily detected at concentrations exceeding the method detection limit. Total polycyclic aromatic hydrocarbon concentrations not normalised to total organic carbon varied widely, from 17.5 $ng.g^{-1}$ at station MHLA in the Mhlanga River estuary to 6248.8 $ng.g^{-1}$ at station DBAY4 in Durban Bay (Figure 1.7). The mean concentration was 1239.1 $ng.g^{-1}$, with a standard deviation of 1495.6 $ng.g^{-1}$. The 25^{th}, 50^{th} and 75^{th} percentiles of the concentration distribution were 222.4, 376.6 and 2010.7 $ng.g^{-1}$ respectively. Thus, total polycyclic aromatic hydrocarbon concentrations at the majority of stations were relatively low. The ubiquitous presence of polycyclic aromatic hydrocarbons in sediment in rivers, estuaries and canals sampled in the eThekwini area was not unexpected since these chemicals are nearly ubiquitous in sediment in other regions of the world, including in non-urbanised catchments (*e.g.* Cundy *et al*., 1997; Neff *et al*., 2005; Garner *et al*., 2009; Tao *et al*., 2010). This ubiquity undoubtedly reflects a multitude of natural and anthropogenic sources of polycyclic aromatic hydrocarbons in the eThekwini area. Low molecular weight isomers contributed proportionally

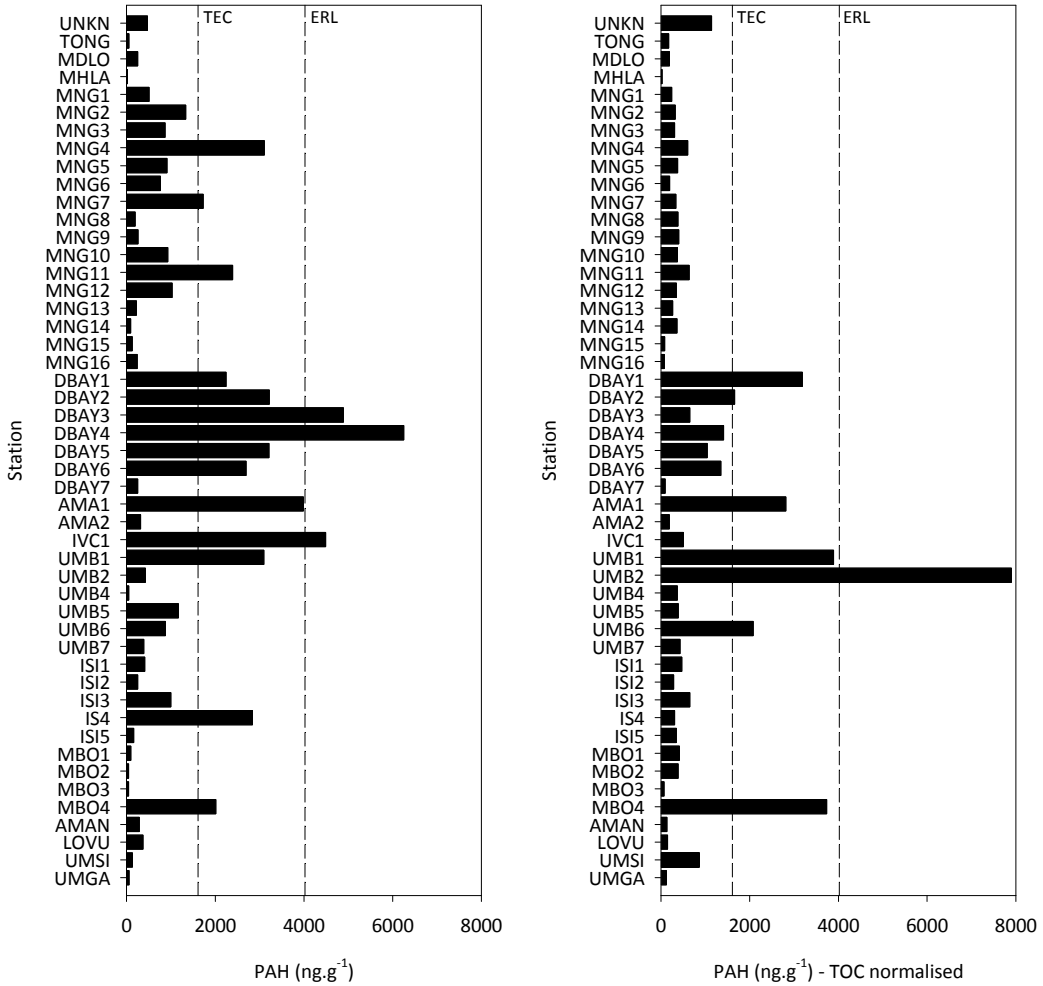

Figure 1.7. Total polycyclic aromatic hydrocarbon (PAH) concentrations not normalised (left) and normalised (right) to total organic carbon (TOC) in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2011. The dashed lines denote the Threshold Effect Concentration (TEC) of the consensus-based sediment quality guidelines derived by MacDonald *et al*. (2000) and the Effects Range Low (ERL) of the sediment quality guidelines derived by Long *et al*. (1995).

less to total polycyclic aromatic hydrocarbon concentrations compared to high molecular weight isomers at all stations. In fact, low molecular weight isomers were not detected or were present at very low concentrations in sediment in several estuaries with rural or lightly urbanised catchments situated to the north and south of the greater Durban area, although it is necessary to reiterate that only a single sediment sample was collected in the latter systems. Low and high molecular weight isomer concentrations for all stations combined were very strongly positively correlated ($r = 0.969$, $p < 0.001$) provided the data for station AMA1 in the Amanzimnyama River and station DBAY3 in Durban Bay were trimmed before correlation analysis (Figure 1.8). At the latter stations, low molecular weight isomers comprised a substantially higher proportion of the total polycyclic aromatic hydrocarbon concentration compared to other stations and were clear outliers. Low molecular weight isomers at station AMA2 in the Amanzimnyama River also comprised a comparatively high proportion of the total polycyclic aromatic hydrocarbon concentration, but the data point does not deviate significantly from the relationship for other stations in Figure 1.8 because the total polycyclic aromatic hydrocarbon concentration at this station was low (317.1 $ng.g^{-1}$).

Total polycyclic aromatic hydrocarbon concentrations were generally higher in sediment collected in rivers, estuaries and canals with highly urbanised and industrialised catchments, alluding to a more significant anthropogenic contribution of these chemicals to these systems. This is a common feature of catchments where land-use is urban and industrial in other regions of the world (*e.g*. Meador *et al*., 1995; Cundy *et al*.,

1997; Kimbrough and Dickhut, 2006; Garner *et al*., 2009; Tao *et al*., 2010). However, as discussed previously the sampling design was strongly biased to urbanised and industrialised catchments and the direct comparison of concentrations between catchments where numerous sediment samples were collected and those where only a single sediment sample was collected should be treated with caution.

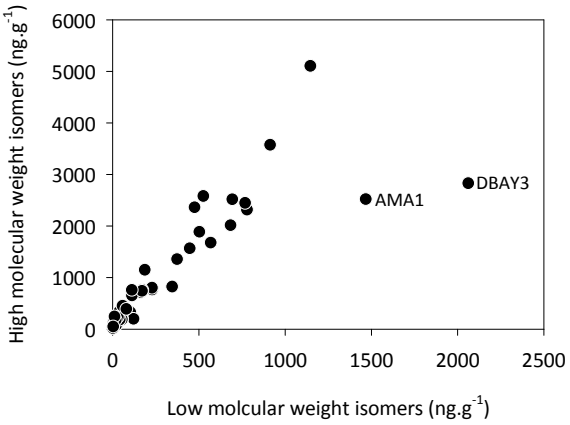

Figure 1.8. Relationship between low and high molecular weight polycyclic aromatic hydrocarbon isomer concentrations in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2011.

Fluoranthene and pyrene typically contributed most to the total polycyclic aromatic hydrocarbon concentration, followed in most cases by phenanthrene. In fact the contribution of phenanthrene was often as high as higher than the contribution of fluoranthene and pyrene. Fluoranthene and pyrene are typically dominant in urban and industrial settings. Isomer contributions to the total polycyclic aromatic hydrocarbon concentration for the majority of stations resembled contributions reported by Brown and Peake (2006) for street dust, stormwater reticulation sump sediment and suspended sediment in surface runoff in Dunedin, New Zealand, and by Gonzalez *et al*. (2000) for surface runoff in Paris, France. A similar isomer composition pattern has also been reported by other workers (*e.g.* Baumard *et al*., 1998; McCready *et al*., 2000).

As stated previously, sediment is the most important sink for polycyclic aromatic hydrocarbons in aquatic ecosystems. Fine-grained sediment with a high particulate organic matter content has a greater potential to accumulate polycyclic aromatic hydrocarbons compared to coarse-grained sand dominated sediment, because of the greater surface area provided by sediment grains for adsorption and because polycyclic aromatic hydrocarbons are partial to adsorption onto organic matter, which usually accumulates in fine-grained sediment (Maruya *et al*., 1996; Di Toro and De Rosa, 1998; Mitra *et al*., 1999; Wang *et al*., 2001). Affinity for the particulate phase generally increases with molecular weight/size of the polycyclic aromatic hydrocarbon molecule (isomer). Total polycyclic aromatic hydrocarbon (and the sum of low and high molecular weight isomer) concentrations for all rivers, estuaries and canals combined were very weakly correlated to the mud, total organic content and total organic carbon fractions of sediment (Figure 1.9). This was partly attributable to high polycyclic aromatic hydrocarbon concentrations in sediment with a low mud, total organic content and total organic carbon fractions. The weak relationships might reflect different sources, types and loadings of polycyclic aromatic hydrocarbons at the catchment specific level.

There were sufficient sediment samples to explore relationships between polycyclic aromatic hydrocarbon concentrations and the mud, total organic and total organic carbon fractions at the catchment scale for only a few catchments. In all cases the relationships were weak. However, there was a strong and statistically highly significant linear relationship between total polycyclic aromatic hydrocarbon concentrations and the mud fraction and total organic content of sediment in the uMngeni River estuary and tributaries of the estuary provided three high concentrations were considered outliers and trimmed from the dataset before regression analysis (Figure 1.10a,b). There was also a statistically highly significant, although somewhat weaker linear relationship between total polycyclic aromatic hydrocarbon concentrations and the total organic carbon fraction of sediment provided two high concentrations were considered outliers and trimmed from the dataset before regression analysis (Figure 1.10c). For the uMngeni River estuary and tributaries of the estuary it would thus appear that polycyclic aromatic hydrocarbons had, for the most part, partitioned onto particulate organic matter and/or mud in the sediment. It was not possible to determine whether particulate organic matter or mud was the more

important binding site since the mud fraction and total organic content were also strongly positively correlated (r^2 = 0.925, $p < 0.001$). The reason for the anomalously high total polycyclic aromatic hydrocarbon concentrations in sediment at the three stations identified as outliers in the uMngeni River estuary and tributaries of the estuary (*i.e.* stations MNG4, MNG7 and MNG11) is uncertain as these stations showed no spatial relationship (see Figure 1.3) and the total organic content of the sediment was not anomalously different to that at other stations on a mud normalised basis. It must, therefore, be presumed there were significant localised anthropogenic sources of polycyclic aromatic hydrocarbons in the vicinity of these stations, although there were no clear anthropogenic sources in the vicinities of the stations apart from the fact that station MNG11 was situated in a canal in an urbanised area.

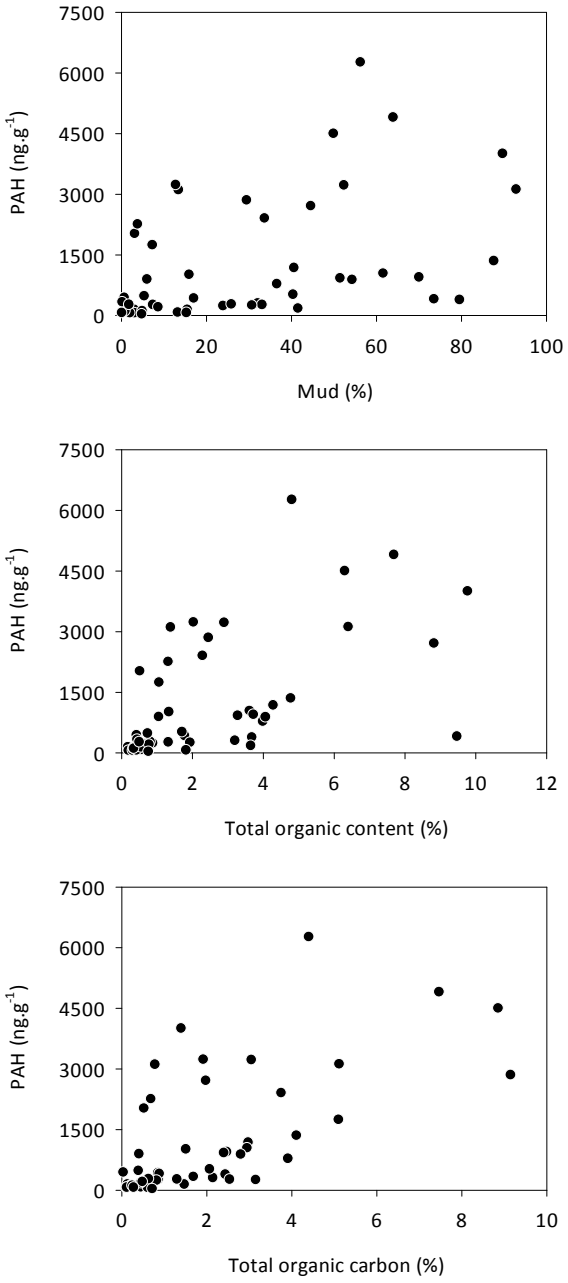

Figure 1.9. Relationship between total polycyclic aromatic hydrocarbon (PAH) concentrations and mud and particulate organic matter indicator fractions in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2011.

Identification of the actual sources of polycyclic aromatic hydrocarbons in the sediment samples is obviously impossible. This is because environmental samples usually contain polycyclic aromatic hydrocarbons from a combination of anthropogenic and natural sources and also undergo transformation before and after deposition (Green and Trett, 1989, Neff *et al*., 2005). However, polycyclic aromatic hydrocarbons in environmental samples collected in urbanised and industrialised areas typically have a predominantly anthropogenic origin, derived mostly from pyrolitic and to a lesser degree petrogenic sources. The analysis of both parent and alkylated polycyclic aromatic hydrocarbons would have aided source identification, but alkylated polycyclic aromatic hydrocarbons were not analysed because of cost implications. The ratio between various isomers is commonly used to discriminate between polycyclic aromatic hydrocarbons that have a predominantly pyrolitic or petrogenic source. The basis is that certain isomers are thermodynamically more stable than others and therefore tend to predominate if the polycyclic aromatic hydrocarbons were derived from combustion related sources, while less thermodynamically stable isomers tend to predominate if the polycyclic aromatic hydrocarbon source was petrogenic (Yunker and Macdonald, 1995; Yunker *et al*., 2002; Neff *et al*., 2005). For example, anthracene has a lower thermodynamic stability compared to phenanthrene and its predominance is indicative of a pyrogenic source, while the opposite is true for a petrogenic source (Buamard *et al*., 1998; Budzinski *et al*., 1997; Webster *et al*., 2002). Although numerous isomer ratios have been used for diagnostic purposes these often provide contradictory evidence because polycyclic aromatic hydrocarbons are usually derived from mixed sources. It would appear that ratios used for diagnostic purposes are sometimes based on those that provide results that

conform best to a predetermined expectation based on sampling site proximity to potential (especially petrogenic) anthropogenic sources of polycyclic aromatic hydrocarbons. The use of more than one ratio increases the level of confidence in diagnosing the source of polycyclic aromatic hydrocarbons, but even then it is necessary to note that diagnostic ratios are indicative of possible rather than unequivocal sources. Wagener *et al*. (2010, 2012) concluded that isometric ratios for parent polycyclic aromatic hydrocarbons are inefficient at discriminating petrogenic sources and tend to diagnose sources as being of a pyrogenic source even though alkylated homologues are indicative of a petrogenic source.

Cross-plots of four isomer ratios were used for diagnostic purposes in this study (Figure 1.11), using petrogenic-pyrogenic transition points defined by Yunker *et al*. (2002). The plots provide evidence that polycyclic aromatic hydrocarbons in the sediment sampled had a predominantly pyrolitic source. None of the plots provided evidence for an exclusively petrogenic source, although there were consistent signals at three stations for a significant petrogenic contribution to the total polycyclic aromatic hydrocarbon concentration. These are station AMA1 in the lower part of the Amanzimnyama River and stations DBAY3 and DBAY7 in Durban Bay. Station DBAY3 was situated at the point where the Amanzimnyama River discharges into Durban Bay. The suggestion of a significant petrogenic contribution of polycyclic aromatic hydrocarbons at stations AMA1 and DBAY3 thus establishes a link between these stations, which were separated by a distance of about 375 m. A significant petrogenic contribution makes sense for the Amanzimnyama River, as an oily sheen is often present on the water surface (B Newman, personal observation). The contribution of isomers to the total polycyclic aromatic hydrocarbon concentration at these stations was also similar, establishing a further link. Station DBAY7 was situated in the Island View Basin area of Durban Bay, which is the site of a bulk liquids import and storage facility. Station DBAY7 was situated near the position where bunker barges berth and near the point where drainage canals (Island View Canal) that pass through the storage facility discharge into this part of the Bay. Petroleum products are often visible on the water surface in one arm of Island View Canal (B Newman, personal observation). The stronger petrogenic signal at station BBAY7 thus probably reflects the input of polycyclic aromatic hydrocarbons leaked from the bulk liquids storage facility and/or (but less likely) contributions from bunker

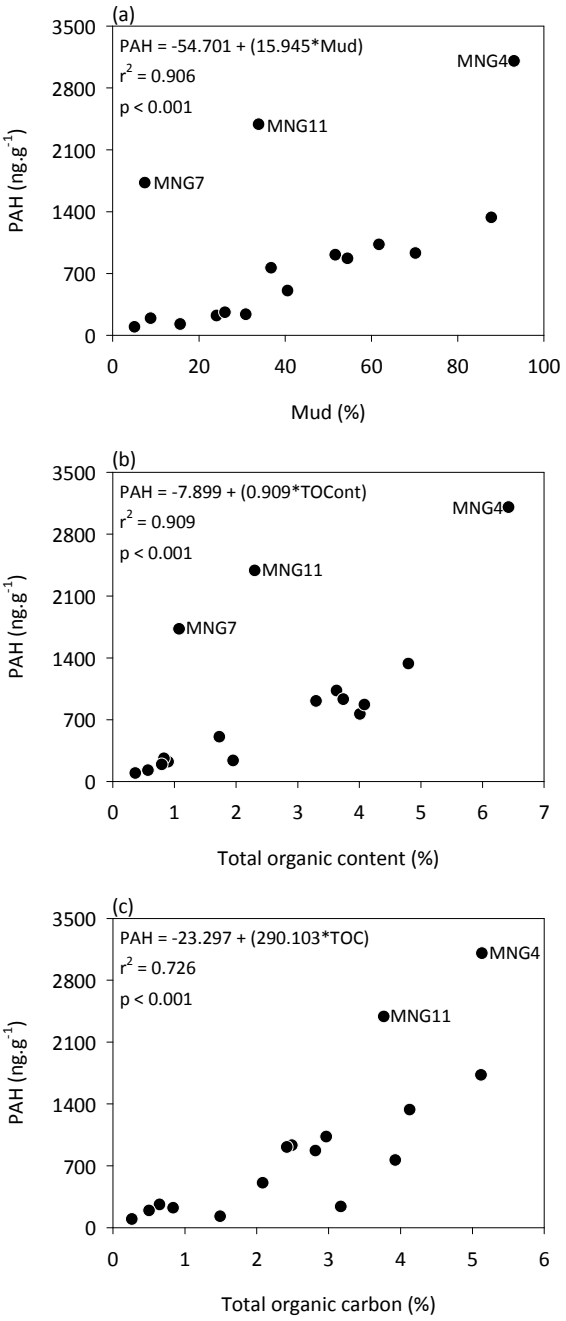

Figure 1.10. Relationship between total polycyclic aromatic hydrocarbon (PAH) concentrations and mud and particulate organic matter indicator fractions in sediment collected in the Mngeni River estuary and tributaries of the estuary in 2011. Parameters for linear regressions fitted to data trimmed of outliers (data points indicated by station identifiers) are given with coefficients of determination (r^2) and statistical significance (p).

barges.

The ratio between low and high molecular weight isomers is also often used to discriminate between polycyclic aromatic hydrocarbons that have a predominantly pyrolitic or petrogenic source (Soclo *et al*., 2000). A limitation of this approach is that it depends on the number of low and high molecular weight isomers analysed. For example, in this study nine low molecular weight and twelve high molecular weight isomers were analysed. Workers that only analyse for the sixteen United States Environmental Protection Agency priority polycyclic aromatic hydrocarbons, in contrast, analyse for six low molecular weight and ten high molecular weight isomers. The ratio between low and high molecular weight isomers in all sediment samples collected in rivers, estuaries and canals in the eThekwini area was less than one (Figure 1.12), confirming the predominantly pyrolitic origin of polycyclic aromatic hydrocarbons identified through the use of isomer ratio cross-plots. The highest ratios were for stations DBAY3 in Durban Bay and AMA1 and AMA2 in the Amanzimnyama River, suggesting the strongest petrogenic contribution at these stations. Two of these stations (stations AMA1 and DBAY3) agree with the findings using the isomer ratio cross-plots. The inclusion of station AMA2 establishes a further link between inputs of polycyclic aromatic hydrocarbons from the Amanzimnyama River and station DBAY3 situated off the inflow of this river, as discussed previously.

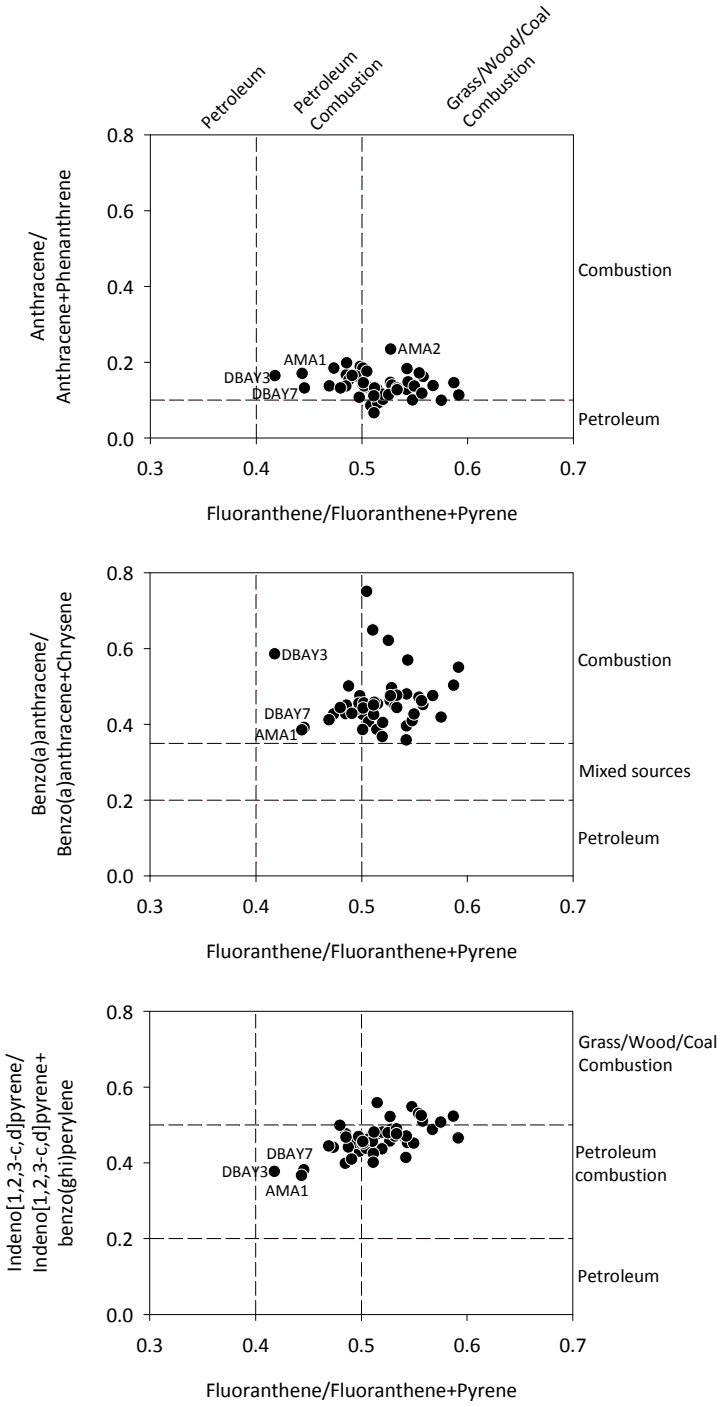

Figure 1.11. Cross plots of ratios of polycyclic aromatic hydrocarbon isomer concentrations in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2011. Selected data points are highlighted by station identifiers.

As discussed above the polycyclic aromatic hydrocarbons in sediment had a predominantly pyrolitic source. This is typical of urbanised and industrialised areas (*e.g.* Sun *et al*., 2009; Tao *et al*., 2010). There is, however, uncertainty on whether the predominant pyrolitic source was the combustion of grass, wood and coal, or combustion of petroleum related products. Each of these potential sources is logical for the study area considering that wood and to a lesser degree coal are burned for heat and cooking in low income households in informal townships and the large volume of vehicle traffic in the eThekwini area, while in the more rural areas there is significant burning of sugar cane to remove leaf foliage prior to harvesting.

As discussed previously, sediment quality guidelines are often used to estimate the toxicological risk posed

by chemicals in sediment when direct measures of such effects (*e.g.* toxicity testing) are not possible. There are no South African sediment quality guidelines for organic chemicals. Therefore, two sets of sediment quality guidelines derived to be protective of sediment-dwelling organisms in North American freshwater (MacDonald *et al*., 2000) and coastal (Long *et al*., 1995) ecosystems were used to interpret the potential toxicological risk posed by polycyclic aromatic hydrocarbons in sediment. None of the low and high molecular weight isomers nor the total polycyclic aromatic hydrocarbon concentration in sediment in estuaries situated to the north or south of the greater Durban area (the upper four and lower four stations in Figure 1.7) exceeded the Threshold Effect Concentration of the sediment quality guidelines derived by MacDonald *et al.* (2000) nor the Effects Range Low of the sediment quality guidelines derived by Long *et al.* (1995). In other words, the polycyclic aromatic hydrocarbons in sediment sampled in these estuaries were not present at concentrations likely to have been acutely toxic to sediment-dwelling organisms. Isomer concentrations in sediment at one, but usually substantially more stations in the remaining rivers, estuaries and canals exceeded the Threshold Effect Concentration or the Effects Range Low. In other words, the polycyclic aromatic hydrocarbon concentrations at these stations may have been acutely toxic to sediment-dwelling organisms. However, no isomer concentrations exceeded the Probable Effect Concentration of the sediment quality guidelines derived by MacDonald *et al.* (2000) or the Effects Range Median of the sediment quality guidelines derived by Long *et al.* (1995). The highest concentrations were in fact well below the latter guidelines, suggesting that the likelihood that polycyclic aromatic hydrocarbons in the sediment were exerting acute toxic effects on sediment-dwelling organisms was relatively low. The most frequent exceedance of isomer specific guidelines, and the number of stations where isomer concentrations exceeded guidelines was highest for sediment in Durban Bay (Figure 1.13). In fact, regardless of the sediment quality guidelines used at least one isomer was present at a concentration exceeding a guideline for sediment at all stations in Durban Bay apart from station DBAY7. The total polycyclic aromatic hydrocarbon concentration in sediment at thirteen stations exceeded the Threshold Effect Concentration (Figure 1.7). Once again the most frequent exceedance was for sediment in Durban Bay. In contrast, the total polycyclic aromatic hydrocarbon concentration at only two stations in Durban Bay and the single station in Island View Canal exceeded the Effects Range Low (Figure 1.7). This difference in the frequency of total polycyclic aromatic hydrocarbon concentration exceedance of the Threshold Effect Concentration and Effects Range Low is due to the fact that the Effects Range Low is about 2.5 times higher than the Threshold Effect Concentration (see Table 1.3). The Long *et al*. (1995) sediment quality guidelines also provide an Effects Range Low and Effects Range Median for the sum of low and high molecular weight isomers. The Effects Range Low for the sum of high molecular weight isomers was far more frequently

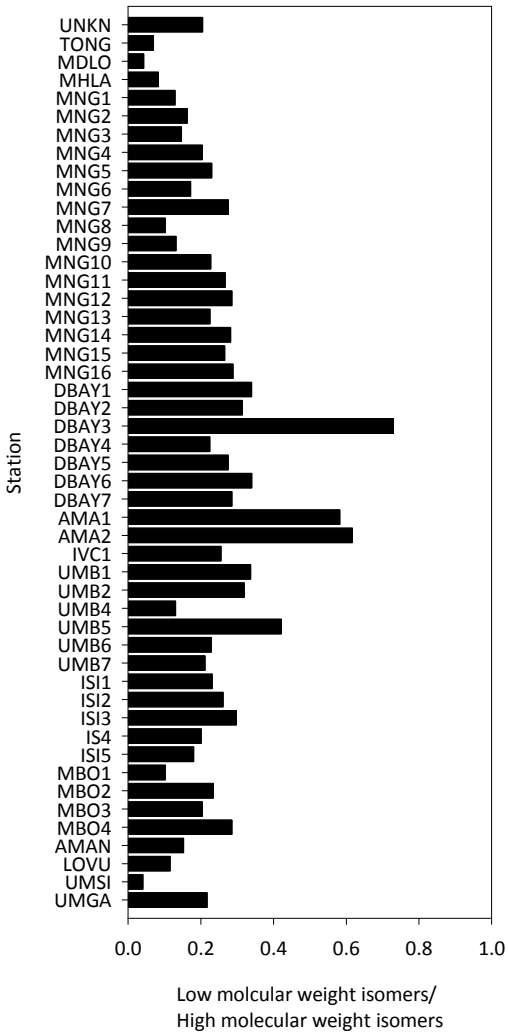

Figure 1.12. Ratio between low and high molecular weight polycyclic aromatic hydrocarbon isomer concentrations in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2011.

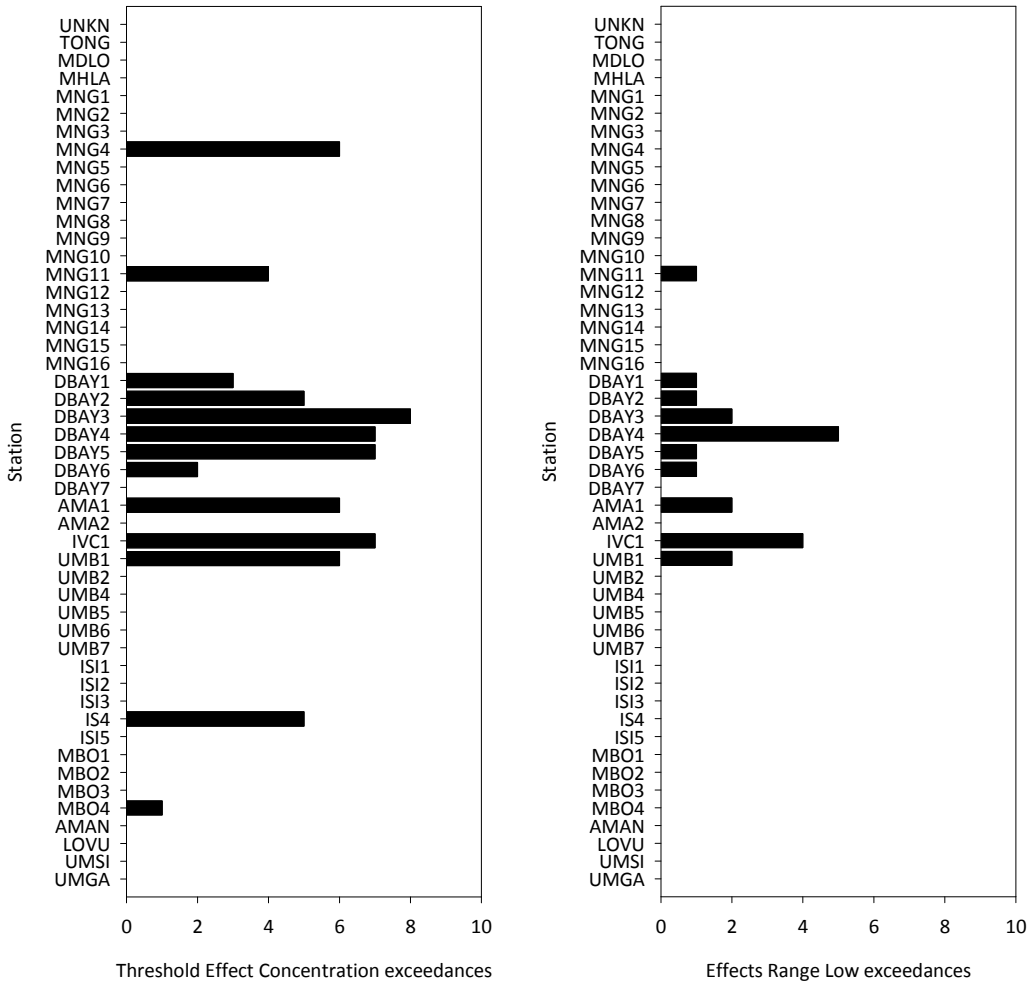

Figure 1.13. Number of low and high molecular weight polycyclic aromatic hydrocarbon isomer concentrations in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2011 that exceeded the Threshold Effect Concentration of the consensus-based sediment quality guidelines derived by MacDonald *et al*. (2000) and the Effects Range Low of the sediment quality guidelines derived by Long *et al*. (1995).

exceeded than the sum of low molecular weight isomers. Thus, based on polycyclic aromatic hydrocarbon concentration exceedances of sediment quality guidelines the greatest toxicological risk posed by these chemicals in sediment to sediment-dwelling organisms was in Durban Bay and Island View Canal, some parts of the uMngeni River estuary and tributaries of the estuary, and isolated parts of the Amanzimnyama, Umbilo, Umhlatuzana, Isipingo and Mbokodweni Rivers.

The above discussion is based on polycyclic aromatic hydrocarbon concentrations that were not normalised to the total organic carbon content of sediment, because both sets of sediment quality guidelines are for non-organic carbon normalised concentrations. Various studies have shown that non-organic carbon normalised sediment quality guidelines predict sediment toxicity as well or better than organic carbon normalised sediment quality guidelines in field-collected sediments (Barrick *et al*., 1988; Long *et al*., 1995; Ingersoll *et al*., 1996; USEPA 1996; MacDonald, 1997). Many workers nevertheless advocate for organic carbon normalisation since total organic carbon theoretically exerts a strong influence on polycyclic aromatic hydrocarbon bioavailability (Di Toro *et al*., 1991; McGroddy *et al*., 1996; Di Toro and De Rosa, 1998; Swartz, 1999). This is because organic contaminants generally adsorb more strongly to particulate organic matter compared to sediment grains, and hence more readily desorb from sediment grains. Some workers contend, however, that sorption to sediment is a complex and variable phenomenon that cannot be captured by simple organic carbon normalisation. For example, soot, which contributes little to the total organic carbon fraction of sediment, is a more important phase for polycyclic aromatic hydrocarbon adsorption. Total organic carbon normalised concentrations of organic contaminants should thus be

interpreted with caution. As a further confounding factor some workers do not normalise organic chemical concentrations to total organic carbon if the latter falls below a certain (but not consistent) fraction of the sediment whilst others normalise regardless of the total organic carbon fraction. Despite the focus of this study on non-organic carbon normalised concentrations it is worthwhile examining the influence of organic carbon normalisation under the assumption the lack of a relationship between total organic carbon and polycyclic aromatic hydrocarbon concentrations for the entire data set was due to high levels of contamination in some systems. Organic carbon normalisation of total polycyclic aromatic hydrocarbon concentrations reduced concentration variability between stations in numerous of the systems studied and resulted in fewer exceedances of sediment quality guidelines (Figure 1.7). Based on total organic carbon normalised concentrations the greatest likelihood for total polycyclic aromatic hydrocarbon concentrations posing a toxicological risk to sediment-dwelling organisms was for sediment in one part of Durban Bay, at one station in the Amanzimnyama River, at two stations in the lower reaches of the Umbilo and Umhlatuzana Rivers, and at a station in the Mbokodweni River (Figure 1.7). The highest risk was at station UMB2, in the lower reach of the Umbilo River. However, the concentration at this station was low, at 424.8 $\mu g.kg^{-1}$, and it seems unlikely this would have resulted in significant acute toxic effects to sediment-dwelling organisms.

2.3.4 Pesticides

Pesticides have societal and economic benefits, including increased agricultural yields through the control of crop pests, the control of pests that damage structures (*e.g.* wooden beams in homes), and the control insects (*e.g.* mosquitoes) that are vectors for microbes that pose a human health risk. However, these benefits are offset by the fact that pesticides may pose a risk to non-target organisms and to humans when present at elevated concentrations. It is in fact because of the significant ecological and human health risks posed by some pesticides that has led to restrictions on their use, or the banning of their production and use under the Stockholm Convention on Persistent Organic Pollutants. Perhaps the best known example is DDT, which is still used for the control of mosquitoes in the malaria belt in South Africa but its use as an agricultural pesticide is banned because of the significant ecological and human health risks posed by this pesticide.

Only three pesticides were detected in sediment at concentrations exceeding the method detection limit. The most frequently detected was DDT and its metabolites, in sediment at 31 of the 49 stations sampled (Figure 1.14). DDX concentrations not normalised to total organic carbon varied widely, from below the method detection limit at 37% of stations to 54.46 $ng.g^{-1}$ at station UMB5 in the Umhlatuzana River. The mean concentration was 4.63 $ng.g^{-1}$, with a standard deviation of 10.76 $ng.g^{-1}$. The ratio between technical DDT and its derivatives is often used to diagnose recent or historical sources of this pesticide. In general a ratio >0.5 for DDE+DDD/DDT is indicative of long-term weathering (Doong *et al*., 2002; Zhou *et al*., 2006). In 22 of the 31 sediment samples where DDT and/or its metabolites were detected at a concentration exceeding the method detection limit, the DDX concentration was comprised exclusively of technical DDT. Where DDE and/or DDD as well as DDT were detected the ratio exceeded 0.5 at only two stations, although it was only at 0.53 at one of these stations. The implication, therefore, is for recent sources of DDT in/to the study area. Although difocol is a (minor) source of technical DDT as it includes several DDT analogs as impurities (Batterman *et al*., 2008), difocol was not detected in any sediment samples. The widespread presence and suggestion of recent sources of DDT in the study area is interesting considering the study area does not fall within a malaria control area. In KwaZulu-Natal, malaria control areas are situated in the northern most part of the province, over 200 km from Durban. Also, as stated previously DDT was deregistered for agricultural use in South Africa in 1976 and banned in 1983 (Bouwman *et al*., 1990). There should, therefore, theoretically be no significant sources of DDT in the eThekwini area. Although DDT has an approximate half-life of 10-20 years it seems unreasonable to expect there is still a substantial reservoir of DDT in sediment in rivers in the eThekwini area. This is because the rivers sampled are relatively small

and typically not of a depositional nature, and are frequently scoured by strong river flow after heavy rains. There may be some historical DDT in estuaries as these are depositional zones, although this also seems unlikely as sediment in estuaries in the eThekwini area is also periodically scoured during floods. Batterman *et al*. (2008) reported the widespread presence of DDT (technical and metabolites) in air samples collected in Durban and suggested that an important source of this pesticide may be long-distance atmospheric transport from malaria control areas. If so then this could account for the widespread presence of DDT in sediment in rivers, estuaries and canals in the eThekwini area. Nevertheless, it seems unlikely diffuse atmospheric deposition could result in the high concentrations detected in sediment at some stations (*e.g.* 54.46 $ng.g^{-1}$ at station UMB5 in the Umhlatuzana River), and suggests there are other localised sources of DDT in the study area.

DDX concentrations were very weakly correlated to the mud, total organic content and total organic carbon fractions of sediment when all stations were considered. However, as was the case for polycyclic aromatic hydrocarbons the relationships were stronger if data for the uMngeni River estuary and tributaries of the estuary were considered alone. The relationship between DDX concentrations and the mud fraction of sediment in the uMngeni River estuary and tributaries of the estuary was strong provided one concentration was identified as an outlier and trimmed before regression analysis (Figure 1.15a). The relationship between DDX concentrations and the total organic content and total organic carbon fractions of sediment was weak, although the relationship improved dramatically for the total organic content relationship if three concentrations were identified as outliers (Figure 1.15b,c). For the uMngeni River estuary and tributaries of the estuary it would thus appear that DDT and its metabolites had, for the most part, partitioned onto particulate organic matter and/or mud in the sediment, as was the case for polycyclic aromatic hydrocarbons. It was not possible to determine whether particulate organic matter or mud was the more important binding site, even though the coefficient of determination is substantially higher for the relationship between DDX concentrations and the mud fraction of sediment, since the mud and total organic content fractions were also strongly positively correlated ($r^2 = 0.925$, $p < 0.001$).

At 20 of the 31 stations where DDT and/or its metabolites were detected the DDX concentration exceeded the Effects Range Low of the sediment quality guidelines derived by Long *et al*. (1995) (Figure 1.14). The concentration in sediment at station UMB5 in the Umhlatuzana River also exceeded the Effects Range Median of these sediment quality guidelines while the concentration at station DBAY1 in Durban Bay was only slightly lower than this guideline. The Threshold Effect Concentration of the sediment quality guidelines derived by MacDonald *et al.* (2000) for DDX is about five times higher than the narratively equivalent Effects Range Low, with the result that DDX concentrations in sediment at only ten of the 31 stations exceeded this guideline (Figure 1.14). No DDX concentrations exceeded the Probable Effect Concentration of these sediment quality guidelines, which is almost twelve times higher than the narratively equivalent Effects Range Median of the sediment quality guidelines derived by Long *et al*. (1995). If exceedance of both the Effects Range Low and Threshold Effect Concentration is taken as a more reliable estimate of the potential toxicological risk posed by DDX concentrations to sediment-dwelling organisms then the greatest risk was at ten stations, the bulk of which (six) were situated in the uMngeni River estuary and tributaries of the estuary (Figure 1.14). However, the greatest potential risks were at station DBAY1 in Durban Bay and station UMB5 in the Umhlatuzana River (Figure 1.14). This said, as mentioned above the DDX concentration at the latter stations was far lower than the Probable Effect Concentration, and Long *et al.* (1995) expressed a low confidence in the guidelines they derived for DDX, which creates uncertainty on whether concentrations at the latter stations were posing a significant toxicological risk to sediment-dwelling organisms.

Total organic carbon normalisation of DDX concentrations significantly reduced concentration variability in the uMngeni River estuary and tributaries of the estuary (Figure 1.15). Total organic carbon normalised DDX concentrations at numerous stations still exceeded the Effects Range Low, but now only a single

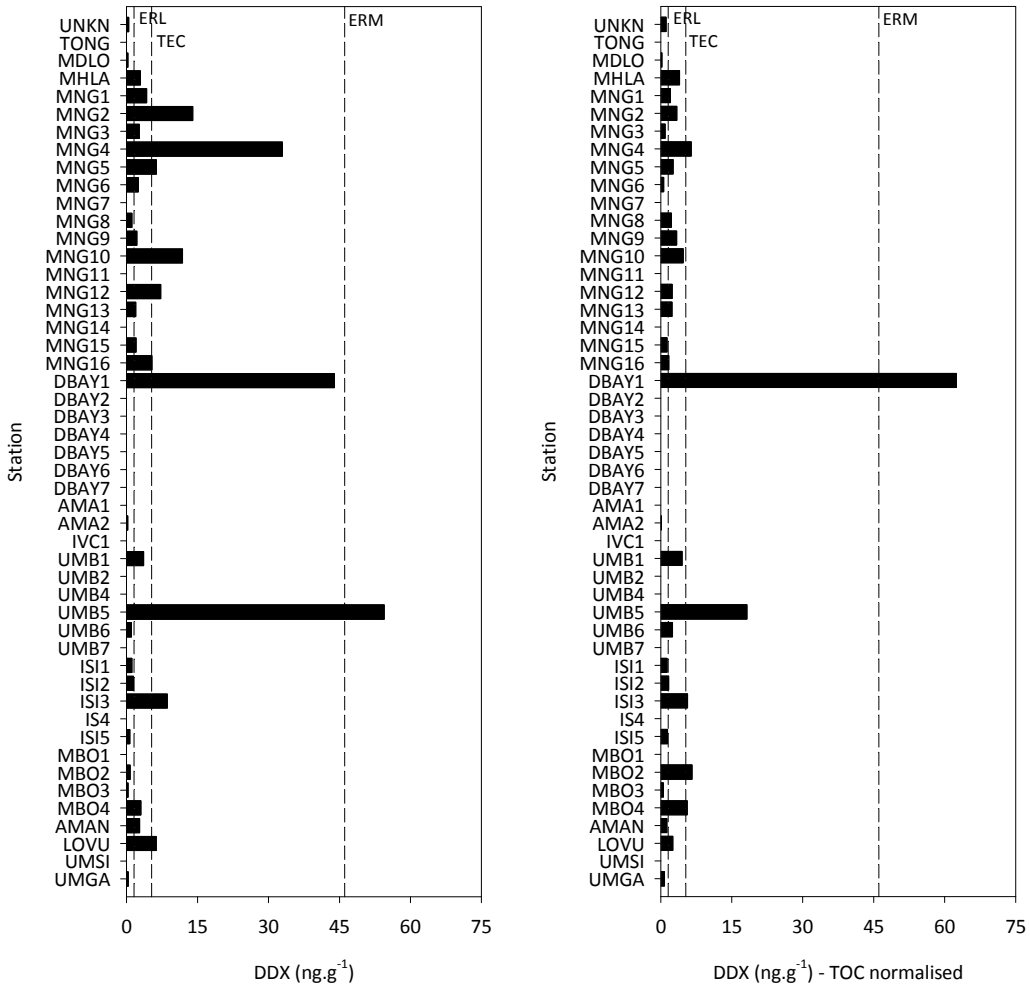

Figure 1.14. DDX concentrations not normalised (left) and normalised (right) to total organic carbon (TOC) in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2011. The dashed lines denote the Threshold Effect Concentration (TEC) of the consensus-based sediment quality guidelines derived by MacDonald *et al*. (2000) and the Effects Range Low (ERL) and Effects Range Median of the sediment quality guidelines derived by Long *et al*. (1995).

concentration exceeded the Threshold Effect Concentration. A generally similar effect was evident in other rivers, estuaries and canals, although here numerous DDX concentrations still exceeded the Threshold Effect Concentration and/or the Effects Range Low. The most significant changes were for stations DBAY1 and UMB5. At station DBAY1 the normalised concentration increased substantially, due to the low total organic carbon fraction (0.70%) of the sediment at this station. As a consequence the concentration exceeded the Effects Range Median of the sediment quality guidelines derived by Long *et al.* (1995) (Figure 1.15). At station UMB5 the opposite effect was evident, with the consequence that the concentration fell substantially below the Effects Range Median.

The detection of chlorpyrifos at relatively high concentrations in sediment at three stations in close proximity in the uMngeni River estuary (stations MNG5, MNG6 and MNG7) suggests a localised source of this organophosphate pesticide (Figure 1.16). Chlorpyrifos was also detected in sediment at station UMB5 in a tributary of the Umbilo River, but at a far lower concentration compared to stations in the uMngeni River estuary. Station UMB5 is the station at which the highest DDT concentration was detected (Figure 1.14). Chlorpyrifos is an insecticide and acaricide found in insecticides used in households and on golf courses, and as a non-structural wood treatment. It also is used to control foliage and soil-borne insects on a variety of food and feed crops (USEPA, 2002a,b). Of these possible applications two golf courses are situated on the banks of the uMngeni River estuary and are possible sources of chlorpyrifos, although any conclusion on sources is speculative. This is especially so considering chlorpyrifos was not detected in

sediment at other stations in the uMngeni River estuary, in spite of these being situated near one of golf courses. The sediment quality guidelines derived by Long *et al.* (1995) and Macdonald *et al.* (2000) do not provide guidelines for chlorpyrifos.

Metabolites of chlordane (cis- and trans-chlordane, and trans-nonachlor) were detected at a concentration exceeding the method detection limit in sediment at a single station, namely station AMA2 in the Amanzimnyama River (Figure 1.16). The ratio of cis- to trans-chlordane was relatively low (0.49), suggesting a recent source of this pesticide (Eitzer *et al*., 2001). The total chlordane concentration exceeded the Threshold Effect Concentration but not the Probable Effect Concentration of the consensus-based sediment quality guidelines derived by MacDonald *et al*. (2000) (Figure 1.16). The sediment quality guidelines derived by Long *et al*. (1995) do not provide a guideline for chlordanes.

The absence of numerous organochlorine pesticides analysed in sediment collected in rivers, estuaries and canals in the eThekwini area, including aldrin, chlordane, hexachlorobenzene and dieldrin, is interesting considering these were detected in air samples collected in Durban by Batterman *et al*. (2008). DDX and hexachlorobenzene were also detected on plastic pellets collected on the shoreline at a location in Durban by Ogata *et al*. (2009), although many of the organochlorine pesticides detected in air samples were not detected on the pellets. The pellets, which are feed stock for the production of plastic products, are unintentionally released to the environment during manufacturing and transport. Because of the nature of the plastic pellet surface, hydrophobic pollutants adsorb onto the pellets from the surrounding water, with concentration factors of up to a million times. Hexachlorocyclohexane (including Lindane) concentrations on pellets collected in Durban were the highest measured for pellets collected at any location in the world. Batterman *et al*. (2008) also reported high Lindane concentrations in air samples collected in Durban. The reason for the absence of hexachlorocyclohexane in sediment in rivers, estuaries and canals in light of its presence in atmospheric samples and on pellets collected on the shoreline in Durban is thus interesting.

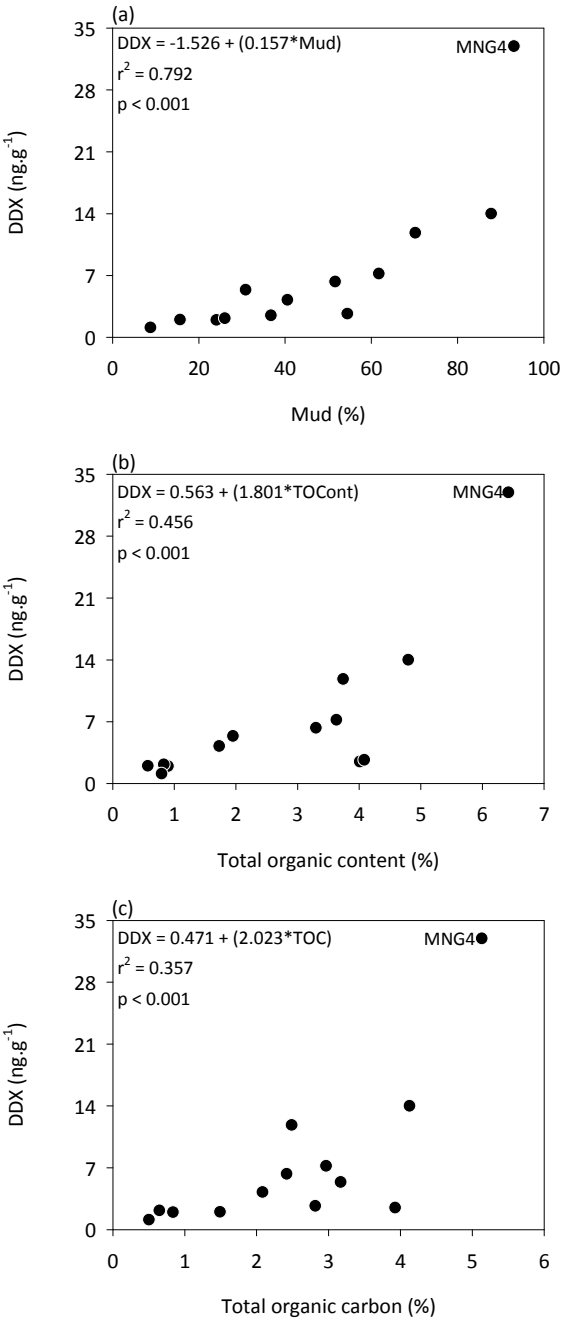

Figure 1.15. Relationship between DDX concentration and mud and particulate organic matter indicator fractions in sediment collected in the Mngeni River estuary and tributaries of the estuary in 2011. Parameters for linear regressions fitted to data trimmed of outliers (data points indicated by station identifiers) are given with coefficients of determination (r^2) and statistical significance (p). Selected data points are highlighted by station identifiers.

2.3.5 Polychlorinated biphenyls

Polychlorinated biphenyls are a class of synthetic organic chemicals that were used extensively as insulating fluids in electrical transformers, capacitors and other heat transfer devices, as lubricants in compressors, and as plasticisers in paints and rubber sealants amongst other uses (ATSDR, 2000). Polychlorinated biphenyls resist thermal and other degradation processes, reflecting their commercial application where chemical stability was required from a safety, operation and durability perspective. This resistance to thermal and other degradation processes means, however, that polychlorinated biphenyls are stable and persist for long periods in the environment. The manufacture and use of polychlorinated biphenyls in the United States of America, the world's major producer of these chemicals, was banned in 1979, and elsewhere in the world via the Stockholm Convention on Persistent Organic Pollutants in 2001 due to toxicological concerns. Polychlorinated biphenyls have a high bioaccumulation and biomagnification potential and are listed as probable carcinogens, and despite a ban on their production and restrictions on their use continue to pose ecological and human health risks in many regions of the world (*e.g.* Baars *et al*., 2004; Diamanti-Kandarakis *et al*., 2009; Stahl *et al*., 2009; Blocksom *et al*., 2010). In the United States of America, for example, polychlorinated biphenyls are responsible for the most fish consumption advisories after mercury (USEPA, 2011).

Polychlorinated biphenyls constitute a class of 209 chemical compounds (or congeners) with different biological activity and toxicity. In practice, however, there are about 100-150 congeners present in polychlorinated biphenyl formulations that were in use and that are found in environmental samples. The so-called dioxin-like congeners exert a wide range of toxic responses particularly focused on the endocrine system, while the ortho-substituted congeners seem to produce neurotoxic effects (Rice and Hayward, 1997). In aquatic ecosystems, polychlorinated biphenyls tend to accumulate in sediments and biota because of their hydrophobic character, low water solubility and persistence (Smedes and de Boer, 1997).
Polychlorinated biphenyls were detected at concentrations exceeding the method detection limit in 24 of the 49 sediment samples collected in rivers, estuaries and canals in the eThekwini area. Sediment at at least one station in each highly urbanised and industrialised catchment with the exception of the Island View Canal revealed contamination by polychlorinated biphenyls (Figure 1.17). Polychlorinated biphenyls were not detected in sediment in estuaries situated to the north and south of the greater Durban area (*i.e.* the upper four and lower four stations in Figure 1.17). The absence of polychlorinated biphenyl contamination of sediment in the latter estuaries makes sense when the primary applications of polychlorinated biphenyls and the nature of anthropogenic activities in these lightly urbanised or rural catchments is considered. The link between polychlorinated biphenyl contamination of sediment and catchment land-use is thus self-evident in these estuaries, although one of the catchments is fairly urbanised (Amanzimtoti River estuary). The relationship between catchment land-use and polychlorinated biphenyl contamination of sediment was not always clearly evident, however, since the Umbilo and Umhlatuzana Rivers flow through highly urbanised and industrialised areas yet there was minimal contamination of sediment by polychlorinated biphenyls (Figure 1.17). This may reflect strong river flow induced scouring of sediment and associated contaminants from these rivers. Total polychlorinated biphenyl concentrations varied widely, from below the method detection limit at 49% of stations to 459.55 $ng.g^{-1}$ at station DBAY3 in Durban Bay (Figure 1.17). The mean concentration was 224.20 $ng.g^{-1}$, with a standard deviation of 77.00 $ng.g^{-1}$. The 25^{th}, 50^{th} and 75^{th} percentile of the concentration distribution was 0.00, 0.00 and 8.68 $ng.g^{-1}$. Thus, polychlorinated biphenyl concentrations at the majority of stations were low. The highest concentrations were detected at stations DBAY3 and DBAY5 in Durban Bay and station AMA2 in the Amanzimnyama River, followed by stations ISI2 and ISI3 in the Isipingo River and estuary (Figure 1.17). The high total polychlorinated biphenyl concentration at station AMA2 in the Amanzimnyama River and station DBAY3 in Durban Bay establishes a link between these stations considering station DBAY3 was situated at the point where the Amanzimnyama River flows into Durban Bay (see Figure 1.3). It is, however, interesting that no polychlorinated biphenyls were detected at station AMA1 in the latter river. The high polychlorinated biphenyl concentration at

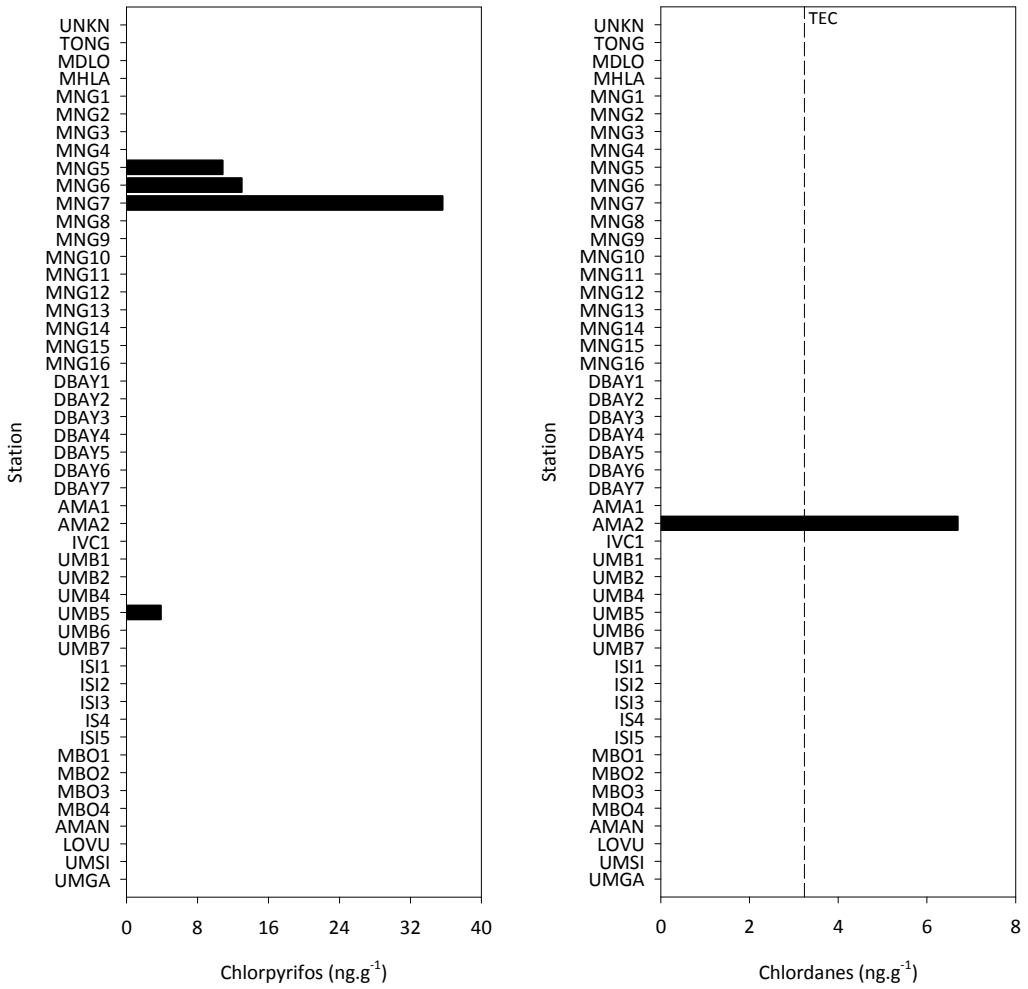

Figure 1.16. Chlorpyrifos and total chlordane concentrations in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2011. The dashed line denotes the Threshold Effect Concentration (TEC) of the sediment quality guidelines derived by MacDonald *et al*. (2000).

station DBAY5 in Durban Bay may have been derived from vessel construction and maintenance activities performed in this part of the Bay. Historically, polychlorinated biphenyl containing paints were applied to the hulls of vessels, as extenders and antifouling agents (Kang *et al*., 2000; UNEP, 1999; Maruyama *et al*., 1983; Sanger *et al*., 1999; Edge *et al*., 2001), and polychlorinated biphenyls in sediment near vessel maintenance and construction facilities have been shown to, or strongly suspected to be derived from paints applied to vessel hulls (*e.g.* Hong *et al*., 2005). The polychlorinated biphenyl concentration at station DBAY2 in Durban Bay probably reflects inputs from the central business district of Durban via surface runoff considering this station was situated at the point where a stormwater outfall discharges into the Bay. Likely sources of polychlorinated biphenyls in the city include leakages at electrical substations. Polychlorinated biphenyls were, however, not detected at station DBAY1, which was situated only 280 m as the crow flies from station DBAY2 and at the point where another stormwater outfall that also has as its catchment part of the central business district discharges into the Bay. The difference in concentrations between these stations suggests localised inputs of polychlorinated biphenyls to stormwater conveyance systems. A similar concentration difference between these stations was evident for DDX (see Figure 1.14), also supporting the contention of localised contaminant inputs to stormwater conveyance systems.

As was the situation for polycyclic aromatic hydrocarbons and DDX, total polychlorinated biphenyl concentrations at all stations were very weakly correlated to the mud, total organic content and total organic carbon fractions of sediment. Here, however, the relationships remained very weak even if concentrations for the uMngeni River estuary and tributaries of the estuary were considered alone.

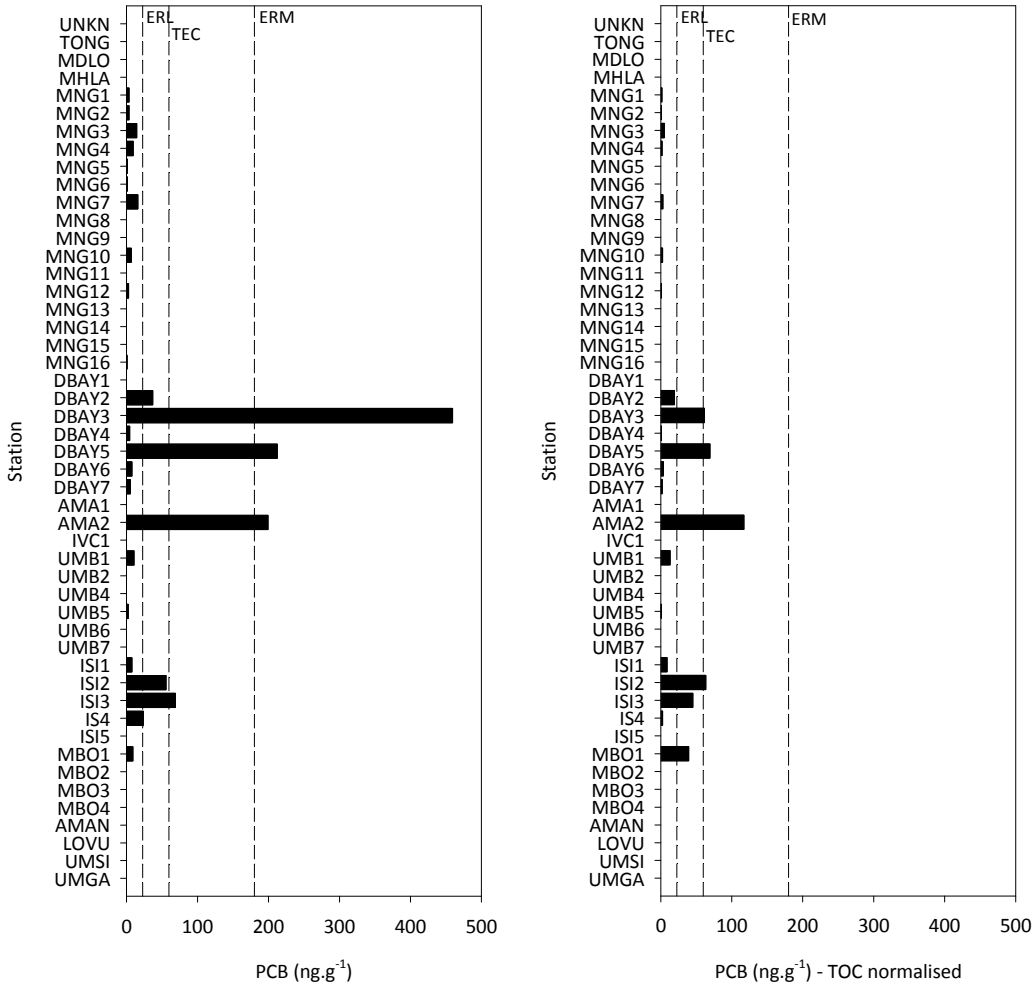

Figure 1.17. Total polychlorinated biphenyl (PCB) concentrations not normalised (left) and normalised (right) to total organic carbon (TOC) in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2011. The dashed lines denote the Threshold Effect Concentration (TEC) of the consensus-based sediment quality guidelines derived by MacDonald *et al*. (2000) and the Effects Range Low (ERL) and Effects Range Median (ERM) of the sediment quality guidelines derived by Long *et al*. (1995).

Total polychlorinated biphenyl concentrations in sediment at four stations, two in Durban Bay and one in each of the Amanzimnyama and Isipingo Rivers exceeded the Threshold Effect Concentration but not the Probable Effect Concentration of the consensus-based sediment quality guidelines derived by MacDonald *et al*. (2000) (Figure 1.17). In comparison, total polychlorinated biphenyl concentrations in sediment at the latter stations and two additional stations in Durban Bay and the Isipingo River exceeded the Effects Range Low of the sediment quality guidelines derived by Long *et al*. (1995), while concentrations at two stations in Durban Bay and a station in the Amanzimnyama River also exceeded the Effects Range Median (Figure 1.17). This difference in exceedance of these sediment quality guidelines is due to the fact that the Threshold Effect Concentration is about 2.6 times higher than the narratively equivalent Effects Range Low, and the Probable Effect Concentration is about 3.6 times higher than the narratively equivalent Effects Range Median. Once again the sediment quality guidelines provide a different understanding of the potential toxicological significance of chemical concentrations in sediment to sediment-dwelling organisms. The highest likelihood that total polychlorinated biphenyl concentrations were posing a toxicological risk to sediment-dwelling organisms was at stations DBAY3 and DBAY5 in Durban Bay and station AMA2 in the Amanzimnyama River. The single highest probability was at station DBAY3, where the concentration substantially exceeded the Effects Range Median (Figure 1.17).

Thus, despite a ban on the production of polychlorinated biphenyls in the late 1970s these chemicals are still entering aquatic ecosystems in the greater Durban area, and in certain rivers, estuaries and canals have

accumulated in sediment to concentrations that are likely posing a toxicological risk to sediment-dwelling organisms.

Organic carbon normalised polychlorinated biphenyl concentrations at numerous stations exceeded the Effects Range Low and Threshold Effect Concentration, but no longer the Effects Range Median (Figure 1.17). The greatest likelihood that total polychlorinated biphenyl concentrations were posing a toxicological risk to sediment-dwelling organisms based on total organic carbon normalised concentrations remained certain parts of Durban Bay, the Amanzimnyama River and Isipingo River and estuary, although there was a likelihood the concentration at station MBO1 in the Mbokodweni River was also posing a risk. The latter concentration was elevated in significance relative to the non-organic carbon normalised concentration due to the low total organic carbon fraction (0.23%) in the sediment at this station.

2.3.6 Metals

As stated previously, although not target analytes the sediment collected at each station was also analysed for a suite of metals, to provide a point for comparison considering that metals and organic chemicals often have similar anthropogenic sources and behave similarly in aquatic ecosystems (*e.g.* sediment is the major sink).

Determining whether sediment is contaminated by chemicals such as polychlorinated biphenyls and DDX is easy since these only have an anthropogenic origin. The mere presence of these chemicals in sediment is thus indicative that the sediment is contaminated. Determining whether sediment is metal contaminated is far more complicated, for several reasons. First, metals are a ubiquitous, naturally occurring component of sediment. The mere presence of metals in sediment does not, therefore, imply the sediment is contaminated. Second, metal concentrations in uncontaminated sediment can vary by orders of magnitude over relatively small spatial scales depending on sediment mineralogy, granulometry and organic content amongst other factors (Wangersky, 1986; Windom *et al*., 1989; Krumglaz *et al*., 1992; Loring and Rantala, 1992; Thomas and Bendell-Young, 1999; Kersten and Smedes, 2002). Within a geologically homogenous area, grain size is the most important factor controlling natural metal concentrations in sediment (Förstner, 1989). This is because aluminosilicates, the dominant natural metal-bearing phase of sediment, predominate in clay. Sand, in contrast, is comprised predominantly of metal deficient quartz. Particulate organic matter in sediment acts as an additional host for metals. High metal concentrations in sediment may thus simply reflect the mineralogy of parent material and/or granulometry and organic content of the host sediment, and not necessarily contamination. Third, despite input and transport dissimilarities, naturally occurring and anthropogenically introduced metals tend to accumulate in the same areas (Loring, 1991, Hanson *et al*., 1993). Because of these complexities an identical metal concentration in two sediment samples collected in the same aquatic ecosystem may reflect contamination in one instance but not the other, because the granulometry and organic content of the sediment is different.

To meaningfully interpret metal concentrations in sediment the mineralogical and granulometric factors that influence the natural variation of metal concentrations must be compensated for before naturally occurring concentrations can be differentiated from anthropogenically enhanced concentrations (*i.e.* concentrations indicative of contamination). This can be accomplished by the procedure of normalisation, which mathematically normalises metal concentrations to a co-occurring conservative element that provides a tracer of crustal decomposition (Hanson *et al*., 1993, Kersten and Smedes 2002). The purpose of normalisation is to compensate for the factors that influence the natural concentrations of metals in sediment. After normalisation, metal concentrations in equally contaminated or uncontaminated sediment samples of a different granulometry should not differ significantly. Two forms of normalisation can be applied, namely primary (or granulometric) and secondary (or geochemical) normalisation. These are not mutually exclusive. In fact, Kersten and Smedes (2002) recommend a two tier normalisation process that incorporates both primary and secondary normalisation. Nevertheless, most workers follow the

geochemical normalisation approach.

The basis for geochemical normalisation is that while metal concentrations vary between crustal material from one region to another, the relative proportions of metals within crustal material from a particular region tend to be fairly constant (*e.g.* Turekian and Wedepohl, 1961; Taylor and McLennan, 1981; Martin and Whitfield, 1983; Wedepohl, 1995; Kersten and Smedes, 2002). Since there is relatively little fractionation between metals and aluminosilicates during weathering (Schropp and Windom, 1988), metal concentrations in uncontaminated sediment tend to reflect the relative proportions of metals in the parent material. This relative constancy of the proportions of metals and the usually strong inverse correlation between metal concentrations and the mud fraction of sediment permits the use of geochemical normalisation, wherein relationships between metal concentrations and the co-occurring concentration of a metal that provides a conservative tracer of crustal decomposition are modelled through linear but occasionally multiple linear regression. Linear regression models defined in this manner are generally referred to as baseline metal concentration models, or simply baseline models. Although several metals may be used as a proxy for the major natural metal-bearing phases of sediment, aluminium and iron are most commonly used for this purpose. Aluminium is generally considered the better normaliser since it is a major constituent of fine-grained aluminosilicates, with which the bulk of trace metals are associated. Consequently, aluminium concentrations are usually strongly inversely correlated to grain size and strongly positively correlated to co-occurring metal concentrations. Aluminium is also stable and not affected by early diagenic processes and strong redox effects commonly observed in sediment (Schiff and Weisberg, 1999; Kersten and Smedes, 2002), and is highly refractory. Although iron is not as tightly incorporated into the crystal lattice of aluminosilicates as aluminium, iron oxide coatings, which serve as a host for metals, are usually associated with sediments in definite quantities related to the sediment surface area (Förstner and Wittman, 1979). Consequently, iron concentrations are also usually strongly inversely correlated to grain size and strongly positively to co-occurring metal concentrations. A potential limitation to the use of iron is that it may be highly mobile in anoxic sediments, leading to its enrichment at the sediment-water interface through the precipitation of iron oxide when exposed to aerobic conditions (Finney and Huh, 1989) or in deeper sediments as a result of co-precipitation with sulphides (Gobeil *et al*., 1997). This natural enrichment may lead to the underestimation of enrichment by other metals when iron is used as the normaliser.

Natural concentrations of aluminium and iron, which are respectively the third and fourth most abundant elements in the earth's crust (Wedepohl, 1995), are orders of magnitude higher than concentrations of metals of concern from a toxicological perspective ($mg.g^{-1}$ versus $\mu g.g^{-1}$ concentrations respectively). The high natural concentrations of aluminium and iron are considered to 'swamp' the usually low anthropogenic inputs of these metals to aquatic ecosystems (acid mine drainage excluded) and their concentrations are, therefore, likely to remain relatively unchanged (or have a low variability) in anthropogenically impacted areas (Schropp *et al*., 1990). The low natural concentrations of trace metals in sediment mean their concentrations are far more sensitive to anthropogenic inputs. This leads to a change in the ratio between a metal and the normaliser, which is the basis for identifying anthropogenic (and natural) metal enrichment of sediment.

Aluminium and iron normalised baseline models were recently defined for a suite of metals in sediment in Durban Bay (CSIR, unpublished data). The procedure used to define the baseline models is not discussed here in detail but is available on request from the authors of this report. The baseline models appear to be suitable for interpreting metal concentrations in sediment in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal, although there is uncertainty associated with the cadmium and mercury models. This is because cadmium and mercury concentrations often do not show a strong linear relationship to other co-occurring metal concentrations.

A theoretical example, based on the baseline model for chromium in sediment in Durban Bay, can be used to demonstrate how the baseline models are used to interpret metal concentrations in sediment (Figure 1.18). The first step is to superimpose metal concentrations that require interpretation onto the baseline model. In Figure 1.18, four hypothetical chromium concentrations are superimposed on the baseline model, each with an identical corresponding aluminium concentration. Metal concentrations that fall between the baseline model prediction limits, such as hypothetical chromium concentration 1, fall within the baseline concentration range and are obviously interpreted as uncontaminated. Concentrations that exceed the baseline model upper prediction limit, such as hypothetical chromium concentrations 2, 3, and 4, are interpreted as enriched. In rare instances metal concentrations may fall below a baseline model lower prediction limit and are interpreted as metal depleted, unreliable, or possibly reflecting enrichment/contamination of the sediment by the normaliser. The chromium baseline model is useful for explaining other features pertinent to baseline models. As stated previously, a metal normaliser, which in the case of Figure 1.18 is aluminium, is used as a proxy for the mud fraction of sediment. Aluminium concentrations on the extreme left of the plot are indicative of sediment with a low mud fraction (*i.e.* coarse, sandy sediment) and on the extreme right of sediment with a high mud fraction. Also evident in Figure 1.18 is that there is no single baseline concentration for chromium (and indeed other metals) in sediment but rather a range of concentrations at any particular aluminium concentration, that is, the range between the prediction limits. The range exists because different material in sediment contributes slightly different concentrations of metals, and because of analytical variability. Also evident is that the baseline concentration range changes in sympathy with the fraction of mud in the sediment, as reflected by the aluminium concentration. To provide an example, the baseline concentration range for chromium at an aluminium concentration of 10 $mg.g^{-1}$, indicative of sand dominated sediment, is between 17.82-46.75 $\mu g.g^{-1}$. In contrast, at an aluminium concentration of 50 $mg.g^{-1}$, indicative of mud dominated sediment, the baseline concentration range is between 120.14-149.07 $\mu g.g^{-1}$. In both cases the baseline concentration range is identical (28.93 $\mu g.g^{-1}$) but the actual concentrations are obviously different. It is these complexities that make it difficult to determine whether sediment is metal contaminated and which must be compensated for before metal concentrations in sediment can correctly be interpreted.

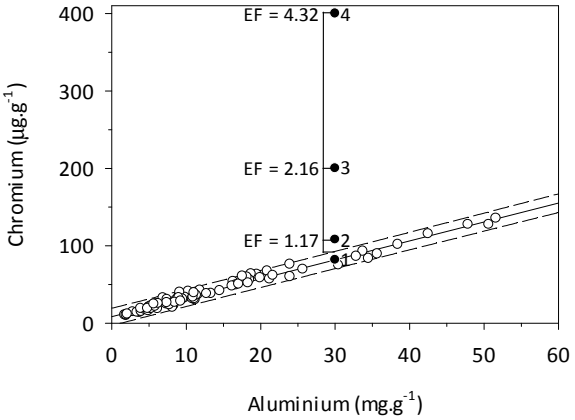

Figure 1.18. Aluminium normalised baseline model for chromium in sediment from Durban Bay. Open symbols represent chromium concentrations used to define the baseline model, while numbered solid symbols represent four hypothetical scenarios: 1. concentration falls within baseline model upper and lower 99% prediction limits (dashed lines flanking solid regression line) and is interpreted as not enriched; 2, 3 and 4. concentrations exceed baseline model upper prediction limit and are interpreted as reflecting various levels of enrichment that can broadly be defined as very low (2) through to high (4). Enrichment Factors (EF) for hypothetical concentrations 2, 3 and 4 are provided. Concentrations 3 and 4 would be interpreted as reflecting enrichment through an anthropogenic contribution with a high level of confidence. Scenario 2 would be interpreted as reflecting enrichment through an anthropogenic contribution with a moderate level of confidence.

A metal concentration that exceeds the baseline model upper prediction limit does not necessarily imply the concentration was enhanced through an anthropogenic contribution (*i.e.* contamination) but rather that the concentration is atypical of the data used to define the baseline model (Horowitz *et al*., 1991). Several reasons in addition to an anthropogenic contribution can lead to a metal concentration exceeding a baseline model upper prediction limit, including analytical errors, poor baseline model assumptions, the probability that concentrations in some samples will naturally exceed the baseline model upper prediction limit (in a normally distributed population, at the 99% prediction level 1 in every 100 concentrations could

conceivably naturally exceed the limit), and natural enrichment not captured by the data set used to define the baseline model (Schropp *et al*., 1990; Rae and Allen, 1993). Interpretation of metal enrichment, and ultimately whether this reflects contamination thus requires consideration of ancillary factors, including possible (bio)geo-chemical processes leading to natural enrichment (*e.g.* diagenesis), the difference between a metal concentration and baseline model upper prediction limit (*i.e.* the magnitude of enrichment), the number of metals in a sediment sample at concentrations that exceed baseline model upper prediction limits, and the position of metal enriched sediment relative to known or suspected anthropogenic sources of metals. The greater the exceedance of a baseline model upper prediction limit by a metal concentration, the greater the number of metals enriched in sediment at a particular location, and the nearer the location is to known or suspected anthropogenic sources of metals the greater the likelihood the metal concentration/s were enhanced through an anthropogenic contribution and thus reflect contamination. In Figure 1.18, hypothetical chromium concentration 2 is interpreted as enriched, but whether this reflects contamination should only be concluded after considering the abovementioned ancillary factors. This is because the concentration only marginally exceeds the baseline model upper prediction limit. In the case of hypothetical chromium concentrations 3 and 4, exceedance of the baseline model upper prediction limit is pronounced and these concentrations would be interpreted as enriched due to an anthropogenic contribution with a high level of confidence, that is, the sediment at these stations is interpreted as being contaminated by chromium. The magnitude of exceedance of the baseline model upper prediction limit by hypothetical chromium concentrations 3 and 4 is in fact sufficient that this interpretation would be made even if no other metals in the sediment were enriched.

The baseline models provide an effective tool for identifying metal enriched sediment. However, it is difficult to visually interpret data in scatterplot format when a large proportion of the metal concentrations exceed the baseline model upper prediction limit, even if the data points are identified by station identifiers. A more effective approach is to calculate and display Enrichment Factors, either with the data for sampling points arranged in a logical sequence in graphs or as spatially explicit plots. An Enrichment Factor is a measure of how many times a metal concentration exceeds or falls below a pre-defined concentration. The benefit of Enrichment Factors is that they can be directly compared, unlike metal concentrations, because the natural factors controlling the variability of metal concentrations in sediment have been compensated for in the Enrichment Factor. Enrichment Factors were calculated using the upper prediction limit of baseline models as the denominator. In other words, the point for comparison is the highest concentration predicted by the baseline model for granulometrically equivalent sediment. Metals in sediment at concentrations below the method detection limit were replaced with a surrogate concentration of one-half the method detection limit for the calculation of Enrichment Factors. Enrichment Factors can be visualised using the same hypothetical example used previously to demonstrate how baseline models are used for interpreting metal concentrations in sediment (Figure 1.18). As expected, the Enrichment Factors for hypothetical concentrations 2, 3 and 4 increase the further the concentration is from the baseline model upper prediction limit. An Enrichment Factor of 4.32, as is the case for hypothetical concentration 4, means that concentration is a little over four times higher than the concentration predicted at the baseline model upper prediction limit. It is important to note that baseline model prediction limits are not linear but biconcave, being narrowest at the average and widest at the extremes of the normaliser distribution. However, prediction limits are near enough linear if the data set used to define the baseline model is large, the concentrations are more or less evenly distributed across the normaliser range, and the concentration variability around the regression line is relatively narrow. The inaccurate estimation of enrichment attributable to the assumption that the upper prediction limit is linear when it is not is small for the baseline models defined for Durban Bay and has little material effect on the interpretation of metal concentrations.

In Figure 1.19, metal concentrations in sediment collected in rivers, estuaries and canals in the eThekwini area are superimposed on aluminium normalised baseline models for metals in sediment in Durban Bay.

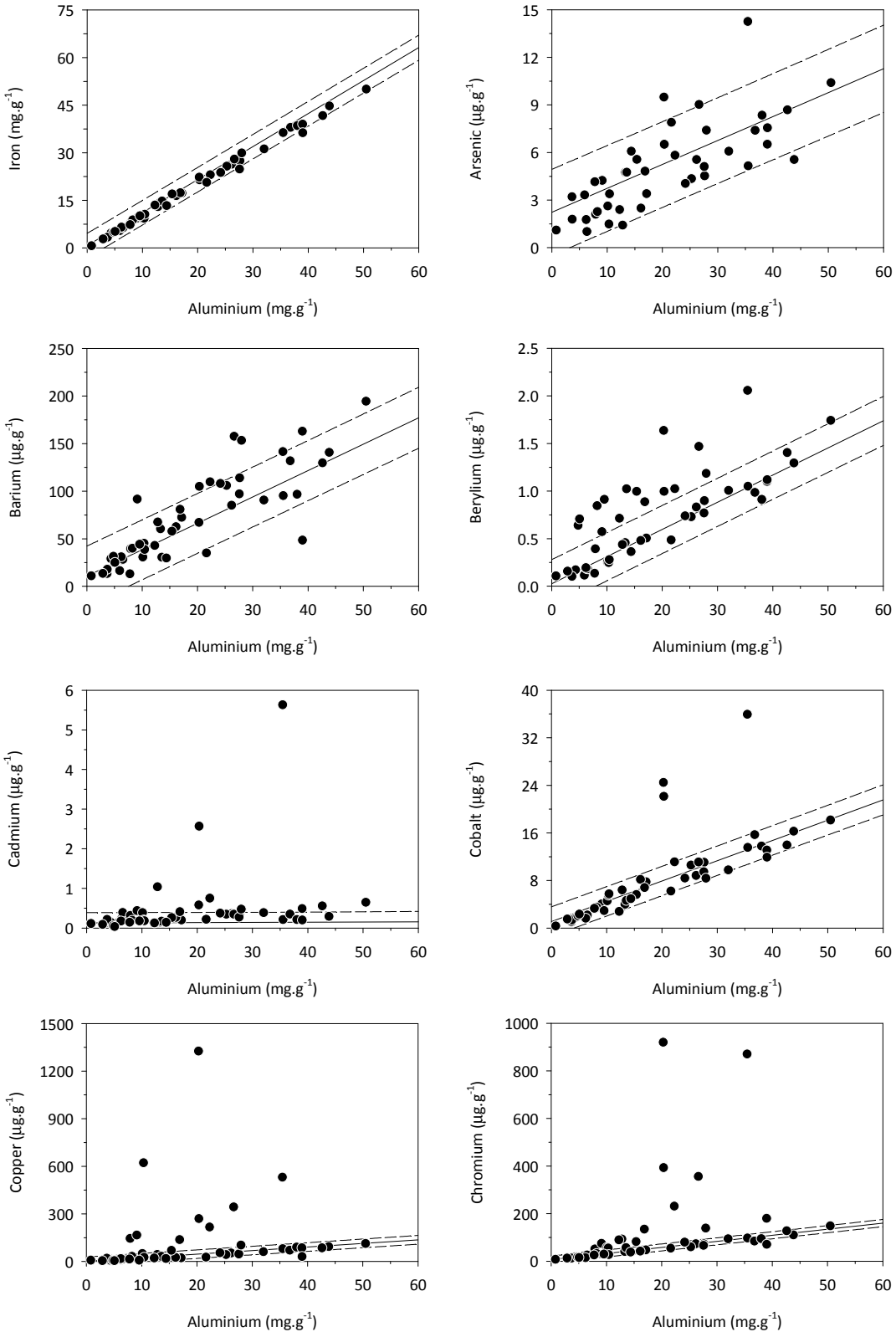

Figure 1.19. Aluminium normalised baseline models for metals in sediment in Durban Bay with metal concentrations in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2011 superimposed.

Metal concentrations in sediment at a large proportion of stations fall within baseline model upper and lower prediction limits, that is, within the concentration range expected for granulometrically equivalent but uncontaminated sediment. However, one or more concentrations of each metal apart from iron exceed a baseline model upper prediction limit, that is, the sediment was metal enriched/contaminated. Figure 1.20 presents Enrichment Factors for each metal. The enrichment of sediment by several metals was

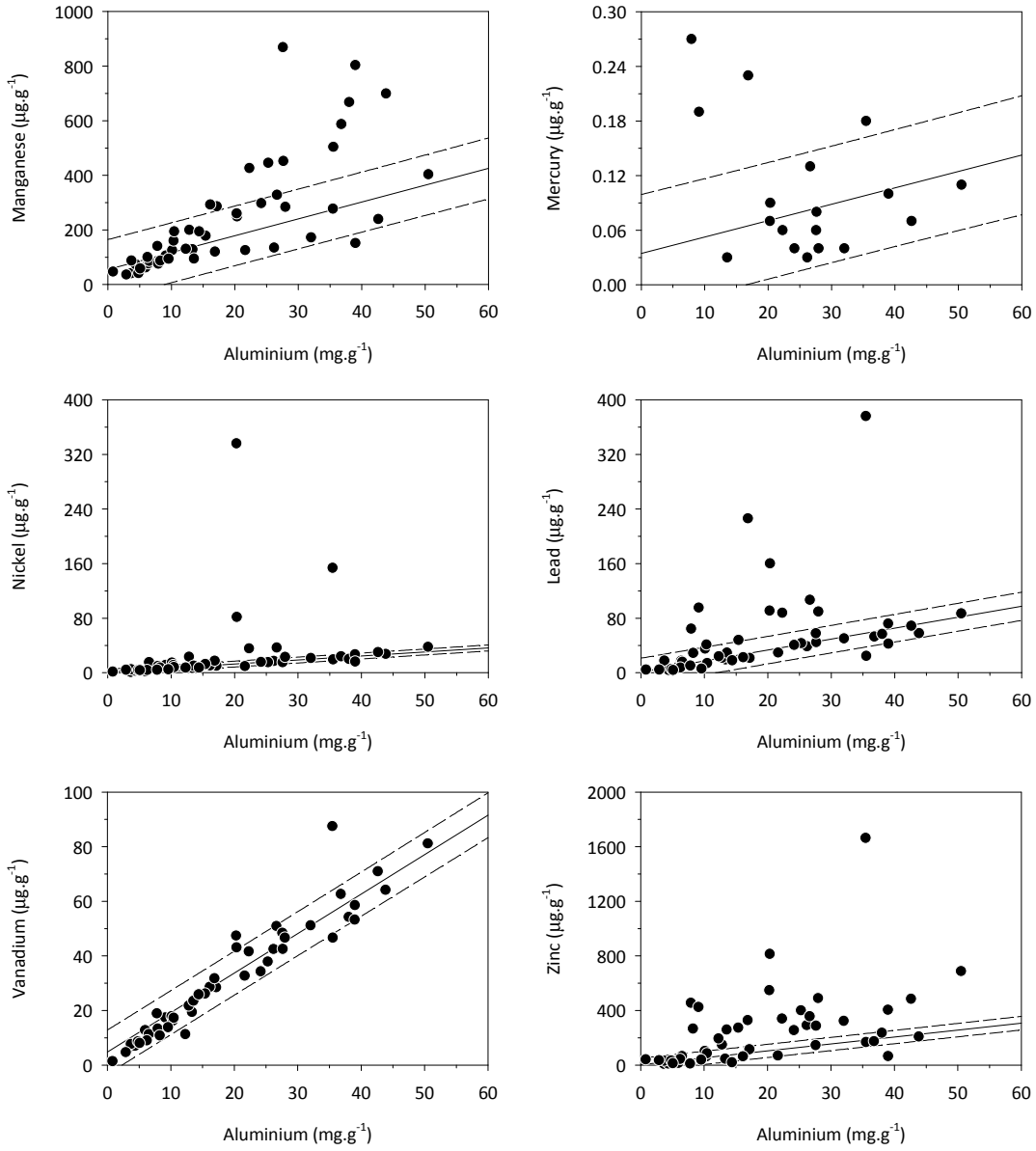

Figure 1.19 continued. Aluminium normalised baseline models for metals in sediment in Durban Bay with metal concentrations in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2011 superimposed.

infrequent and/or of a low magnitude (*e.g.* arsenic, barium, cobalt). The most severely contaminated sediment from a cumulative Enrichment Factor perspective was at station IVC1 in Island View Canal, followed by station AMA1 in the Amanzimnyama River and station DBAY 3 in Durban Bay (Figure 1.21). The most frequently enriched metal was zinc (at 47% of stations), followed by beryllium and chromium (33% of stations each) and cadmium (27% of stations). No metals were enriched in sediment in estuaries situated to the north and south of the greater Durban area (*i.e.* the top four and lower four stations in Figures 1.20 and 1.21). This lack of metal enrichment/contamination in the latter estuaries agrees with lack of or minimal contamination of sediment in these estuaries by pesticides and polychlorinated biphenyls, and low polycyclic aromatic hydrocarbon concentrations. Again, it is necessary to reiterate that only single sediment samples were collected in these systems.

In other catchments the sediment at one but usually more stations was metal enriched/contaminated. The most frequently metal enriched/contaminated sediment was in Durban Bay, the Amanzimnyama River, Island View Canal, and Isipingo River and its estuary (Figure 1.21). For example, sediment at station AMA1 in the Amanzimnyama River was contaminated by 11 metals, while sediment at stations DBAY3 and DBAY6

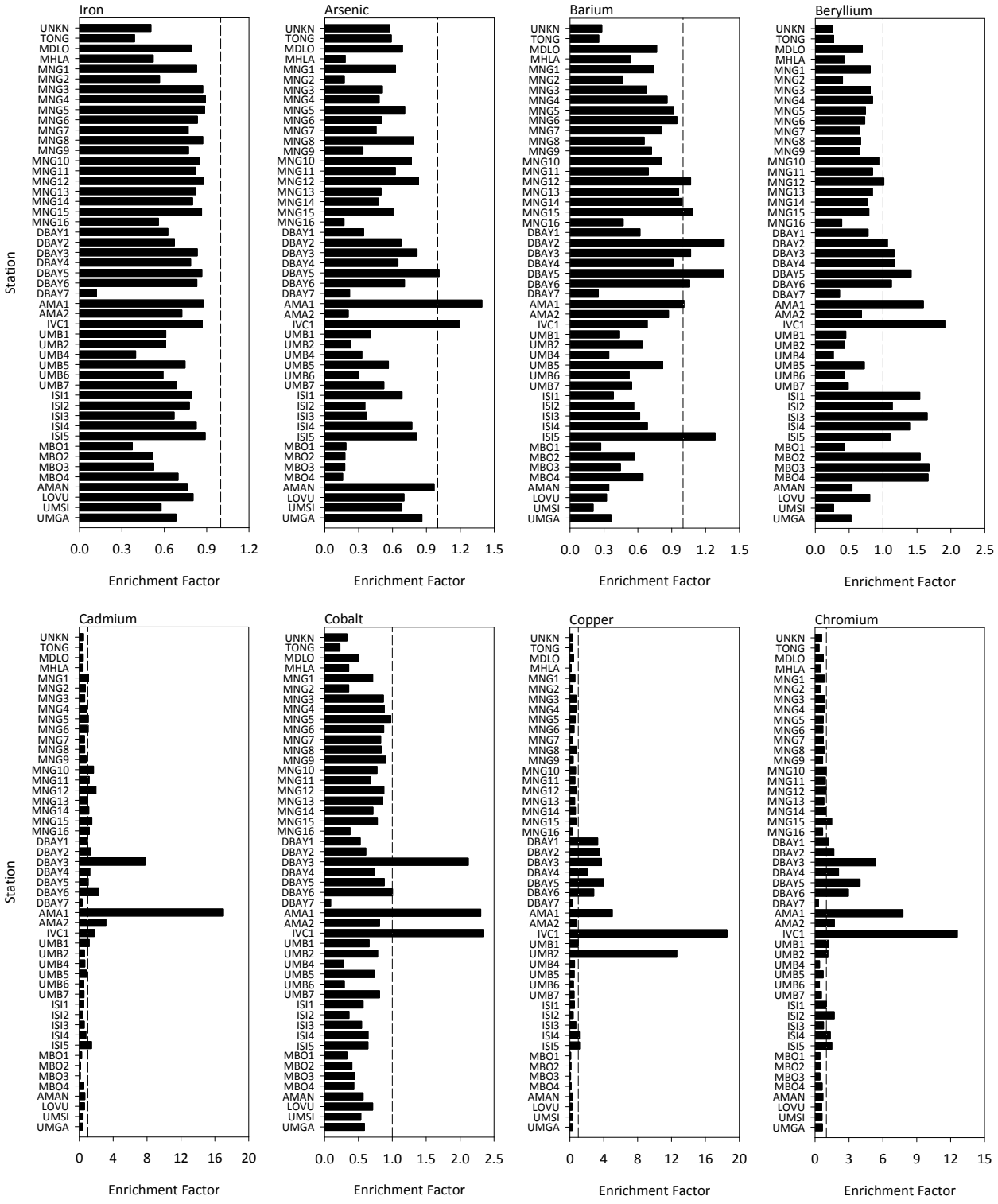

Figure 1.20. Enrichment Factors for metals in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2011. The dashed lines represent an Enrichment Factor of one.

in Durban Bay and IVC1 in Island View Canal was contaminated by 10 metals (Figure 1.20).

Some metal concentrations and associated Enrichment Factors were extremely high. For example, Enrichment Factors for copper and nickel in sediment at station IVC1 in Island View Canal were 18.53 and 19.42 respectively, that is, 18.53 and 19.42 times higher than the highest copper and nickel concentrations expected in granulometrically equivalent but uncontaminated sediment. There was infrequent, yet significant metal contamination of sediment in some systems (*e.g.* copper at station UMB2 in the Umhlatuzana River) (Figure 1.20). It is beyond the scope of this study to speculate on the anthropogenic

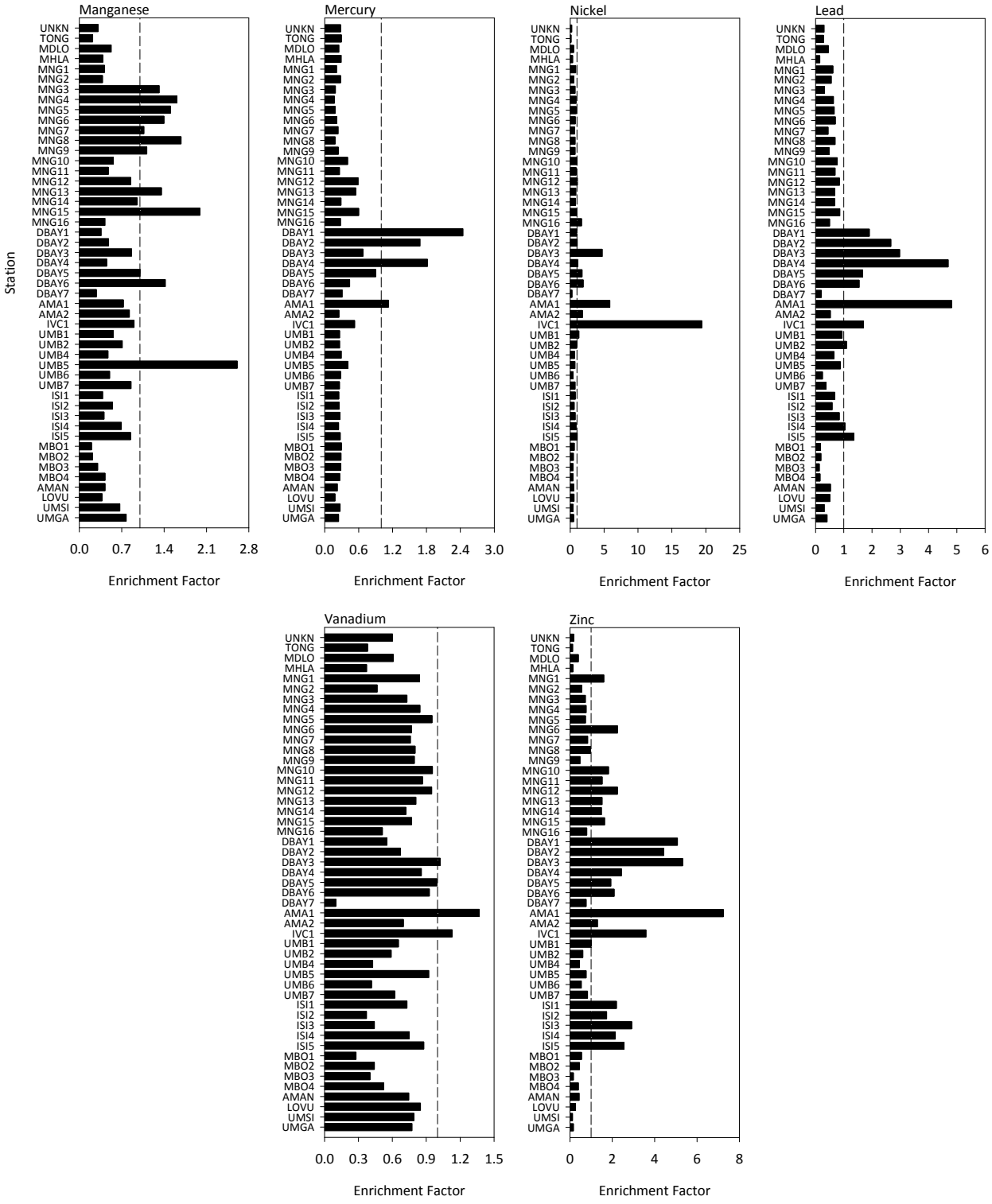

Figure 1.20 continued. Enrichment Factors for metals in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2011. The dashed lines represent an Enrichment Factor of one.

sources of metals in cases where the Enrichment Factors were high enough to suspect contamination save to state that there are numerous anthropogenic sources of metals to aquatic ecosystems in urbanised and industrialised areas. In Durban Bay this also includes port associated activities.

Interesting enrichment patterns were evident for some metals, as follows. First, beryllium enrichment of sediment was evident in Durban Bay, the Amanzimnyama River, Island View Canal, Isipingo River and estuary, and Mbokodweni River (Figure 1.20). These systems are situated in the so-called South Durban Basin and the frequency of beryllium enrichment suggests there was an anthropogenic source of beryllium

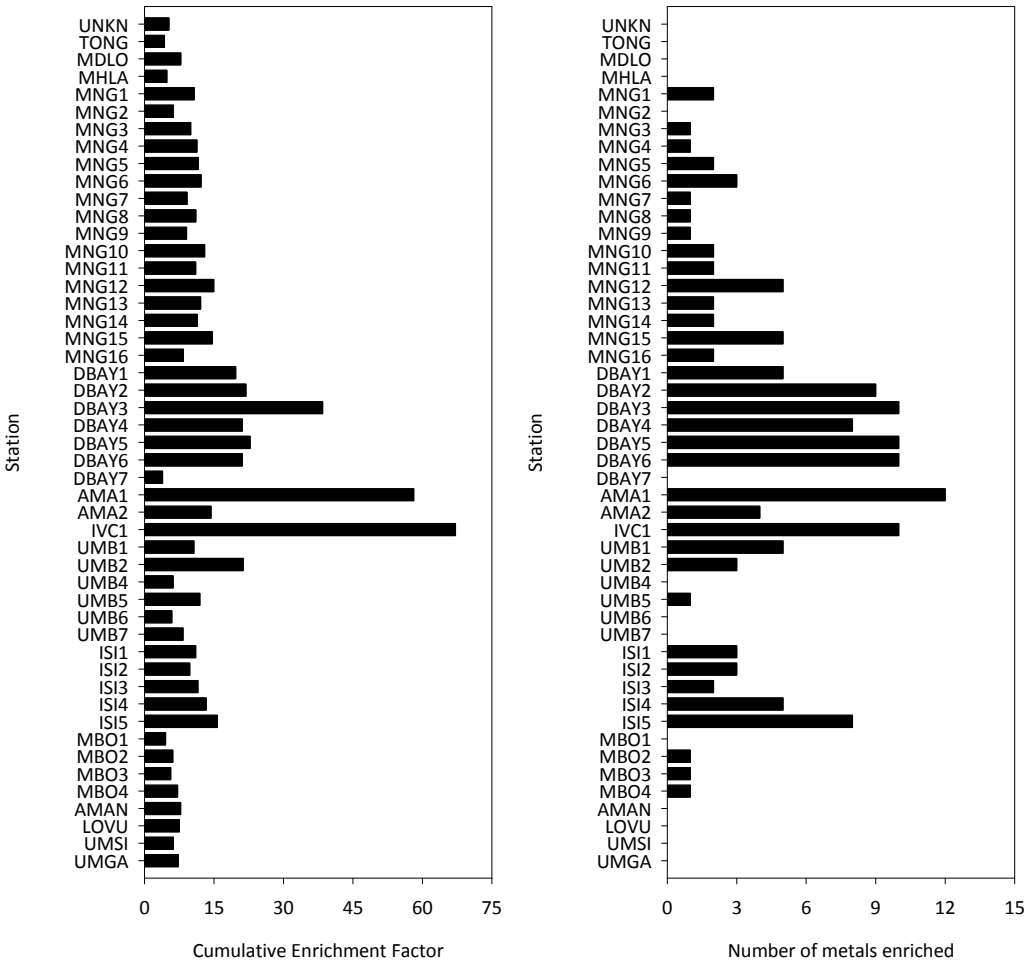

Figure 1.21. Cumulative Enrichment Factors (left) and number of metals at enriched concentrations (right) in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2011.

in the area. However, there was over extraction of beryllium in three batches of sediment samples analysed, which included samples from these systems, and the enrichment might thus represent apparent rather than real enrichment. Second, sediment at station IVC1 in the Island View Canal and at station AMA1 in the Amanzimnyama River was contaminated by cobalt (Figure 1.20). The sediment at station DBAY3, situated in Durban Bay off the Amanzimnyama River inflow, was also contaminated by cobalt and establishes a link between contamination in the river and this part of the Bay. This is interesting since cobalt is rarely a contaminant of sediment in South African coastal ecosystems (CSIR, unpublished data). Sediment is periodically exported through the Coal Terminal in Durban Bay and sediment in the vicinity of this terminal is usually contaminated by cobalt (CSIR, unpublished data), but is too far from the Island View Canal and particularly the Amanzimnyama River for the same anthropogenic source to be relevant at the latter stations. The source of cobalt in the Island View Canal may reflect inputs from a rail truck cleaning yard situated adjacent to the canal, but the source of cobalt to the Amanzimnyama River is uncertain. Third, there was widespread manganese enrichment of sediment in the uMngeni River estuary and to a lesser degree tributaries of the estuary. In contrast, the sediment at only three stations in other systems was enriched by manganese (Figure 1.20). It is difficult to determine whether the manganese enrichment represents contamination since this metal is highly mobile in sediment under certain conditions (*e.g.* anoxia), leading to its natural enrichment at the sediment-water interface.

Although the sediment quality guidelines derived by MacDonald *et al*. (2000) and Long *et al*. (1995) that were used to interpret the potential toxicological significance of organic chemical concentrations in sediment also provide guidelines for metals, these are inappropriate for application in South African aquatic ecosystems. This is because the guidelines for several metals are lower than the baseline

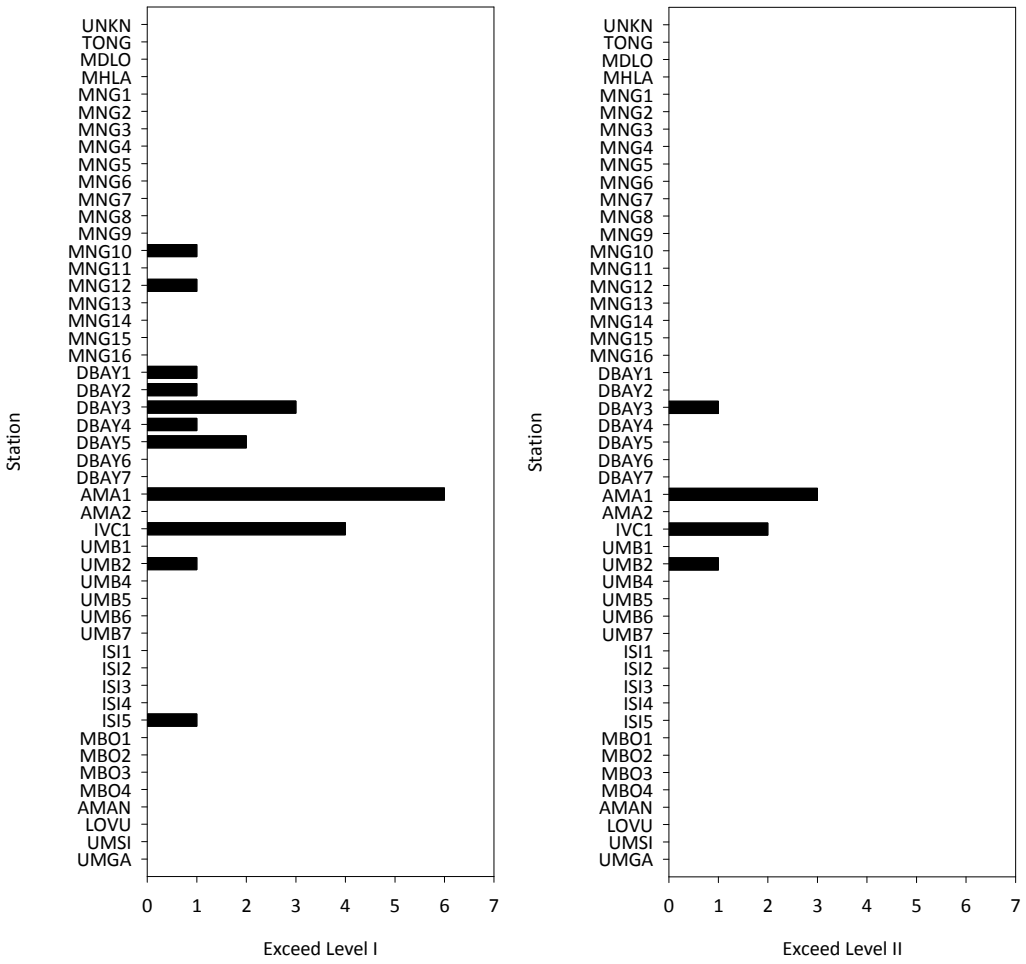

Figure 1.22. Number of metal concentrations in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2011 that exceeded the Level I and Level II of sediment quality guidelines used to regulate the disposal of dredged material in South African coastal waters.

concentrations for these metals in sediment from South African coastal waters, particularly along the KwaZulu-Natal coastline (CSIR, unpublished data).

For example, the Effects Range Low of the sediment quality guidelines derived by Long *et al*. (1995) for chromium is 81 $\mu g.g^{-1}$. Of the 135 chromium concentrations that define the baseline model for this metal in Figure 1.19, 30 (or 22%) exceed the Effects Range Low. In other words, these concentrations would be identified as posing a potential toxicological risk to sediment-dwelling organisms yet are identified through the baseline model as naturally occurring concentrations. The situation is even more extreme if the sediment quality guidelines derived by MacDonald *et al*. (2000) are considered, since the narratively equivalent Threshold Effect Concentration prescribes a chromium concentration of only 43.4 $\mu g.g^{-1}$. If this guideline is used then 63 (or 47%) of the baseline concentrations would be identified as posing a potential toxicological risk to sediment-dwelling organisms. In fact, 14 of the baseline concentrations also exceed the Probable Effect Concentration of these guidelines and would thus be interpreted as posing a high toxicological risk to sediment-dwelling organisms. The low concentrations prescribed by the sediment quality guidelines derived by MacDonald *et al.* (2000) and Long *et al.* (1995) presumably reflect a difference in the geology (geochemistry) of parent material giving rise to sediment in South Africa and the conterminous United States of America. The only sediment quality guidelines available for interpreting the potential toxicological significance of metal concentrations in sediment in South Africa are those used to determine if sediment identified for dredging in South African coastal waters is of a suitable quality for unconfined openwater disposal. The sediment quality guidelines were adopted from guidelines used to regulate dredging and dredged material disposal in North American aquatic ecosystems, after consideration

of baseline metal concentrations in sediment along the South African coastline. The sediment quality guidelines identify three guidelines for metals, namely the Warning Level, Level I and Level II. The Level I and Level II are used for decision-making. The Warning Level is only used to provide a warning of incipient metal contamination. Sediment with metals at concentrations equivalent to or lower than the Level I is regarded as posing a low toxicological risk to sediment-dwelling organisms and is thus of a suitable quality for unconfined openwater disposal. Sediment with metals at concentrations between the Level I and Level II is regarded as posing a potential toxicological risk to sediment-dwelling organisms, with the degree of risk increasing as the Level II is approached. A decision on whether this sediment is of a suitable quality for unconfined openwater disposal is made after considering the number of metal concentrations that exceed the Level I at a particular location and the magnitude of exceedance. Additional testing (*e.g.* metal analysis of sediment elutriates) may be requested to assist decision-making. Sediment with metals at concentrations equal to or higher than the Level II is regarded as posing a high toxicological risk to bottom-dwelling organisms and in the absence of other data to refute this conclusion is considered unsuitable for unconfined openwater disposal. However, if additional testing (*e.g.* toxicity testing of sediment elutriates, benthic invertebrate community analysis) shows the metals are not posing an unacceptable toxicological risk then the sediment may be considered for unconfined openwater disposal.

If the South African sediment quality guidelines are considered then it is evident that concentrations of numerous metals at numerous stations exceeded the Warning Level. Relatively few metal concentrations exceeded the Level I, with exceedances generally restricted to sediment in Durban Bay, Island View Canal and the Amanzimnyama River (Figure 1.22). Metal concentrations in sediment at four stations exceeded the Level II, with concentrations of three metals at station AMA1 exceeding this guideline (Figure 1.22).

2.3.7 Sediment quality guideline quotients

To account for the fact that sediment is frequently contaminated by a mixture of chemicals yet sediment quality guidelines only cater for individual chemicals, the mean sediment quality guideline quotient approach has been advocated for interpreting the potential toxicological significance of chemical concentrations in sediment. In this approach chemical concentrations are divided by their respective Probable Effect Concentration or Effects Range Median, to derive a quotient. The quotients are then summed and the mean value, which is unitless, is then calculated. Mean sediment quality guideline quotients calculated using the Probable Effect Concentration and Effects Range Median are presented in Figure 1.23 (note that metals were not included in quotient calculation as there is far more uncertainty as to whether these are in a bioavailable form compared to organic chemicals). As is evident, the mean quotients differ depending on the sediment quality guideline used, because the concentrations (guidelines) prescribed for chemicals differ between the sediment quality guidelines. Nevertheless, regardless of the sediment quality guideline used the highest mean quotients were for sediment collected over much of Durban Bay, in Island View Canal, and in parts of the Amanzimnyama River. The mean quotients were generally lower for sediment collected in the uMngeni, Umhlatuzana, Umbilo and Isipingo Rivers and where applicable their estuaries, although the quotients for sediment at some stations in the latter systems were comparable to Durban Bay, Island View Canal and the Amanzimnyama River. Quotients for estuaries situated to the north and south of the greater Durban area (*i.e.* the upper four and lower four stations in Figure 1.23) were generally the lowest or amongst the lowest.

Mean Probable Effect Concentration quotients have been related to the probability for toxicity based on the analysis of matching chemical and toxicity data from a large database for freshwater sediment in North America (Crane *et al*., 2002). The proportion of samples in mean Probable Effect Concentration quotient ranges of <0.1, 0.11-0.5, 0.51-1.0, 1.1-5.0 and >5 were determined to coincide with incidences of acute toxicity of ≤10%, 16%, 27%, 36%, and 100%. Mean Probable Effect Concentration quotients for sediment in rivers, estuaries and canals in the eThekwini area were below 0.1 at all but thirteen stations, with the

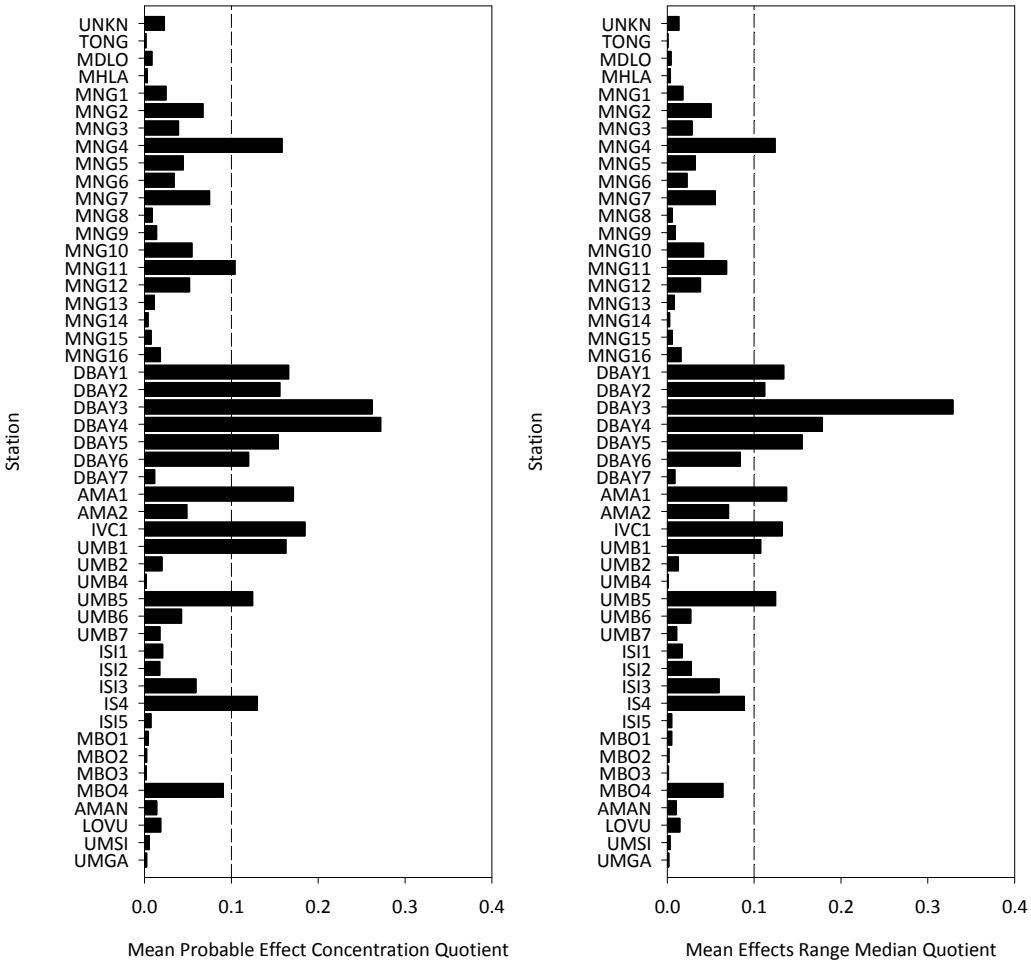

Figure 1.23. Mean Probable Effect Concentration and Effects Range Median quotients for sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2011. The dashed lines denote quotient ranges that coincide with incidences of acute toxicity provided in the text.

highest quotient of 0.27 (Figure 1.23). This suggests there was a relatively low likelihood (about 16% or less) that organic chemicals in the sediment were acutely toxic to sediment-dwelling organisms.

Mean Effects Range Median quotients have also been related to the probability for toxicity based on the analysis of matching chemical and toxicity data from a large database for estuaries in North America (Long *et al*., 2000). The proportion of samples in mean Effects Range Median quotient ranges of <0.1, 0.11-0.5, 0.51-1.5, and >1.5 were determined to coincide with incidences of acute toxicity of ≤10%, 25-30%, 50%, and ≥75%. Mean Effects Range Median quotients for sediment in rivers, estuaries and canals in the eThekwini area were below 0.1 at all but ten stations, with the highest quotient of 0.33 (Figure 1.23). These data also suggest there was a relatively low likelihood (about 30% or less) that chemicals in the sediment were acutely toxic to sediment-dwelling organisms.

The highest likelihood (about 16-30% depending on the guidelines used) that organic chemicals in the sediment were acutely toxic to sediment-dwelling organisms was thus at the majority of stations sampled in Durban Bay, in Island View Canal, in the lower part of the Amanzimnyama River, at a station below the confluence of the Umbilo and Umhlatuzana Rivers, and at a station in the uMngeni River estuary (Figure 1.23).

2.4 CONCLUSIONS

- Polycyclic aromatic hydrocarbons, DDX, polychlorinated biphenyls, and certain metals were frequent and in some cases significant contaminants of sediment sampled in rivers, estuaries and canals in the

eThekwini area of KwaZulu-Natal in September 2011.

- Polycyclic aromatic hydrocarbons were ubiquitous in sediment. The highest total polycyclic aromatic hydrocarbon concentrations were detected in sediment in rivers, estuaries and canals in the greater Durban area, that is, in catchments where the major land-use is urban and industrial. This suggests a major proportion of the total polycyclic aromatic hydrocarbon concentration had an anthropogenic source. At the system specific level the highest total polycyclic aromatic hydrocarbon concentrations were detected in sediment in Durban Bay, the Amanzimnyama River and Island View Canal, although concentrations were relatively high at a single stations in the uMngeni River estuary and a tributary of the estuary, in the Isipingo River, and below the confluence of the Umbilo and Umhlatuzana Rivers immediately prior to where these rivers discharge into Durban Bay. The Amanzimnyama River and Island View Canal discharge riverine and surface runoff into Durban Bay.
- Based on the ratio between various isomers, polycyclic aromatic hydrocarbons in sediment in the rivers, estuaries and canals sampled were diagnosed as being derived predominantly from combustion (pyrogenic) sources. Only at a few stations was there evidence for a strong petroleum or oil (petrogenic) contribution, albeit at no stations was there a dominant petrogenic source signal.
- Based on the comparison of polycyclic aromatic hydrocarbon concentrations to sediment quality guidelines derived to be protective of sediment-dwelling organisms in North American freshwater and coastal ecosystems there seems a likelihood that concentrations in sediment at some stations were posing an acute toxic risk to sediment-dwelling organisms. The greatest risk was for sediment in Durban Bay and Island View Canal, parts of the uMngeni River estuary and a tributary of the estuary, and parts of the Amanzimnyama, Umbilo/Umhlatuzana, Isipingo and Mbokodweni Rivers. The catchments of these systems are urbanised and/or industrialised. Polycyclic aromatic carbon concentrations in sediment in estuaries with lightly urbanised or rural catchments were too low to pose a risk to sediment-dwelling organisms.
- Only two organochlorine pesticides and one organophosphate pesticide were detected in sediment. DDT and its metabolites were widespread and in some cases significant contaminants of sediment in rivers, estuaries and canals. The source of the DDT is uncertain, but may include long-range atmospheric transport from malaria control areas in northern KwaZulu-Natal, where this pesticide is still used to control mosquitoes. However, this does not explain the high DDX concentrations in sediment in some systems and it is likely there are local sources of DDT to aquatic ecosystems in the eThekwini area. Chlordane was detected at a single station while chlorpyrifos was detected at four stations, three of which were situated in close proximity to one another in the uMngeni River estuary.
- Based on a comparison of pesticide concentrations to sediment quality guidelines derived to be protective of sediment-dwelling organisms in North American freshwater and coastal ecosystems there seems a likelihood that DDX in sediment at some stations was posing an acute toxic risk to sediment-dwelling organisms. The highest risk was for sediment in the uMngeni River estuary and tributaries of the estuary, and at single stations in Durban Bay and the Umhlatuzana River.
- Polychlorinated biphenyls were widespread and in some cases significant contaminants of sediment in rivers, estuaries and canals in the greater Durban area, that is, in catchments where the major land-use is urban and industrial. The highest concentrations were detected in sediment in Durban Bay, the Amanzimnyama River, and Isipingo River and its estuary. Polychlorinated biphenyls were not detected in sediment in estuaries with lightly urbanised or rural catchments.
- Based on a comparison of polychlorinated biphenyl concentrations to sediment quality guidelines derived to be protective of sediment-dwelling organisms in North American freshwater and coastal ecosystems there seems a likelihood that concentrations in sediment at some stations were posing an acute toxic risk to sediment-dwelling organisms. The highest risk was for sediment in parts of Durban Bay and the Amanzimnyama and Isipingo Rivers.
- Sediment in Island View Canal, the Amanzimnyama River and Durban Bay was most frequently and severely metal contaminated. Based on a comparison of metal concentrations to sediment quality

guidelines used to regulate the disposal of dredged material in South African coastal waters there seems a likelihood that concentrations in sediment in parts of the latter systems and at isolated locations in other systems were posing an acute toxic risk to sediment-dwelling organisms.

- The mean sediment quality guideline quotient approach to estimating the potential toxicological significance of multiple chemicals in sediment suggested that the greatest likelihood for adverse effects posed by organic chemicals to sediment-dwelling organisms was for sediment in parts of Durban Bay, Island View Canal, Bayhead Canal and the Amanzimnyama River.
- Although the comparison of chemical concentrations to sediment quality guidelines suggests the likelihood that polycyclic aromatic hydrocarbons, DDX, polychlorinated biphenyls and metals in sediment at some stations in rivers, estuaries and canals were likely posing an acute toxic risk to sediment-dwelling organisms, the magnitude and probability of the risk differed depending on which the sediment quality guidelines used to interpret the data. This creates uncertainty on whether toxic effects were likely manifesting and identifies the need for the toxicity testing or some other form of biological assessment to resolve this uncertainty.
- The most frequent and severe organic chemical and metal contamination of sediment was in rivers, estuaries and canals with densely urbanised and industrialised catchments. Sediment in rivers and estuaries with lightly urbanised or rural catchments was not contaminated. This agrees with the scientific literature and highlights the impact of catchment development on aquatic ecosystem contamination and health.

CHAPTER 3: POLYCYCLIC AROMATIC HYDROCARBON, PESTICIDE, POLYCHLORINATED BIPHENYL AND METAL CONTAMINATION, AND TOXICITY OF SEDIMENT IN THREE CATCHMENTS IN THE ETHEKWINI AREA OF KWAZULU-NATAL

3.1 INTRODUCTION

The findings of the survey discussed in Chapter 1 showed that while polycyclic aromatic hydrocarbons were ubiquitous in sediment, the most significant contamination was by and large restricted to urbanised and industrialised catchments, while polychlorinated biphenyl and metal contamination of sediment was almost exclusively restricted to urbanised and industrialised catchments. Based on these findings the decision was made to perform a more detailed assessment of sediment contamination by organic chemicals and metals in the Durban Bay and uMngeni and Isipingo River catchments. The need for biological assessment to identify the toxic effects of contaminants was also identified, since estimates of such effects using sediment quality guidelines differed considerably between the two sets of sediment quality guidelines used. Furthermore, the use of sediment quality guidelines assumes that the entire concentration of the chemical is in a bioavailable form, which is not necessarily the case. The only way to resolve whether chemicals are in a bioavailable form is to use some form of biological assessment, such as toxicity testing.

There were several objectives for the research discussed in this chapter. The first was to determine whether sediment contamination trends evident through the survey discussed in Chapter 1 were temporally consistent. This was considered necessary since sediment in the riverine portions of catchments is often scoured by strong water flow during periods of heavy rainfall, which may lead to significant temporal variation in contaminant concentrations. If so, then this will influence the frequency of sediment contaminant monitoring to aid decision-making in terms of the need for management. Alternately, if trends are temporally consistent then surveys can be conducted at longer intervals, with significant cost implications.

The second objective was to determine, at a higher resolution compared to the survey discussed in Chapter 1, whether sediment contamination in the estuarine portions of catchments reflected contamination in the riverine portions, particularly in the suite of chemicals identified as contaminants of sediment. The purpose was to determine whether sediment contaminant monitoring in the estuarine reach can be used to identify the need for monitoring in the riverine reach of catchments. This was considered necessary since sediment contaminant monitoring in rivers is not only usually more difficult and dangerous compared to monitoring in estuaries, but has obvious cost implications. If estuaries provide a faithful record of contaminants entering the riverine reaches of catchments then this negates the need for (frequent) sediment contaminant monitoring in these reaches, with obvious benefits.

The third objective was to determine whether sediment quality guidelines for polycyclic aromatic hydrocarbons and polychlorinated biphenyls provide a reliable estimate of the toxicological risk posed by these chemicals in sediment in rivers, estuaries and canals in the eThekwini area, by performing bioassays on the sediment and comparing the findings to predictions of toxicity based on the comparison of chemical concentrations to sediment quality guidelines derived to be protective of sediment-dwelling organisms. Genetically modified rat hepatoma H4IIE cells, widely used as an *in vitro* screening tool (Behnisch *et al*., 2002; Brack, 2003), were used for this purpose. The H4IIE reporter gene bioassay works on the principle that certain pollutants, such as polycyclic aromatic hydrocarbons, polychlorinated biphenyls, polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzo furans, bind to the aryl hydrocarbon receptor (AhR) present in the cytoplasm of most vertebrate cells (Behnisch *et al.*, 2001). The AhR-ligand the complex is then translocated to the nucleus of the cell, which results in the transcription of genes and

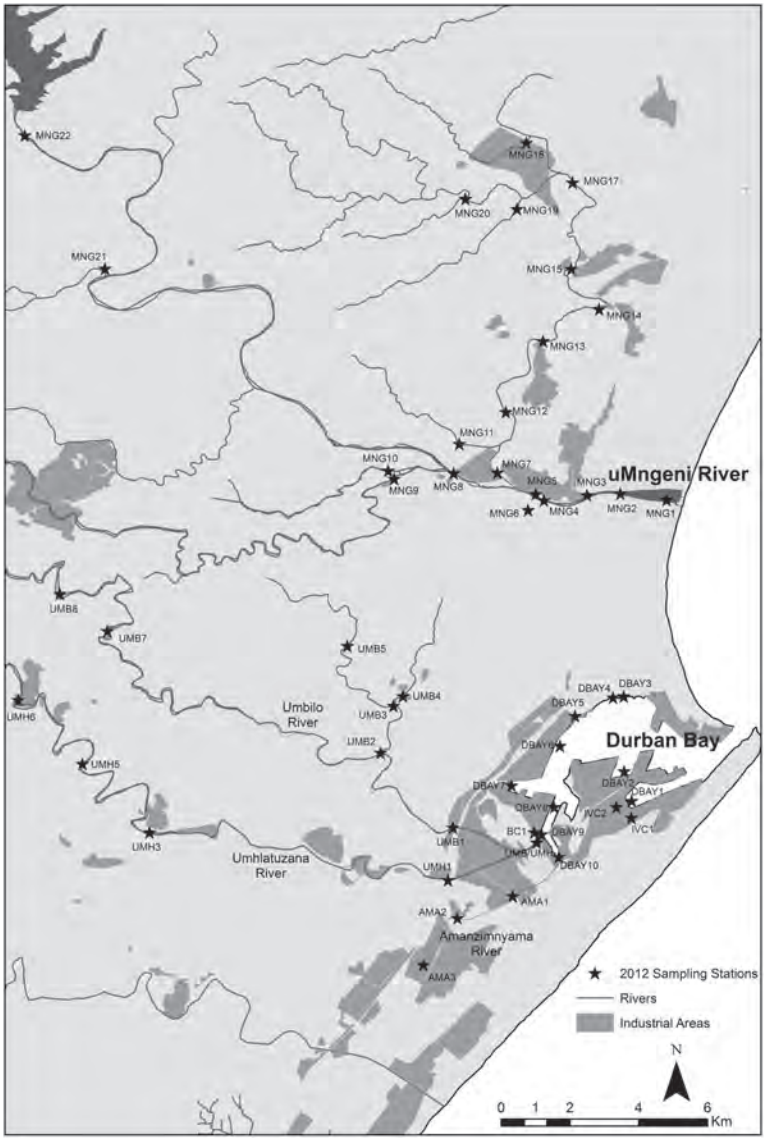

Figure 2.1. Map showing the positions where sediment samples were collected in the uMngeni River and Durban Bay catchments in May 2012.

subsequently the production of proteins, one of which is CYP1A. In the genetically modified cell line the transcribed fire-fly luciferase is expressed. When this enzyme receives its substrate luciferin a light-producing reaction is catalysed. The amount of light produced is directly proportional to the amount of AhR antagonistic compounds present. The response elicited by a sample extract is reported in relation to the response caused by a known positive control and expressed as a bioassay equivalent. It is then possible to semi-quantify the effect these pollutant mixtures will have on biota (Behnisch *et al*., 2001).

3.2 EXPERIMENTAL

3.2.1 Sampling design

Surface sediment (upper 5-10 cm) was the focus of attention since this is the biologically active zone and provides a record of the most recent chemical contamination, as opposed to deeper sediment that may represent historical contamination depending on the hydrological regime of the system of concern. The majority of sediment samples were collected from bridges spanning rivers, estuaries and canals and, with the exception of some estuaries where a vessel was used to collect samples, constrained this component of the sampling design to areas in catchments where bridges crossed rivers, estuaries and canals. A total of 54 sediment samples were collected in the catchments of Durban Bay and the uMngeni and Isipingo Rivers in May 2012 (Figures 2.1 and 2.2). Station positioning within catchments attempted to represent conditions in

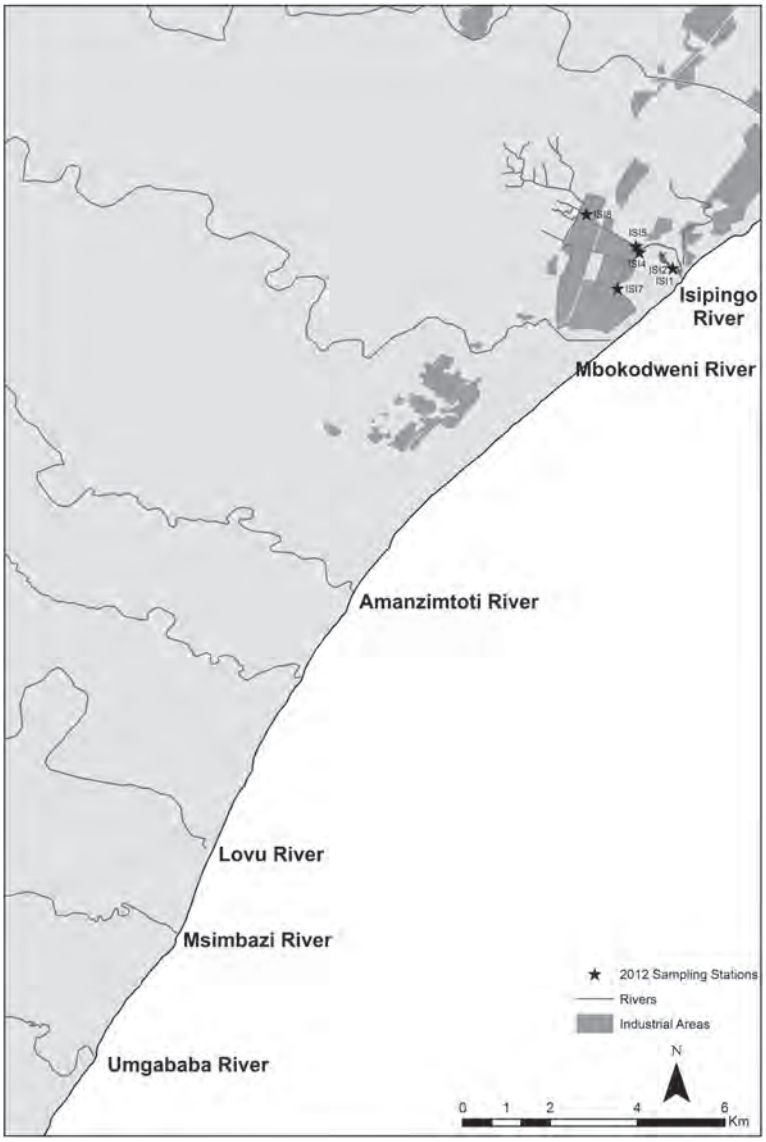

Figure 2.2. Map showing the positions where sediment samples were collected in the Isipingo River catchment in May 2012.

tributaries by sampling upstream and downstream of confluences. Sediment was absent or could not be collected at some pre-identified sampling stations. In some cases the stations were moved to a nearby location, but this was not always possible. Original sampling station identifiers are retained since other measurements not reported on here were also made and this accounts for the sometimes irregular chronology of station identifiers for a particular catchment. Four classes of organic chemicals were identified for analysis, namely polycyclic aromatic hydrocarbons, organochlorine pesticides, organophosphorous pesticides and polychlorinated biphenyls.

3.2.2 Fieldwork

Before entering the field all sampling equipment, including grabs, bowls, scoops and cooler boxes were scrubbed with a hard brush, rinsed with tap water and allowed to dry in a clean room. Once dry the equipment was rinsed with deionised water followed by hexane (using a spray bottle where appropriate) and allowed to dry in a clean room. Where possible (*e.g.* bowls, spoons) equipment was sealed in Ziploc® bags when dry. Sediment sample storage jars (amber glass or high density polyethylene) were sequentially rinsed in tap water, hexane and deionised water. Aluminium foil liners for lids were treated similarly. Glass containers and aluminium foil liners were then placed in an oven at 100°C for 24 hrs. The jars were then stored individually in Ziploc® bags.

As stated previously, most sediment samples were collected from bridges. A vessel was used to collect sediment samples in the uMngeni River estuary and at most stations in Durban Bay. Sediment was collected using a stainless steel van Veen grab. On retrieval excess water overlying sediment in the grab was drained through a bleeder hole, taking care not to lose fine-grained material. Three sediment samples were collected about 2-3 m apart at each station and composited in a glass bowl. The sediment was homogenised to a uniform consistency and colour using a stainless steel spoon. During homogenation fieldworkers (wearing powder free latex gloves) removed material not representative of the sediment when detected, including small pebbles, twigs, leaves, and plastic material. After homogenation, aliquots of sediment were transferred to two high density polyethylene containers for metal and grain size analysis and an amber glass jar for organic chemical analysis. The apertures of glass jars were sealed with an aluminium foil liner before the lid was screwed on, taking care not to puncture the liner in the process. The glass jars were then wrapped in aluminium foil to limit photo-degradation of light sensitive chemicals. Samples were kept on ice in the field and immediately frozen on return to the laboratory.

To limit cross contamination of samples in the field the van Veen grab, compositing bowl, spoons and scoops were scrubbed with a hard brush, sprayed with hexane and rinsed with deionised water between sample collections.

3.2.3 Laboratory analyses

3.2.3.1 Sample preparation

Sediment destined for chemical and total organic carbon analysis was freeze dried and ball milled to a fine consistency. The milled sediment was transferred to new storage containers cleaned according to the same procedure described above.

3.2.3.2 Grain size composition

Sediment grain size composition was determined by wet and dry sieving the sediment into seven grain size classes, namely mud (<0.063 mm), very fine-grained sand (0.063-0.125 mm), fine-grained sand (0.125-0.250 mm), medium-grained sand (0.25-0.50 mm), coarse-grained sand (0.5-1.0 mm), very coarse-grained sand (1.0-2.0 mm) and gravel (>2.0 mm). The contribution of each grain size class is expressed as a fraction of bulk sediment dry weight.

3.2.3.3 Total organic content

About 1 mg of sediment was oven dried, weighed, and organic matter in the sediment then degraded using hydrogen peroxide. The sediment was then washed in distilled water, re-dried and re-weighed, and the difference in dry weight before and after organic matter degradation was used to determine the total organic content. The total organic content is expressed as a fraction of bulk sediment dry weight.

3.2.3.4 Total organic carbon

About 1-2 mg of dried sediment was weighed into silver boats. A small volume of hydrochloric acid (10%) was added to the sediment to degrade inorganic carbon. The addition of acid continued until foaming ceased. The sediment was then dried in an oven at 65^{o}C overnight. The boats were crimped and the total organic carbon measured using an Exeter CHN Model 440 CE analyser at 985^{o}C. Certified reference material BCCS-1 SRM was used to determine recovery. Blanks and the certified reference material were analysed with every batch of 10 samples. The method detection limit was 0.03%. Total organic carbon is expressed as a fraction of bulk sediment dry weight.

3.2.3.5 Organic chemicals

Polycyclic aromatic hydrocarbon, organochlorine and organophosphorous pesticide, and toxaphene

analyses were performed by Physis Environmental Laboratories Inc. in United States of America, using USEPA method 8270C. Analysis of procedural blanks, matrix spikes and sample replicates was used to check for laboratory contamination, accuracy and precision with each batch of 12 or less samples. Method extraction efficiency was evaluated by analysing Standard Reference Material (SRM) 1944 (National Institute of Standards and Technology). All chemicals were present in procedural blanks at concentrations below the method detection limit. With few exceptions surrogate recoveries from spiked blanks and matrix spikes fell within data quality objectives of 50-150%. Also with few exceptions the precision (relative percent difference) of analyses of laboratory blanks, spiked blanks, matrix spikes and certified reference material was below the data quality objective of 30%. Recoveries from SRM 1944 ranged between 76-125% for organochlorine pesticides and 75-125% for polycyclic aromatic hydrocarbon isomers (Table 2.1).

Polychlorinated biphenyl analyses were performed by Advanced Analytical (Australia). Analysis of procedural blanks, matrix spikes and sample replicates was used to check for laboratory contamination, accuracy and precision. All chemicals were present in procedural blanks at concentrations below the method detection limit. Surrogate recoveries from spiked blanks and matrix spikes fell within data quality objectives of 50-150%. Also with few exceptions the precision (relative percent difference) of analyses of laboratory blanks and matrix spikes was below the data quality objective of 30%. A Standard Reference Material was not analysed.

3.2.3.6 Metals

Metal analysis of sediment was performed at the Analytical Services Laboratory on the CSIR campus in Stellenbosch. Approximately 1 g of sediment was digested in HNO_3-HCl-H_2O_2 according to USEPA method 3050B. This is a 'near-total' digestion method that will dissolve most elements that could become 'environmentally available', but is not designed to dissolve metals bound in silicate structures (USEPA, 1996). Precision and recovery of the digestion and metal determination procedures were evaluated by

Table 2.1. Recovery (%) of pesticides and polycyclic aromatic hydrocarbons from Standard Reference Material 1944 (National Institute of Standards and Testing).

		Replicate				
Class	**Compound**	**1**	**2**	**3**	**4**	**Mean**
Pesticides	o,p'-DDD	111	111	95	76	98
	o,p'-DDE	125	118	94	121	115
	p,p'-DDD	86	77	77	118	90
	p,p'-DDE	105	119	115	109	112
	p,p'-DDT	81	98	76	87	86
	trans-Nonachlor	110	123	101	118	113
Polycyclic aromatic hydrocarbons	Anthracene	122	124	96	102	111
	Benz[a]anthracene	79	76	75	76	77
	Benzo[a]pyrene	77	75	80	75	77
	Benzo[b]fluoranthene	76	75	77	76	76
	Benzo[e]pyrene	75	75	75	75	75
	Benzo[g,h,i]perylene	87	108	80	84	90
	Benzo[k]fluoranthene	75	91	80	81	82
	Chlordane-alpha	125	121	113	76	109
	Chrysene	75	76	80	79	78
	Dibenz[a,h]anthracene	125	76	84	80	91
	Dibenzothiophene	125	113	123	91	113
	Fluoranthene	75	79	125	98	94
	Hexachlorobenzene	115	115	110	115	114
	Indeno[1,2,3-c,d]pyrene	97	121	94	88	100
	Naphthalene	112	79	105	96	98
	Perylene	75	79	76	76	77
	Phenanthrene	79	88	121	79	92
	Pyrene	81	81	100	92	89

analysing marine Standard Reference Material PACS-2 (National Research Council of Canada) with each batch of 10 sediment samples. Since the reference material is certified for total digestion the recovery of refractory metals (*e.g.* aluminium, chromium) was, as expected, somewhat below 100% (Table 2.2).

3.2.3.7 Bioassays

3.2.3.7.1 Sample extraction and clean-up

The sediment samples were air dried in stainless steel pans, protected from ultraviolet light. The sediment was then ball-milled to a fine consistency and stored in amber jars with foil-lined lids until analysis. The sediment was extracted at high temperature and pressure using an accelerated solvent extractor. A mixture of 20 g of sediment and anhydrous sodium sulphate was placed into a 60 ml stainless steel extraction cylinder, between two 30 mm cellulose filters. A mixture of dichloromethane and hexane (3:1) was then passed into the cell at 100°C and 11 032 kPa. The system was set to a 10 minute static time and five minute heat time. Analytes were purged from the cells into collection bottles with a 300 second purge with nitrogen gas. The extraction procedure was run twice per sample. Two separate extracts were prepared per sample, one that targeted polychlorinated biphenyls and the other that targeted polycyclic aromatic hydrocarbons. The extracts were concentrated to dryness using a Turbo-Vap® II, with nitrogen gas used to evaporate the solvents at 35°C.

An acid wash was performed on the extracts that targeted polychlorinated biphenyls, by washing the extract with 98% sulphuric acid. The aim was to destroy most of the non-target compounds, by oxidation of those compounds that are not chemically stable (*e.g.* polycyclic aromatic hydrocarbons) (Behnisch *et al*., 2001; Lamoree *et al*., 2004). Evaporated samples were resuspended in 15 ml hexane within a separation funnel and repeatedly washed with an equal volume of concentrated sulphuric acid, tapping off the acid layer once the layers had separated after approximately one hour (Khim *et al*., 1999). The samples were washed with acid until the acidic layer was clear, but not exceeding six washes. The extract was further washed with 15 ml of 20% sodium chloride, followed by 5% potassium hydroxide, not exceeding a 15 minute separation time, and finally an additional sodium chloride wash to remove any trace of potassium hydroxide. The samples were then evaporated to dryness using a Turbo-Vap® II.

It should be noted that this acid washed fraction will, apart from the targeted polychlorinated biphenyls, also contain other persistent compounds such as the dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs). The non-acid-washed extract will contain all of the persistent compounds and polycyclic aromatic hydrocarbons and other compounds able to act as ligands to the AhR (Behnisch *et al*., 2001; Lamoree *et al*., 2004).

Both extracts were run through gel permeation chromatography to select the fraction of the extract most likely to contain polychlorinated biphenyls or polycyclic aromatic hydrocarbons. This process was also used to remove sulphur in the samples as it is toxic to the H4IIE cells. Compounds were separated on the grounds of size selection using a Waters 717 plus auto-sampler, Waters 1515 isocratic HPLC pump, Waters dual λ absorbance detector, a Waters fraction collector III, and two Envirogel gel permeation

Table 2.2. Recovery (%) of metals from Standard Reference Material PACS-2 (National Research Council of Canada).

Replicate	Al	As	Be	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn
1	44.6	82.8	97.0	95.7	84.4	63.6	94.5	73.6	67.8	87.0	95.3	74.0	101.8
2	43.8	83.1	83.0	95.9	79.2	63.1	91.1	71.7	60.5	85.1	88.9	66.3	93.5
3	44.8	85.7	91.3	90.3	81.1	61.0	100.8	74.0	64.3	86.0	88.1	71.2	93.7
4	46.2	94.4	91.8	96.9	87.0	58.3	95.9	68.3	57.7	74.2	89.7	74.0	92.2
5	45.8	79.0	90.1	94.2	85.6	66.8	98.5	76.8	56.8	75.5	83.4	70.6	88.2
6	44.4	87.9	99.9	94.0	85.0	69.7	93.3	71.5	57.2	74.2	96.0	68.1	89.5
Mean	44.9	85.5	93.1	94.5	83.7	63.8	95.7	72.6	60.7	80.4	90.2	70.7	93.1
Precision	2.0	6.2	13.3	2.5	3.5	6.4	3.7	3.9	7.4	7.8	5.2	4.4	5.1

chromatography clean-up columns (19 × 150 mm and 19 × 300 mm) connected in series. A gel permeation chromatography standard solution, containing corn oil, phthalate, methoxychlor, perylene and sulphur, was used to calibrate the system and determine the collection time of the solution where polychlorinated biphenyls are known to elute. A polycyclic aromatic hydrocarbon standard was used to determine the polycyclic aromatic hydrocarbon collection period.

The evaporated sample was reconstituted to 2 ml with dichloromethane through a 1 µl glass fibre filter into a recovery vial before injection into the gel permeation chromatography. The recovery vials were weighed before and after filling with the sample as well as after injection, to determine the mass fraction lost to the gel permeation chromatography process. Polychlorinated biphenyl samples were collected from 9.5-20.5 minutes, while the polycyclic aromatic hydrocarbon samples were collected from 15.5-20.5 minutes. The system was set to a flow rate of 5 ml per minute for 30 minutes, with dichloromethane as the mobile phase. The fraction of sample was evaporated to dryness, as above.

To further target the chemicals of interest the samples were passed through Dual Layer Superclean silica Florisil columns (LC-Si, 2 g/2 g), which trapped polar compounds and allowed apolar, target compounds through the column. The columns were conditioned with 6 ml hexane and followed by 6 ml of the sample, suspended in hexane. The column was washed with a 12 ml dichloromethane and hexane mixture (1:1) followed by 2 ml of dichloromethane to elute the column. The sample was evaporated to dryness and reconstituted to 1 ml with hexane in an amber glass vial and stored at -80°C.

3.2.3.7.2 Bioassay

The H4IIE cells used for the bioassay were donated by Professor John Giesy, currently at the University of Saskatoon in Canada. The tissue culture was maintained in a sterile environment, where all work areas were routinely cleaned with 70% ethanol. The cells were grown in tissue culture dishes (100/20 mm) with Dulbecco's Modified Eagles Medium (DMEM) containing L-glutamine, 1000 $mg.l^{-1}$ glucose without phenol red, and supplemented with 10% foetal bovine serum. They were maintained in a humidified environment with 5% CO_2 and 95% air at 37°C within an incubator.

Prepared extracts were diluted to different concentrations to allow for the generation of a dose response curve. In this case a three times dilution factor was used. Concentrations of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) (120, 30, 7.5, 1.9, 0.5 and 0.1 pg TCDD) per well were used as a reference compound to convert the data into bioassay equivalency (BEQ) values.

The assay required five days to complete. On the first day the cells were trypisinised (0.25% trypsin and 0.1% versene Ethylene-Diamine-Tetra-Acetic-Acid (EDTA)) in Ca^{2+} and Mg^{2+} free phosphate buffered saline from the tissue culture dishes. A suspension of the cells was made using hormone-free FBS supplemented DMEM, because hormones could influence the response of the cells. A 96-microwell plate, with white walls and a clear base, was seeded with a cell suspension with approximately 20 000 cells per well into the interior 60 wells, while the outer wells were filled with phosphate buffered saline, to create a homogenous microclimate across all wells. The plates were incubated for 24 hours.

The cells received 2.5 µl of the extract dilution, in triplicate, in descending concentration. TCDD was dosed in the same way. Each plate contained a solvent control (hexane) and blank controls. The plates were incubated for 72 hrs. A visual inspection of the cells was performed to determine confluency of the cells, whether cytotoxicity occurred or bacteria had infected the wells. The media was removed and the cells washed with phosphate buffered saline containing added Ca^{2+} and Mg^{2+}. The added salts were a precaution to ensure absence of limiting factors during the light producing reactions. Lysis buffer for mammalian cultured cells (Sigma-Aldrich) was added to cell-containing wells before the plates were frozen at -80°C, to ensure complete rupture of the cell membranes.

The plates were subsequently thawed and placed into a plate reading luminometer (Berthold multi-mode micro-plate reader, model-LB941). The thawing and reading of luminescence was performed in a darkened laboratory to prevent false excitation by UV rays. The injector automatically added luciferase assay reagent (LAR), containing 20 mM of tricine, 1.07 mM $Mg(CO_3)_4Mg(OH)_2.5H_2O$, 2.67 mM $MgSO_4.7H_2O$, 0.1 mM EDTA-disodium salt, 33.3 mM dithiothreitol, 270 µM coenzyme A, 530 µM ATP and 470 µM beetle luciferin (Villeneuve *et al*., 2009), to each of the wells. Luciferin was digested by the luciferase, during which light was emitted. The luminescence of the wells was measured as relative light units (RLU). The amount of light produced is directly proportional to the amount of AhR agonists to which the cells were exposed (Giesy *et al*., 2002; Hong *et al*., 2012).

3.2.3.7.3 Bioassay equivalency

The luminescence created by samples was expressed as a percentage of the maximum luminescence elicited by the positive reference compound and was denoted %TCDD max. The dose response curves for the positive reference compound and samples were created with the logarithm of the TCDD concentration (or log of µl sample per well) on the x-axis and %TCDD max on the y-axis. The effective concentration (or effective volume for the sample) was calculated for those concentrations (all volumes) responsible for the 20, 50 and 80% (EC 20-80) luminescence. The relative potency of a sample was calculated by dividing the samples effective concentration by the corresponding effective concentration of the reference compound. The relative potencies were back calculated to take the mass of the sediment initially extracted into consideration. This resulted in a TCDD-eq.g^{-1}, or bioassay equivalent (Nieuwoudt *et al*., 2009, Villeneuve *et al*., 2009). A limit of detection was calculated by determining the mean of all EC 0 of the TCDD dose responses, to which was added the 95% confidence interval and then converted to ng TCDD.g^{-1} limit of detection (Thomsen *et al*., 2003; Nieuwoudt *et al*., 2009). The limit of quantification was considered 15% %TCDD max.

3.2.3.7.4 Cell viability through MTT

To determine viability of the cells once they had been exposed to a sample, the hydrogen accepter 3-(4,5-dimethylthiazol-2-yl)-2,5 diphenyltetrazolium bromide (MTT) assay was used. The assay serves to prove that where the luminescence assay provided 'below level of detection' results or low responses this was not a result of cytotoxicity, but rather low concentrations of AhR agonists. Methods for the MTT were identical to those for the reporter gene bioassay until day five, with the exception that the cells were seeded into clear 96-well microplates. After washing the cells with phosphate buffered saline the cells received MTT solution (0.5 mg.ml^{-1} MTT in non-supplemented DMEM), prepared on the day. This and subsequent steps were performed in a darkened room. The plates were incubated for 30 minutes under normal growing conditions. The living cells metabolised the yellow MTT solution to form blue formazan crystals. The MTT solution was removed from the wells and dimethyl sulphoxide added to the wells, to dissolve the formazan crystals. The plates were left at room temperature for 30 minutes. The absorbance of the plates was then measured at 560 nm using a Bertohold multi-mode micro plate reader (Vistica *et al*., 1991).

To determine the viability of cells absorbance values from the individual sample and wells were divided by the mean of the solvent control wells. This was expressed as a percentage. Low cell viability could result in the reduced responses of cells in the reporter gene assay. The MTT of the xCELLigence plate was analysed in the same manner.

3.2.3.7.5 Cell viability through xCELLigence

The MTT assay is labour intensive and can only measure the endpoint of the cell's fitness at the end of the exposure. Due to the assay utilising optic based detection and absorbance there may be distortions and compound interferences (Urcan *et al*., 2010). It was thus decided to utilise an automated system that can

determine the real-time physiological state of the cells, thereby allowing monitoring of proliferation, viability and cytotoxicity before and during exposure to the extracts. This method was used to monitor any changes in cell growth during the exposure period, which would be lost as an endpoint reading, such as in an MTT assay (Urcan *et al.*, 2010).

This technique utilises the Real-Time Cell Analyser Single Plate (RTCA SP®) (Roche) developed by Biosensor Technologies (Quereda *et al*., 2010). This consists of a 96-well microtiter plate, with the bottom of each well being 80% covered by incorporated gold sensor arrays. The plate fits inside the RTCA SP® station, inside the incubator, in the same conditions as previously mentioned for cell growth. The station is connected to the RTCA analyser and a computer with integrated software (Zhu *et al*., 2006; Urcan *et al.*, 2010). The sensors allow the contents of the wells to be monitored by measuring impedance of the electrodes. Voltage is applied (approximately 20 mV) and impedance between electrodes measured. These data are represented as the Cell Index, which was calculated as the difference between impedance at a particular point in time and impedance at the start, divided by 15 (Urcan *et al.*, 2010; Wu *et al*., 2010). The impedance measured depends on electrode geometry, ion concentration in the well, and whether cells have attached to the electrodes (Zhu *et al*., 2006; Urcan *et al*., 2010). A high Cell Index represents a greater number of healthy attached cells whereas a low Cell Index corresponds to cell death, cytotoxicity or morphological changes (Quereda *et al*., 2010; Urcan *et al*., 2010).

A background reading was obtained by placing 100 µl of supplemented media (DMEM) into each well and placed into the station, and set to do six one minute sweeps (Urcan *et al*., 2010; Quereda *et al*., 2010). The cells were seeded at 80 000 cells.ml^{-1}, as in the luminescence assay, in a 96 well E-plate. Three wells that contained only supplemented media served as a negative control. Proliferation was monitored for 24 hours, with a reading interval of 15 minutes. After 24 hours the cells were dosed in triplicate with the most concentrated sample extraction. A solvent control and blank controls were represented in each plate. The xCELLigence was left to monitor the cells for 72 hours, the same period of exposure as the luminescence and MTT assays.

As an additional measure of quality control and viability an MTT assay was performed using the xCELLigence plate, after the 72 hour exposure was completed (Zhu *et al*., 2006). The method followed was identical to the ordinary MTT.

Data from the xCELLigence was expressed as a Cell Index per time period per individual well. Triplicate wells per sample exposure were analysed. A mean, standard deviation and coefficient of variation of the replicate wells was determined. If the coefficient of variation exceeded 15% the well causing the high coefficient of variation was removed before further analysis. To determine the viability of cells the Cell Index for individual wells was expressed as a proportion of the Cell Index for the solvent control (Zhu *et al*., 2006; Quereda *et al*., 2010; Wu *et al*., 2010).

3.2.4 Data analysis

3.2.4.1 Basic procedures

Total polycyclic aromatic hydrocarbon and total polychlorinated biphenyl concentrations are the sum of all isomers or congeners analysed respectively unless otherwise stated. Isomers or congeners at concentrations below the method detection limit were assigned a value of zero for the purpose of total concentration calculation. DDX concentrations represent the sum of technical DDT and metabolites. Total chlordane concentrations represent the sum of cis- and trans-chlordane, cis- and trans-nonachlor, and oxychlordane. Total endosulfan concentrations represent the sum of endosulfan I, endosulfan II and endosulfan-sulphate. For pesticides concentrations below the method detection limit were also assigned a value of zero for purpose of total concentration calculation.

Correlation and linear regression analysis was used to examine the nature and strength of linear relationships between sediment parameters and/or chemical concentrations. Further details on data analysis procedures are provided in relevant sections of the text.

3.2.4.2 Estimate of potential toxicological risk posed by chemicals to sediment-dwelling organisms

The same approach used in Chapter 1 to estimate the potential toxicological risk posed by chemicals in sediment to sediment-dwelling organisms was followed for this study.

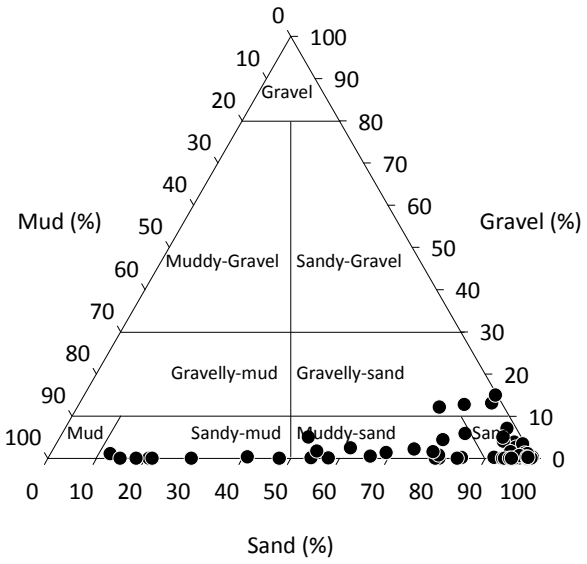

Figure 2.3. Ternary plot illustrating the proportional contribution of gravel, sand and mud to bulk sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2012.

3.2.4.3 Bioassays

Data normality was checked using Kolmogorov-Smirnov test. If the data was not normally distributed a Box-Cox transformation was used to approximate a normal distribution. Parametric or non-parametric (if the data was still not normally distributed after transformation) tests were used to analyse the data. Spearman rank R was used for non-parametric correlation analysis, and Kruskal-Wallis Analysis of Variance for comparisons between treatments, followed where appropriate by a post-hoc test.

3.3 RESULTS AND DISCUSSION[2]

3.3.1 Sediment grain size composition

The significance of grain size in the context of contaminant accumulation in sediment was provided in Chapter 1. There is again little point discussing in detail the grain size composition of sediment in the rivers, estuaries and canals sampled since these systems are naturally disparate in nature and the grain size composition can thus be expected to vary considerably between the systems. The primary purpose for analysing the grain size composition of sediment was to determine whether the mud fraction can account for the variability in organic chemical and metal concentrations in sediment. Nevertheless, a ternary plot revealed that, from a textural perspective there were important differences between catchments or parts of catchments sampled (Figure 2.3). The sediment at all but eight stations was dominated by sand, with the mud contribution to bulk sediment weight frequently <10%. Sediment at the latter stations was dominated by mud-sized sediment, although at none of the stations was the sediment classified texturally as mud (*i.e.* mud contribution >90%). The dominance of sand, in part, reflects the fact that many sediment samples were collected in the fast-flowing reaches of rivers, where fine-grained material is easily winnowed from the sediment by currents. Sediment in the estuarine reaches of catchments was often dominated by fine-grained material, but here too in many cases sand was also the dominant textural class. The grain size composition of sediment sampled in the rivers, estuaries and canals spans a sufficient range to allow for the identification of unifying features in terms of organic chemical and metal association with fine-grained material, provided unifying features are evident.

3.3.2 Particulate organic matter

The significance of particulate organic matter in the context of contaminant accumulation in sediment was

[2] Results of physical and chemical analyses of sediment are presented in Appendices 8-13.

provided in Chapter 1. Baseline models were defined in the same manner discussed in Chapter 1. As indicated by the coefficients of determination (r^2), the relationship between mud and total organic content fractions of sediment was far stronger than the relationship between mud and total organic carbon fractions (Figure 2.4a,b). The baseline model for total organic content identified the sediment at four stations as enriched with particulate organic matter while the model for total organic carbon identified the sediment at six stations as enriched, although the magnitude of enrichment at station DBAY7 in Durban Bay was low for both models. Only three stations where the sediment was identified as enriched by the baseline models were coincident, namely stations DBAY3 and DBAY7 in Durban Bay and station ISI4 in the Isipingo River (Figure 2.4a,b). The cause of the mismatch was the large difference in the proportion of bulk sediment comprised by total organic content and total organic carbon in sediment at several stations (Figure 2.4c). Sediment at station BC1 in Bayhead Canal, for example, was identified as amongst the most enriched with particulate organic matter using the baseline model for total organic carbon, but not by the baseline model for total organic content. A similar mismatch between the total organic content and total organic carbon fractions of sediment was evident for the survey discussed in Chapter 1 (see section 3.2). Since these indicators provide a measure of the contribution of particulate organic matter to sediment the relationship between them should theoretically be very strong. That this was not the case for some stations makes it difficult to determine which provides the most reliable indicator of particulate organic matter enrichment of sediment, and consequently which is the most suitable normaliser of organic chemical concentrations. Nevertheless, where organic chemical concentrations were normalised this followed the convention of using total organic carbon as the normaliser.

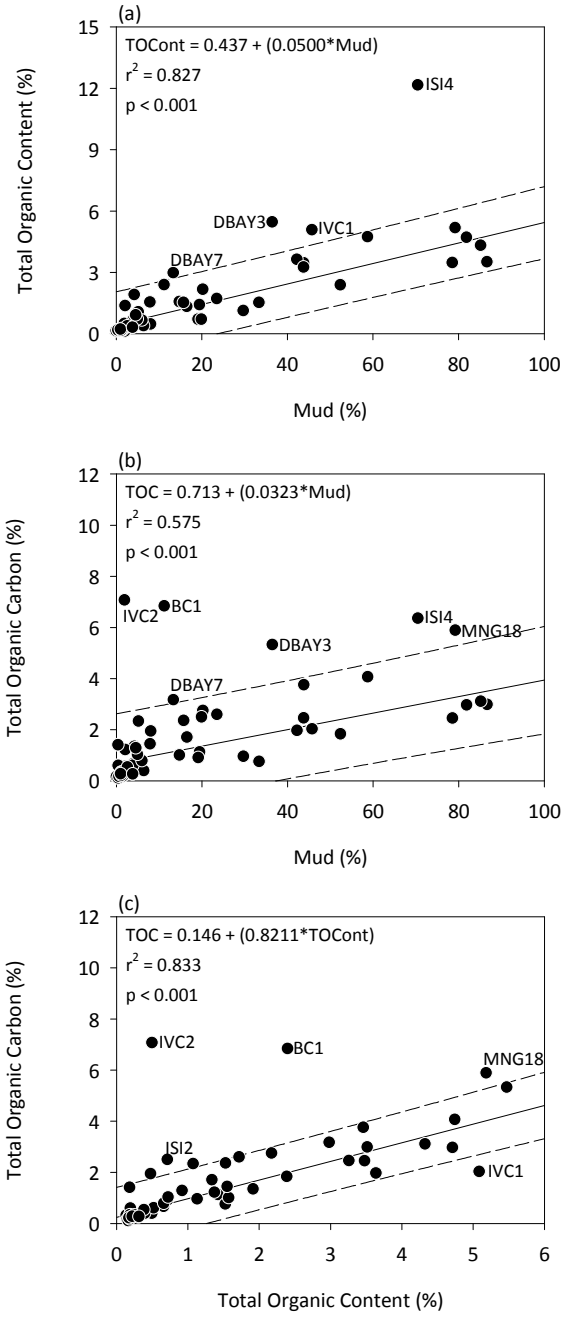

Figure 2.4. Relationship between mud and particulate organic matter indicator fractions in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2012. Linear regressions fitted to data trimmed of outliers (data points indicated by station identifiers) are given with 99% prediction limits, fitted parameters, coefficients of determination (r^2) and statistical significance (p). Selected data points are highlighted by station identifiers.

3.3.3 Polycyclic aromatic hydrocarbons

Background information on the sources and significance of polycyclic aromatic hydrocarbons as contaminants of sediment was provided in Chapter 1. Polycyclic aromatic hydrocarbons were detected at concentrations exceeding the method detection limit in sediment at all stations (Figure 2.5), although all isomers were not necessarily detected at concentrations exceeding the method detection limit. The ubiquitous presence of polycyclic aromatic hydrocarbons in sediment agrees with the findings for the

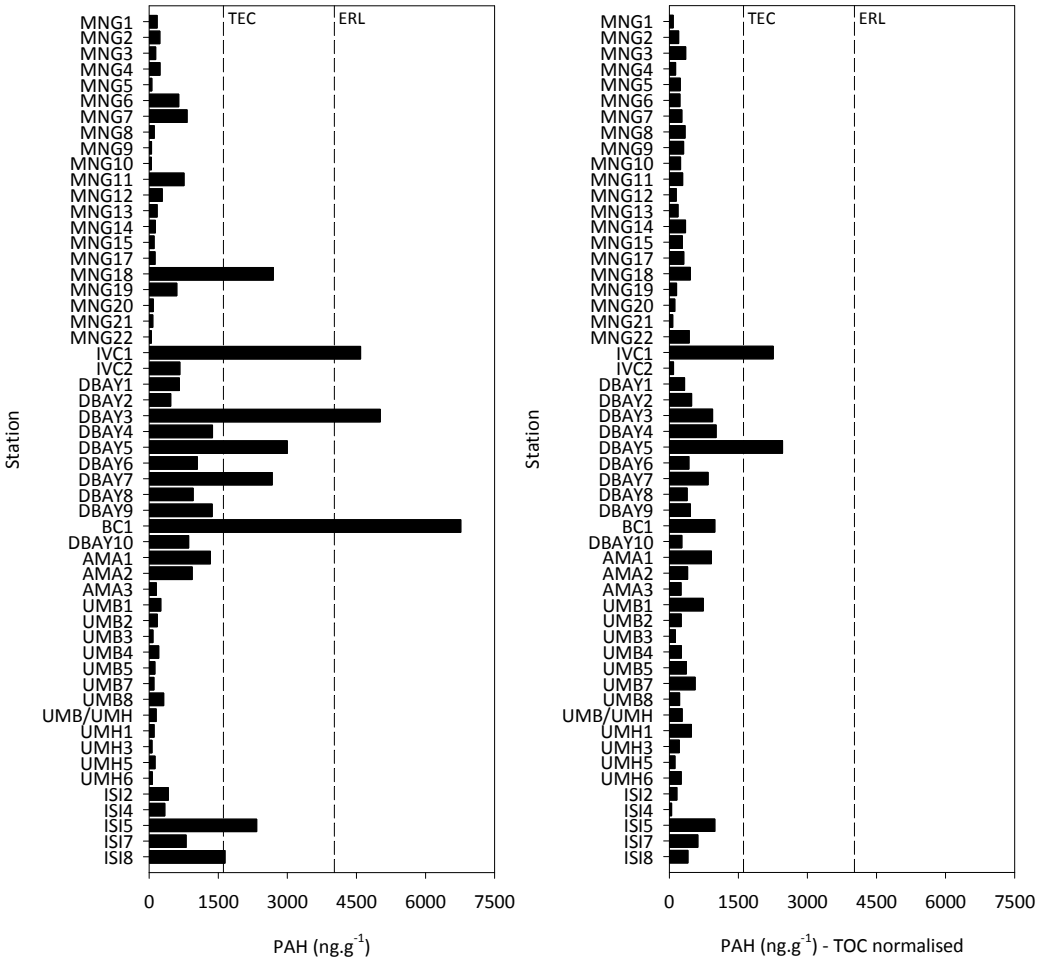

Figure 2.5. Total polycyclic aromatic hydrocarbon (PAH) concentrations not normalised (left) and normalised (right) to total organic carbon (TOC) in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2012. The dashed lines denote the Threshold Effect Concentration (TEC) of the consensus-based sediment quality guidelines derived by MacDonald *et al*. (2000) and the Effects Range Low (ERL) of the sediment quality guidelines derived by Long *et al*. (1995).

survey discussed in Chapter 1. As discussed in Chapter 1, the ubiquity of polycyclic aromatic hydrocarbons in sediment in rivers, estuaries and canals in the eThekwini area was not unexpected since polycyclic aromatic hydrocarbons are nearly ubiquitous in sediment in other regions of the world, including non-urbanised catchments (*e.g.* Cundy *et al*., 1997; Neff *et al*., 2005; Garner *et al*., 2009; Tao *et al*., 2010). The ubiquity undoubtedly reflects a multitude of natural and anthropogenic sources of polycyclic aromatic hydrocarbons in the eThekwini area. Total polycyclic aromatic hydrocarbon concentrations not normalised to total organic carbon varied widely, from 46.7 ng.g^{-1} at station MNG10 in a tributary of the uMngeni River estuary to 6766.5 ng.g^{-1} at station BC1 in Bayhead Canal, which discharges surface runoff into the upper part of Durban Bay. The mean concentration was 865.9 ng.g^{-1}, with a standard deviation of 1352.5 ng.g^{-1}. The 25^{th,} 50th and 75th percentiles of the concentration distribution were 122.9, 299.7 and 915.9 ng.g^{-1} respectively. Thus, the total polycyclic aromatic hydrocarbon concentration at the majority of stations was relatively low. Total polycyclic aromatic hydrocarbon concentrations were, on average, highest in sediment in Durban Bay and the Amanzimnyama River, Island View Canal and Bayhead Canal (Figure 2.5). Total polycyclic aromatic hydrocarbon concentrations were, in turn, generally higher in the Isipingo River and estuary compared to the uMngeni River, its estuary and tributaries of the estuary. The lowest concentrations were generally evident in the Umbilo and Umhlatuzana Rivers. To place the concentrations in the different catchments into perspective, the total polycyclic aromatic hydrocarbon concentration in sediment at only four stations in the uMngeni River, its estuary and tributaries of the estuary exceeded 350 ng.g^{-1}, while in the Umbilo and Umhlatuzana Rivers no concentrations exceeded 350 ng.g^{-1}. In contrast, the

total polycyclic aromatic hydrocarbon concentration in sediment at only a single station in Durban Bay, the Amanzimnyama River, Island View Canal, Bayhead Canal and the Isipingo River and estuary was below 350 $ng.g^{-1}$.

Fluoranthene and pyrene typically contributed most to the total polycyclic aromatic hydrocarbon concentration, followed in most cases by phenanthrene. In fact, the contribution of phenanthrene was often as high or higher than for fluoranthene and pyrene. Fluoranthene and pyrene are typically dominant in urban and industrial settings. Isomer contributions for the majority of samples resembled contributions reported by Brown and Peake (2006) for street dust, stormwater reticulation sump sediment and suspended sediment in surface runoff in Dunedin, New Zealand, and by Gonzalez *et al*. (2000) in surface runoff in Paris, France. A similar isomer composition pattern has also been reported by other workers (*e.g.* Baumard *et al*., 1998; McCready *et al*., 2000).

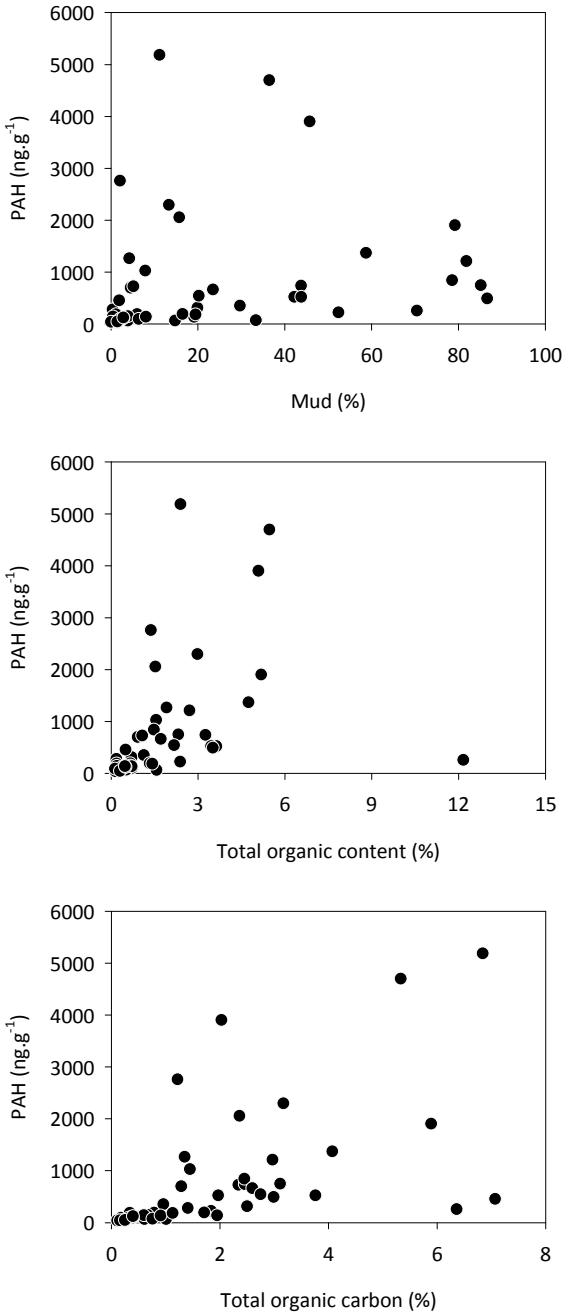

Figure 2.6. Relationship between total polycyclic aromatic hydrocarbon (PAH) concentrations and mud and particulate organic matter indicator fractions in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2012.

As stated elsewhere in this report, because of their particle reactive nature and hydrophobicity, sediment is the most important sink for polycyclic aromatic hydrocarbons in aquatic ecosystems. Fine-grained sediment with a high particulate organic matter content has a greater potential to accumulate polycyclic aromatic hydrocarbons compared to coarse-grained sand dominated sediment, because of the greater surface area provided by fine-grained sediment for adsorption and because polycyclic aromatic hydrocarbons are partial to adsorption onto organic matter, which typically accumulates in the same areas as fine-grained sediment (Maruya *et al*., 1996; Di Toro and De Rosa, 1998; Mitra *et al*., 1999; Wang *et al*., 2001). Affinity for the particulate phase generally increases with molecular weight/size of the polycyclic aromatic hydrocarbon molecule. Total polycyclic aromatic hydrocarbon concentrations (and the sum of low and high molecular weight isomers) concentrations for all rivers, estuaries and canals combined were very weakly correlated to the mud, total organic content and total organic carbon fractions of sediment (Figure 2.6). This was partly attributable to high polycyclic aromatic hydrocarbon concentrations in sediment with a low mud, total organic content and total organic carbon fraction. Because of the weak relationships, polycyclic aromatic hydrocarbon concentrations were not normalised to total organic content or total organic carbon. The weak relationships might reflect different sources, types and loadings of polycyclic aromatic hydrocarbons at the catchment specific level. The relationships did not improve in strength at the catchment specific level with the exception of the uMngeni River, its estuary and tributaries of the estuary provided one high concentration was considered an outlier and trimmed from the dataset before regression analysis (Figure

2.7). The strongest relationship was with total organic carbon (Figure 2.7c). For the uMngeni River, its estuary and tributaries of the estuary, polycyclic aromatic hydrocarbons thus appear for the most part to have preferentially adsorbed onto particulate organic matter, as represented by total organic carbon. This is contrary to the situation to the survey for the uMngeni River, its estuary and tributaries of the estuary discussed in Chapter 1, where the strongest relationship was between the mud and total organic content fractions of the sediment fraction and the relationship between the mud and total organic carbon fractions was weakest.

The use of ratios between isomers to diagnose whether polycyclic aromatic hydrocarbons were derived from pyrogenic or petrogenic sources was discussed in Chapter 1. Cross-plots of four ratios are presented in Figure 2.8, using petrogenic-pyrogenic transition points defined by Yunker *et al*. (2002). Although there is some contradiction between the ratios, some commonalities are evident. First, a strong petrogenic (petroleum) source for polycyclic aromatic hydrocarbons in sediment was evident for a single station, namely station IVC2 situated in one arm of Island View Canal. This makes sense considering the Island View area of Durban Bay is the site of a bulk liquids import and storage facility, and hydrocarbons are commonly visible on the water surface in the arm of the canal where station IVC2 was situated (B Newman, personal observation). The implication is that bulk liquids containing polycyclic aromatic hydrocarbons were leaking into or otherwise entering the canal, although the total concentration in the sediment was not particularly high (666.1 $ng.g^{-1}$). However, this probably reflects the fact that the sediment had a very low mud fraction (1.9% of bulk sediment weight) and was dominated by medium-grained sand (59.7% of bulk sediment weight) rather than a low loading of polycyclic aromatic hydrocarbons. Ratios indicative of a mixed petrogenic/petroleum combustion source were evident for polycyclic aromatic hydrocarbons in sediment at the station in the other arm of the Island View Canal, at two stations in the Amanzimnyama River, at stations in Durban Bay off or near inflows of Island View Canal and the Amanzimnyama River, a station situated immediately adjacent to the dry dock in Congella Basin, a station in the uMngeni River estuary, and a station in a tributary of the latter estuary (Figure 2.8). The source signal for the latter mentioned stations in Durban Bay makes sense since these were situated off inflows of canals and rivers in which there was a strong

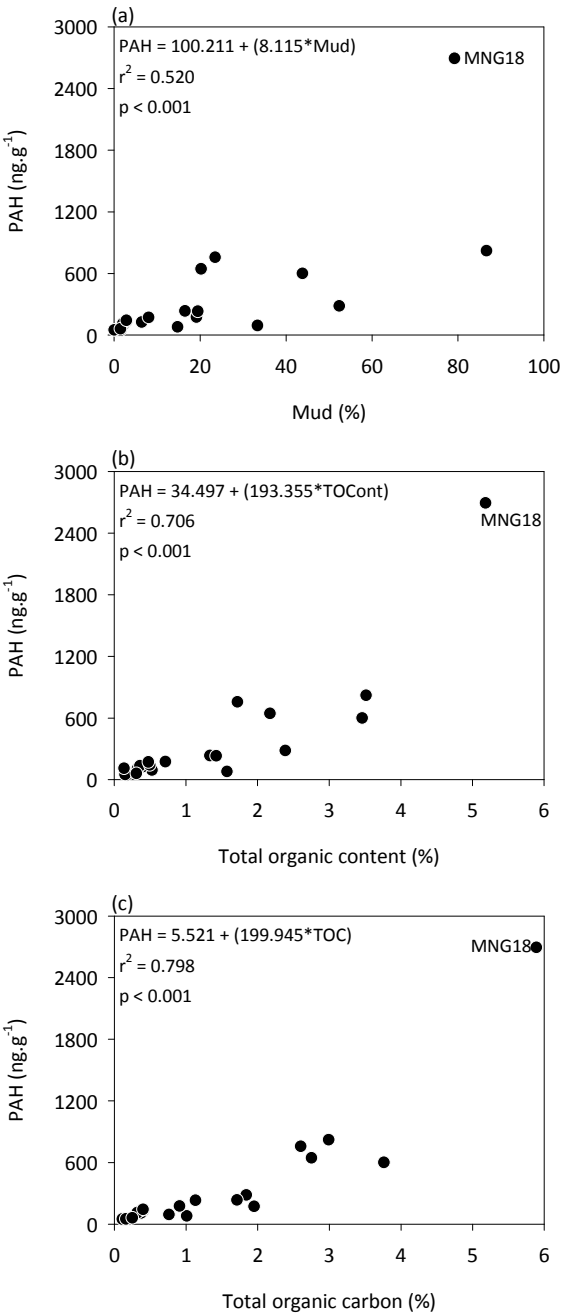

Figure 2.7. Relationship between total polycyclic aromatic hydrocarbon (PAH) concentrations and mud and particulate organic matter indicator fractions in sediment collected in Mngeni River, its estuary and tributaries of the estuary in 2012. Parameters for linear regressions fitted to data trimmed of outliers (data points indicated by station identifiers) are given with coefficients of determination (r^2) and statistical significance (p). Selected data points are highlighted by station identifiers.

petrogenic/petroleum combustion source signal, providing a link between the inflow and immediately adjacent sediment depositional area in the Bay, or were situated in areas where there is a reasonable expectation for the introduction of petrogenic polycyclic aromatic hydrocarbons due to port-associated activities (*e.g.* vessel maintenance and repair facilities). Isomer ratios at the majority of stations were, nevertheless, diagnostic of a predominantly pyrogenic source for polycyclic aromatic hydrocarbons, either from petroleum combustion or grass, wood and coal combustion. A predominantly pyrogenic source for polycyclic aromatic hydrocarbons is typical of urbanised and industrialised areas (*e.g.* Sun *et al*., 2009; Tao *et al*., 2010). The anthracene/anthracene+ phenanthrene and fluoranthene/ fluoranthene+pyrene cross-plot is interesting in that it shows a generally strong separation between stations in Durban Bay, Island View Canal, Bayhead Canal and Amanzimnyama River and other stations. The same separation was not, however, evident for other cross-plots. Although not reported on here the use of other ratios implied a strong petrogenic source of polycyclic aromatic hydrocarbons at two stations in the Amanzimnyama River (AMA1 and AMA2) and a station in a tributary of the uMngeni River estuary (MNG15). This makes sense for the Amanzimnyama River, where an oily sheen is often present on the water surface (B Newman, personal observation).

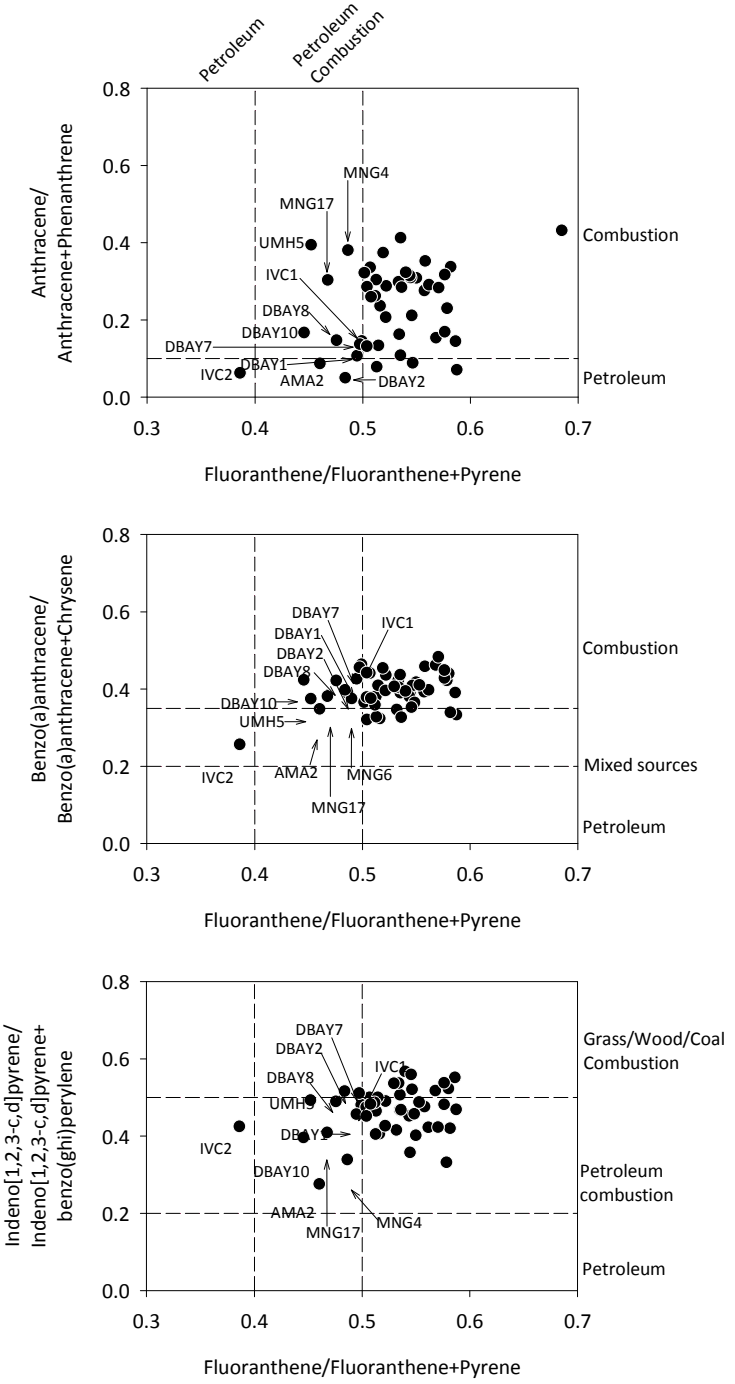

Figure 2.8. Cross plots of ratios of polycyclic aromatic hydrocarbon isomer concentrations in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2012. Selected data points are highlighted by station identifiers.

The ratio between low and high molecular weight isomers is also often used for diagnostic purposes. Limitations of this approach were discussed in Chapter 1. The ratio between low and high molecular weight isomers in sediment collected in rivers, estuaries and canals was below one at the majority of stations (Figure 2.9), confirming the predominantly pyrolitic origin of polycyclic aromatic hydrocarbons identified through the use of cross-plots. The ratio exceeded one at five stations in the uMngeni River, its estuary and tributaries of the estuary, at single stations in Durban Bay, the Amanzimnyama River and Island View Canal, and single stations in the Umbilo and Umhlatuzana Rivers. Although a petrogenic source at many of these stations is logical based on anthropogenic activities nearby, this was not always the case.

As discussed in Chapter 1, two sets of sediment quality guidelines derived for application in North American freshwater and coastal ecosystems were used to interpret the toxicological significance of polycyclic aromatic hydrocarbons in sediment. This is because there are no South African sediment quality guidelines for organic chemicals. The total polycyclic aromatic hydrocarbon concentration in sediment at eight stations exceeded the Threshold Effect Concentration of the sediment quality guidelines derived by MacDonald *et al*. (2000), but the concentration at only three stations exceeded the Effects Range Low of the sediment quality guidelines derived by Long *et al*. (1995) (Figure 2.5). The most frequent exceedances of isomer specific guidelines and the number of stations where isomer concentrations exceeded guidelines was for sediment in Durban Bay (Figure 2.10). Thus, based on polycyclic aromatic hydrocarbon concentration exceedances of sediment quality guidelines the greatest potential toxicological risk posed by these chemicals to sediment-dwelling organisms was for sediment in some parts of Durban Bay, in Island View Canal, and in Bayhead Canal.

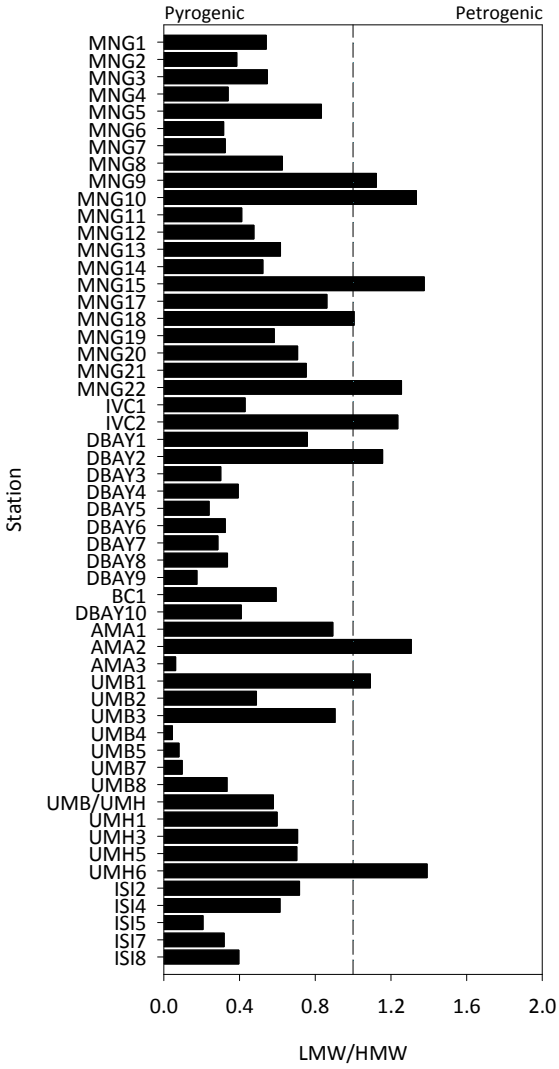

Figure 2.9. Ratio between low and high molecular weight polycyclic aromatic hydrocarbon isomer concentrations in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2012. The dashed line marks the transition between pyrogenic and petrogenic sources.

The above discussion is based on polycyclic aromatic hydrocarbon concentrations that were not normalised to total organic carbon, because both sets of sediment quality guidelines are for non-organic carbon normalised concentrations. Nevertheless, it is worthwhile examining the influence of organic carbon normalisation under the assumption the lack of a relationship between total organic carbon and polycyclic aromatic hydrocarbon concentrations for the entire data set was due to high level contamination in some systems. Organic carbon normalisation of total polycyclic aromatic hydrocarbon concentrations did not substantially alter trends but did decrease concentration variability between and within some systems (Figure 2.5). The most significant influence of normalisation was that only two concentrations exceeded the Threshold Effect Concentration of the sediment quality guidelines derived by MacDonald *et al*. (2000) and no concentrations exceeded the Effects Range Low of the sediment quality guidelines derived by Long *et al*. (1995) (Figure 2.5).

The direct comparison of polycyclic aromatic hydrocarbon concentrations between the survey discussed in this chapter and the survey discussed in Chapter 1 for catchments sampled in both surveys is difficult as the sampling station positions were not always coincident. Although total polycyclic aromatic hydrocarbon concentrations were generally slightly higher in the 2011 survey, the same trend of concentrations generally being higher in Durban Bay and in rivers and canals flowing into the Bay compared to other systems was evident in both surveys (Figure 2.11). In the 2012 survey, total polycyclic aromatic hydrocarbon concentrations in the uMngeni River, its estuary and tributaries of the estuary, and in the Umbilo and Umhlatuzana Rivers were generally more comparable between these systems compared to the 2011 survey.

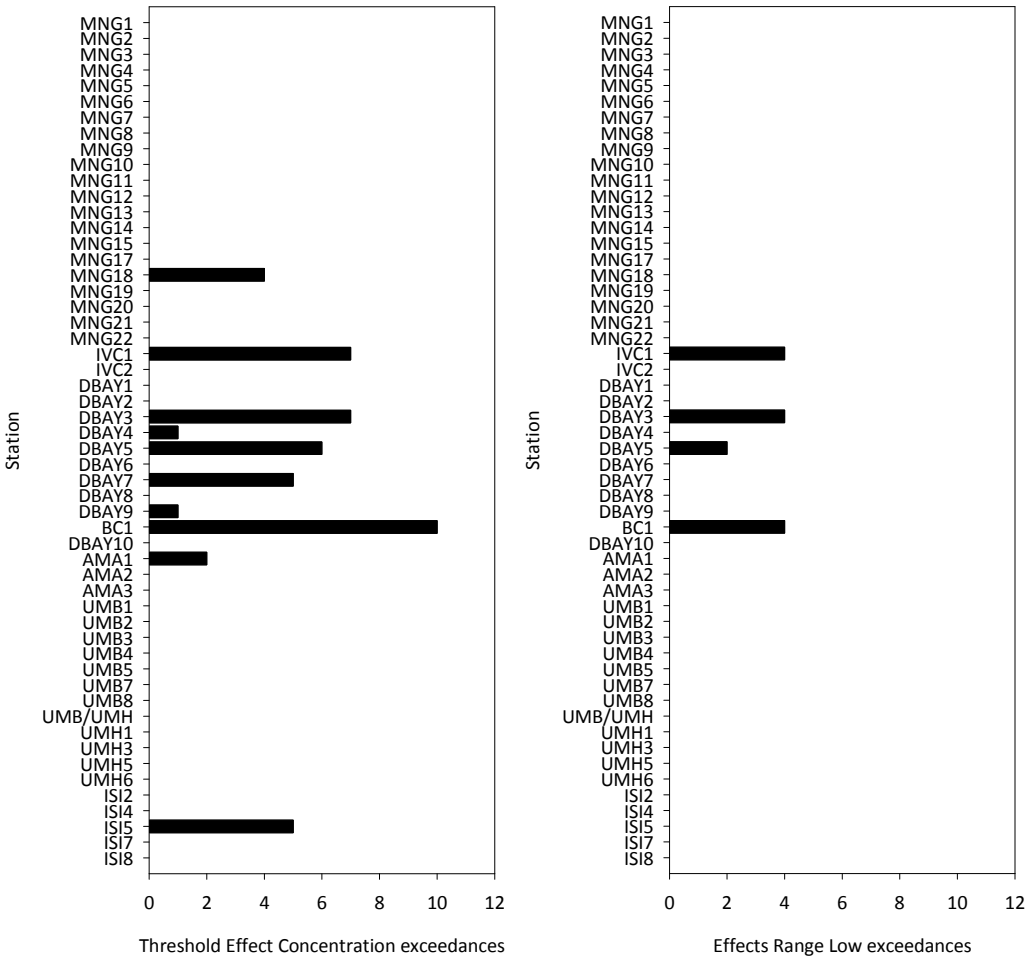

Figure 2.10. Number of low and high molecular weight polycyclic aromatic hydrocarbon isomer concentrations in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2012 that exceeded the Threshold Effect Concentration of the consensus-based sediment quality guidelines derived by MacDonald *et al*. (2000) and the Effects Range Low of the sediment quality guidelines derived by Long *et al*. (1995).

Few studies have reported on polycyclic aromatic hydrocarbon concentrations in sediment in South African aquatic ecosystems, and even fewer have provided raw data to allow for comparisons. Figure 2.12 compares polycyclic aromatic hydrocarbon concentrations reported for sediment in South African aquatic ecosystems to concentrations in sediment for the surveys discussed in Chapter 1 (2011) and this chapter (2012). To allow direct comparison between the studies, only concentrations of the sixteen isomers identified by United States Environmental Protection Agency as priority pollutants were compared. Roos *et al*. (2011) reported polycyclic aromatic hydrocarbon concentrations between 132.1-5408 $ng.g^{-1}$ (mean and median concentrations of 1145.7 and 691.6 $ng.g^{-1}$ respectively) for 27 sediment samples collected at numerous locations in South Africa, including a station near the mouth of the uMngeni River estuary. Nieuwoudt *et al*. (2011) reported total polycyclic aromatic hydrocarbon concentrations of between 44.0-2799.0 $ng.g^{-1}$ (mean and median concentrations of 639 and 330 $ng.g^{-1}$ respectively) for nine sediment samples collected in rivers in industrialised, urbanised and agricultural areas in the Vaal Triangle area. Polycyclic aromatic hydrocarbons were recently measured in 62 sediment samples collected in the Orange-Senqu River Basin (ORASECOM, 2013), with concentrations ranging between 6-867 $ng.g^{-1}$ (mean and median concentrations of 113.6 and 47.0 $ng.g^{-1}$ respectively). In comparison, polycyclic aromatic hydrocarbon concentrations for the survey discussed in Chapter 1 ranged between 13.5-5501.0 $ng.g^{-1}$ (mean and median concentrations of 1054.1 and 411.3 $ng.g^{-1}$ respectively) and for the survey discussed in this chapter between 37.1-5186.3 $ng.g^{-1}$ (mean and median concentrations of 719.8 and 209 $ng.g^{-1}$ respectively). Polycyclic aromatic hydrocarbon concentrations in sediment collected in rivers, estuaries and canals in the eThekwini area in 2011 and 2012 were thus generally higher than concentrations reported for

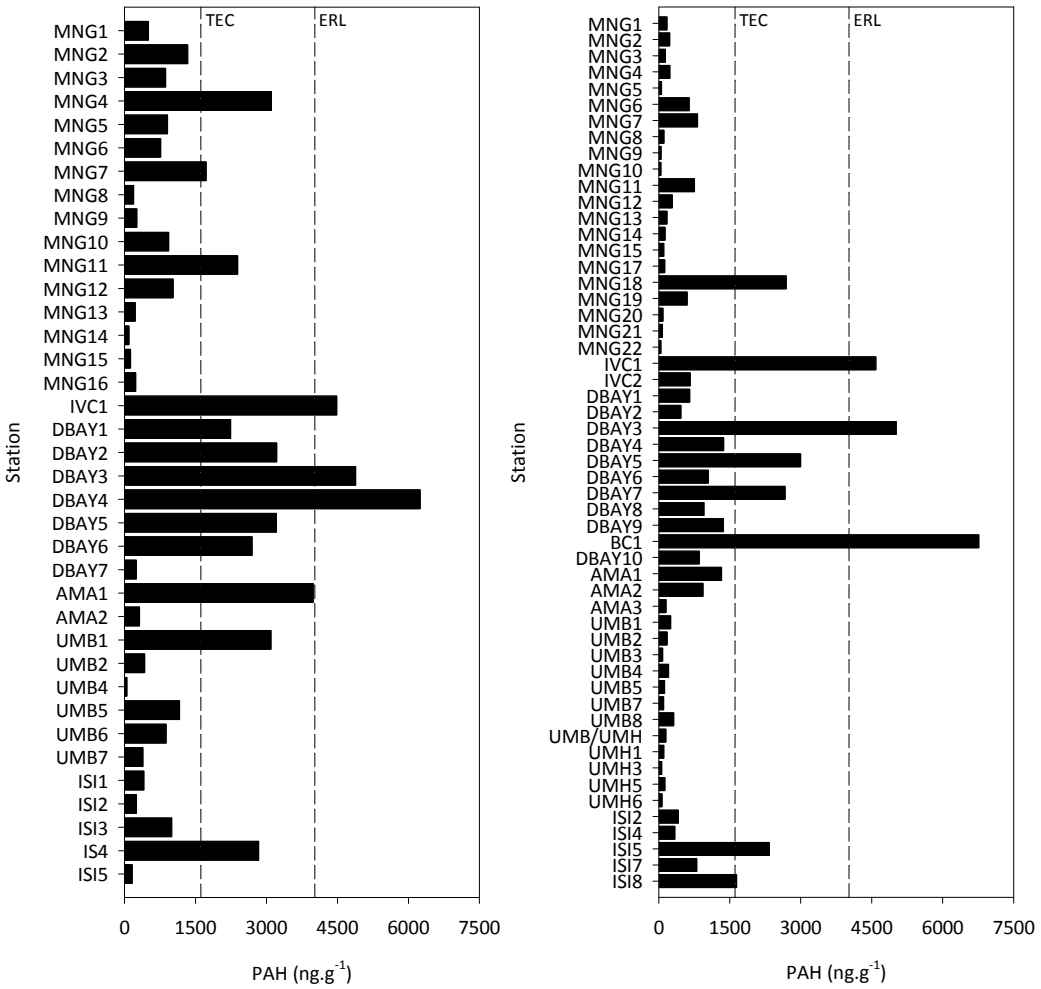

Figure 2.11. Comparison of total polycyclic aromatic hydrocarbon (PAH) concentrations in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2011 (left) and 2012 (right). The dashed lines denote the Threshold Effect Concentration (TEC) of the consensus-based sediment quality guidelines derived by MacDonald *et al*. (2000) and the Effects Range Low (ERL) of the sediment quality guidelines derived by Long *et al*. (1995).

other areas of South Africa, but more so for the 2011 survey, although the second highest concentration measured in any study was for a sediment sample collected in the Soweto/Lenasia area by Roos *et al*. (2011) (Figure 2.12). In a study performed in 2013 (CSIR, unpublished data), a polycyclic aromatic hydrocarbon concentration of 14 530.0 $ng.g^{-1}$ was measured in a sediment sample collected in the Port of Cape Town. In fact, concentrations in sediment at several stations in the Port of Cape Town exceeded the highest concentrations reported in this study and the other South African studies mentioned above. For each of the studies mentioned above the conclusion was also that polycyclic aromatic hydrocarbons in sediment were derived predominantly from pyrogenic sources.

For further comparative purposes, total polycyclic aromatic hydrocarbon concentrations measured in sediment collected in rivers, estuaries and canals in the eThekwini area in 2011 and 2012 are compared to concentrations reported for studies performed in other parts of the world (Figure 2.13). The reader should note that the number of isomers analysed in the comparative studies varied widely, from 12-31, although for the majority of studies 16-21 isomers were analysed.

Although polycyclic aromatic hydrocarbon concentrations in sediment collected in rivers, estuaries and canals in the eThekwini area in 2011 and 2012 (and by implication sediment in the other South African studies mentioned above) do not appear especially high compared to other parts of the world, this is partly because numerous extremely high concentrations reported for some international studies skew the data. These concentrations were generally for sediment collected in industrialised areas of the United States of

America (*e.g.* Ashley and Baker, 1999; Gunther *et al*., 2001; WDE, 2005), although high concentrations were also reported for sediment in Guanabara Bay in Brazil (Wagener *et al*., 2012) and Kaohsiung Harbour in Taiwan (Chen *et al*., 2011). By far the majority of concentrations (95%) reported in international studies used for the comparison in Figure 2.13 were below 10 000 $ng.g^{-1}$, while 65% were below 1000 $ng.g^{-1}$. Of the 1383 concentrations included in Figure 2.13, the highest concentration for the eThekwini area was in position 1259 (6766.5 $ng.g^{-1}$), for sediment collected in Bayhead Canal in the 2012 survey. In fact, 13 of the 103 concentrations analysed in sediment collected in the eThekwini area (9 for 2011 survey and 4 for 2012 survey) are within the highest 20% of concentrations in Figure 2.13, and 45 concentrations are within the highest 50% of concentrations. In other words, a relatively small proportion of the concentrations were 'high' by international standards, although these are still well below the extremely high concentrations reported in some studies. In fact, a large proportion of the concentrations exceed the median concentration reported in comparator studies (Figure 2.13).

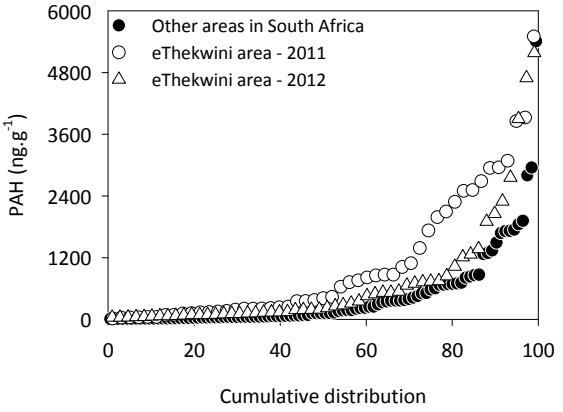

Figure 2.12. Comparison of total polycyclic aromatic hydrocarbon (PAH) concentrations in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2011 and 2012 and in other areas of South Africa (data from Nieuwoudt *et al*., 2011; Roos *et al*., 2011; ORASECOM, 2013).

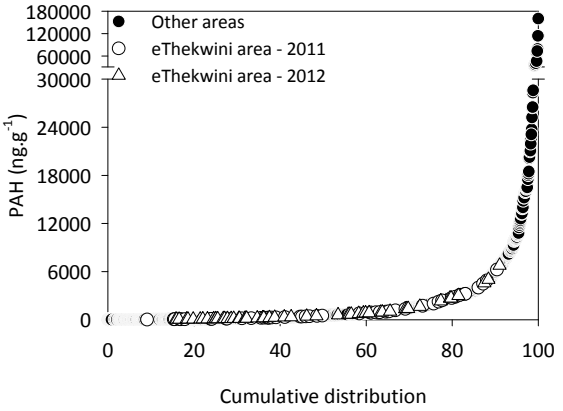

Figure 2.13. Comparison of total polycyclic aromatic hydrocarbon (PAH) concentrations in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2011 and 2012 and in various areas of the world (data from Buamard *et al*., 1998; Ashley and Baker, 1999; Daum *et al*., 2000; Gunther *et al*., 2001; Basheer *et al*., 2003; WDEC, 2005; Martínez-Lladó *et al*., 2007; Pait *et al*., 2007; Vane *et al*., 2007; Wade *et al*., 2008; Acquavita *et al*., 2009; Antizar-Ladislao, 2009; Khairy *et al*., 2009; Mohrherr *et al*., 2009; Sun *et al*., 2009; Shim *et al*., 2010; Chen *et al*., 2011; Choi *et al*., 2011; Gnandi *et al*., 2011; Kanzari *et al*., 2012; Ridgway *et al*., 2012; Wagener *et al*., 2012; Massone *et al*., 2013; Pan *et al*., 2014; Wagener *et al*., 2010).

3.3.4 Pesticides

Background information on the sources and significance of pesticides as contaminants of sediment was provided in Chapter 1. Organophosphorous pesticides were not detected in sediment at concentrations exceeding the method detection limit. Four organochlorine pesticides and/or their metabolites were detected at concentrations exceeding the method detection limit in sediment at 24 stations.

Chlordanes were detected in sediment at nine of the 54 stations sampled. The most frequent detection was in the uMngeni River estuary and tributaries of the estuary (five stations), although in a spatially sporadic manner (Figure 2.14). Chlordanes were also detected in sediment at a station in one arm of Island View Canal, at one station in Durban Bay, and at two stations in the Isipingo River. The ratio between α- and γ-chlordane in technical mixtures of chlordane, which comprises a mixture of over 140 compounds, is about 0.77. In the environment γ-chlordane degrades more easily than α-chlordane (Eitzer *et al*., 2001). Ratios for the sediment samples analysed in this study ranged between 0.66-1.25. The ratio at only two stations was <0.77, although the ratio at one other station was only 0.78. While this suggests a mix of new and historic sources of chlordane the ratio at the majority of stations implies a historic source. Of the trans- and cis-chlordanes, cis-nonachlor was detected in one sediment sample and trans-nonachlor in six samples, also implying a historical source

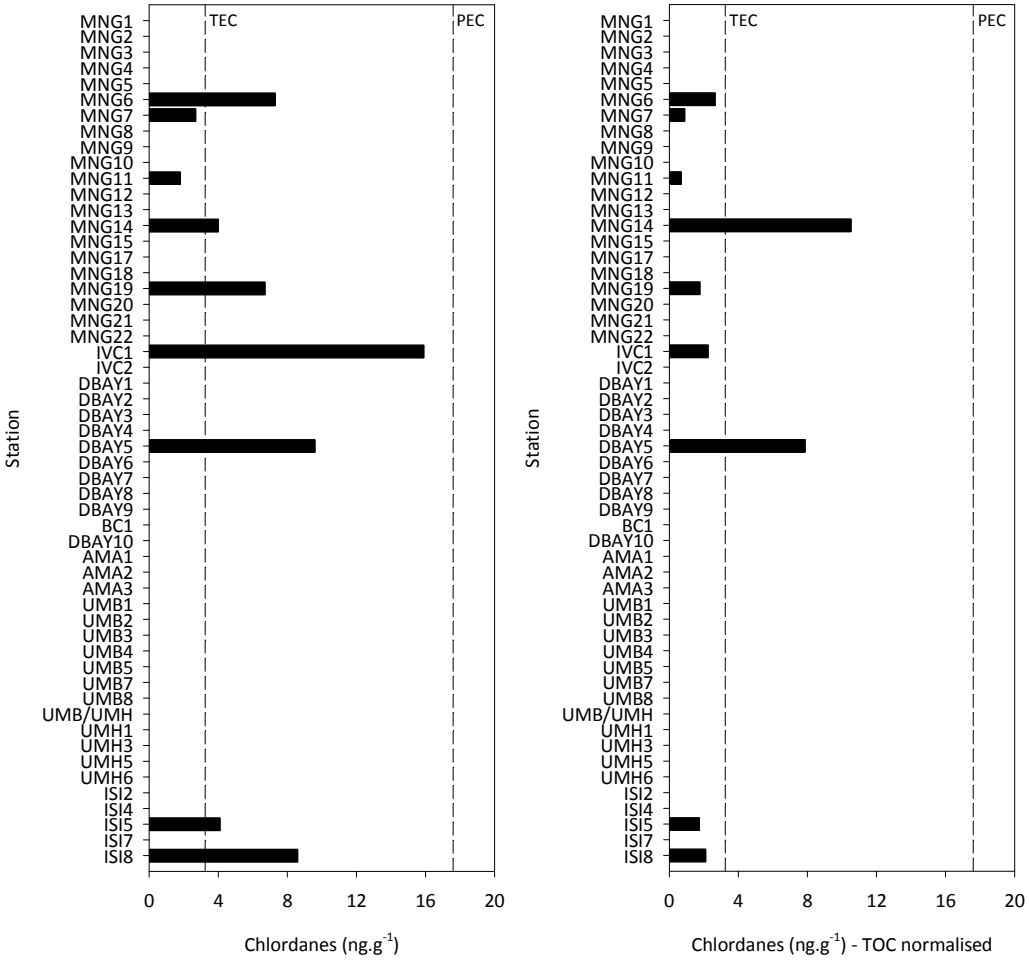

Figure 2.14. Total chlordane concentrations not normalised (left) and normalised (right) to total organic carbon (TOC) in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2012. The dashed lines denote the Threshold Effect Concentration (TEC) and Probable Effect Level (PEC) of the consensus-based sediment quality guidelines derived by MacDonald *et al*. (2000).

(Eitzer *et al*., 2001). At all stations where chlordanes were detected the total concentration at all but two stations exceeded the Threshold Effect Concentration of the consensus-based sediment quality guidelines derived by MacDonald *et al*. (2000), but no concentrations exceeded the Probable Effect Concentration of these guidelines. The concentration at one station in Island View Canal was, however, only slightly lower than the Probable Effect Concentration, implying a high likelihood that this concentration was exerting an acutely toxic effect to sediment-dwelling organisms (Figure 2.14). The sediment quality guidelines derived by Long *et al*. (1995) do not provide a guideline for chlordanes.

DDT and/or metabolites were the most frequently detected pesticide, albeit sporadically within each system studied (Figure 2.15). The DDX concentration at two stations in the Amanzimnyama River, represented in both cases by p'p'-DDE, was extremely high, at 373.9 and 364.5 $ng.g^{-1}$. Concentrations at other stations were far lower, albeit still relatively high at some stations. At all stations where DDT and/or metabolites were detected the DDX concentration exceeded the Effects Range Low of the sediment quality guidelines derived by Long *et al*. (1995) and usually also the Threshold Effect Concentration of the sediment quality guidelines derived by MacDonald *et al*. (2000) (Figure 2.15). The concentration at station IVC1 in Island View Canal and at stations AMA1 and AMA2 in the Amanzimnyama River also exceeded the Effects Range Median of the sediment quality guidelines derived by Long *et al*. (1995), but not the Probable Effect Concentration of the sediment quality guidelines derived by MacDonald *et al*. (2000). Although exceedance of the Effects Range Median suggests a high likelihood that DDX concentrations were acutely toxic to sediment-dwelling organisms at the relevant stations there is uncertainty in this regard considering the

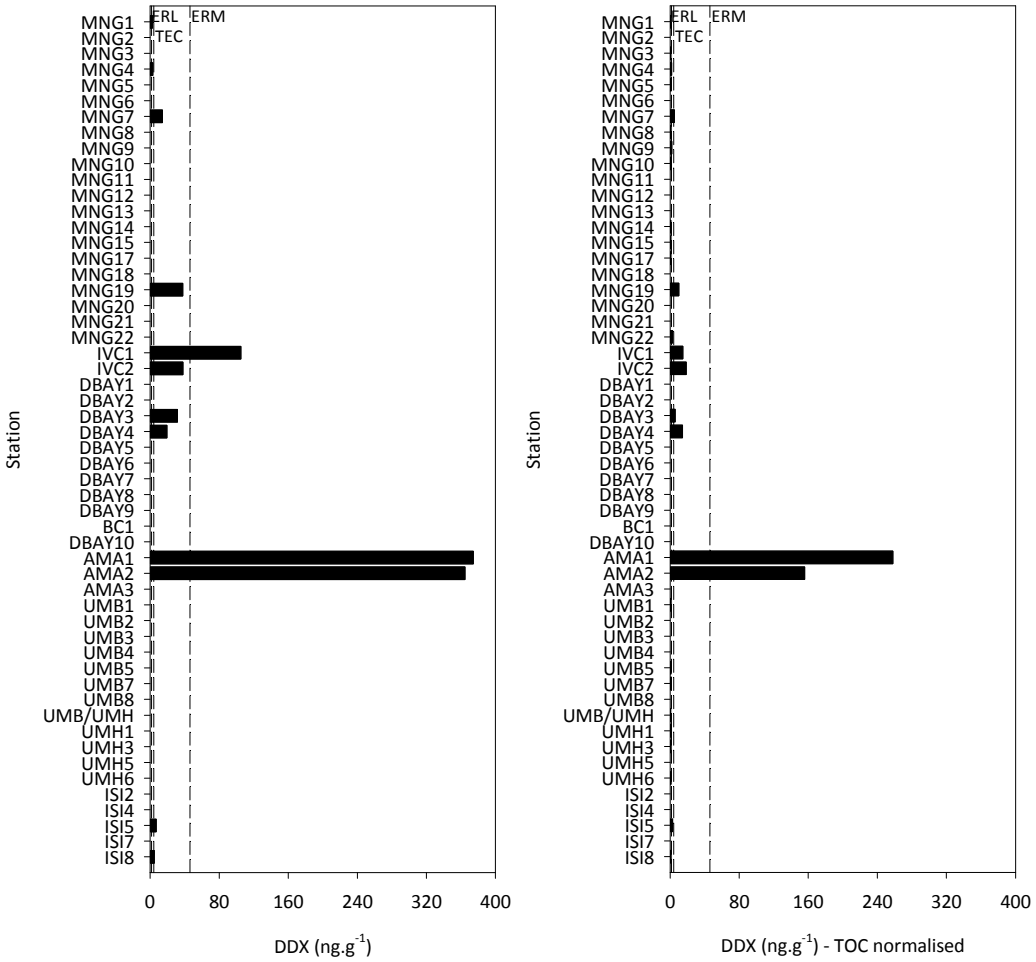

Figure 2.15. DDX concentrations not normalised (left) and normalised (right) to total organic carbon (TOC) in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2012. The dashed lines denote the Threshold Effect Concentration (TEC) of the consensus-based sediment quality guidelines derived by MacDonald *et al*. (2000) and the Effects Range Low (ERL) and Effects Range Median (ERM) of the sediment quality guidelines derived by Long *et al*. (1995).

concentration prescribed by the Effects Range Median is 46.1 ng.g^{-1}, but 572 ng.g^{-1} for the narratively equivalent Probable Effect Concentration of the sediment quality guidelines derived by MacDonald *et al*. (2000). Also, Long *et al.* (1995) assigned a low level of confidence to the guidelines for DDX. Thus, depending on which sediment quality guidelines are used a very different interpretation of the potential toxicological significance of DDX concentrations is reached, although it is necessary to reiterate that the sediment quality guidelines derived by MacDonald *et al*. (2000) are freshwater ecosystems and those derived by Long *et al*. (1995) are for estuarine and marine ecosystems.

Endosulfans were detected in sediment at a single station, namely station DBAY4 in Durban Bay (Figure 2.16). The sediment quality guidelines used for this study do not provide guidelines for endosulfans.

Toxaphene was detected in sediment at all but one station in Durban Bay, but only at one station in the various rivers and canals that discharge into the Bay, namely station BC1 in Bayhead Canal (Figure 2.17). This suggests there was a significant source of toxaphene in Durban Bay, although this pesticide was detected in sediment at the points where rivers and surface runoff discharge into the Bay and external sources may also be important. Toxaphene was also detected at two stations in the Isipingo River and at one station in a tributary of the uMngeni River estuary. Toxaphene concentrations at numerous stations were high, but particularly so at station ISI5 in the Isipingo River. The sediment quality guidelines used for this study do not provide guidelines for toxaphene. Batterman *et al*. (2008) detected five homologues of

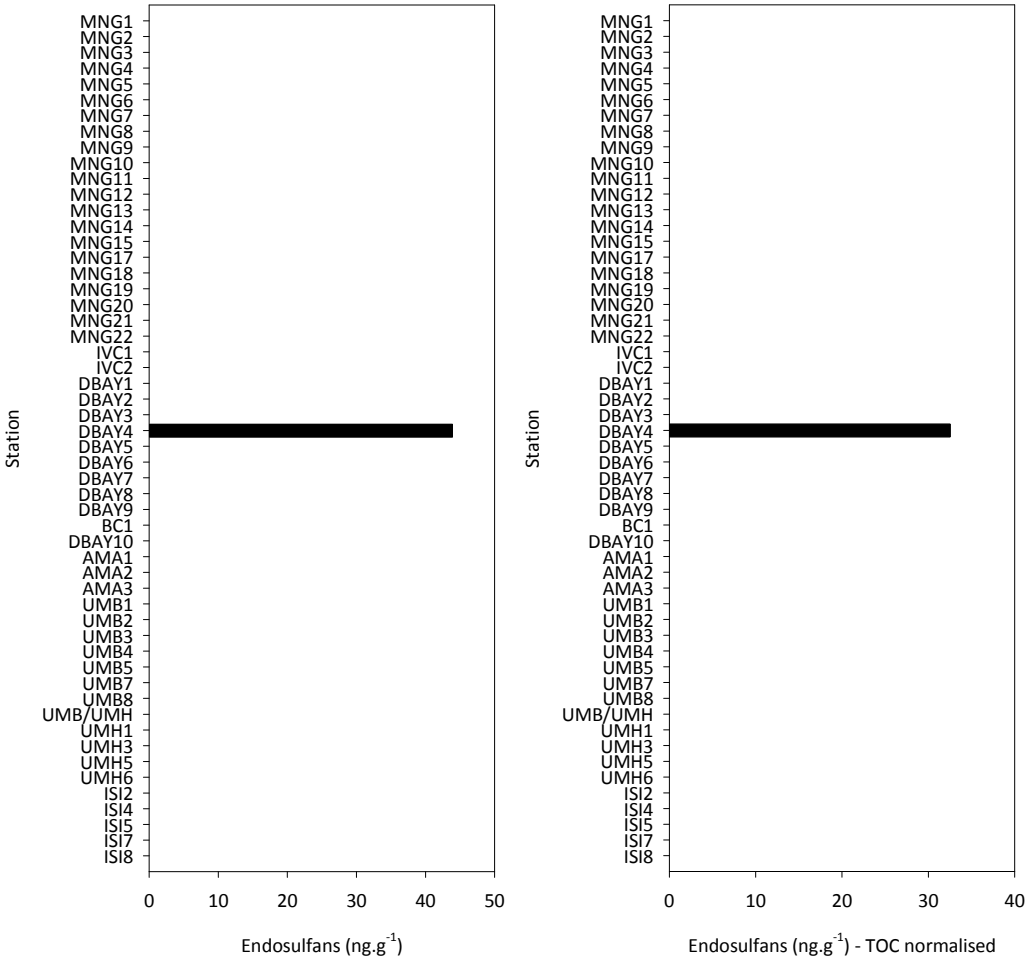

Figure 2.16. Total endosulfan concentrations not normalised (left) and normalised (right) to total organic carbon (TOC) in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2012.

toxaphene in air samples collected at three widely spaced sampling sites in the Durban area and concluded that the toxaphene was derived from both local sources and via long-range atmospheric transport. The potential sources of the toxaphene in the Durban area are uncertain since its primary application was as an insecticide for the control of pests on agricultural crops and on livestock and poultry (ticks and mites).

As is the case for other organic chemicals, fine-grained (muddy) sediment with a high particulate organic matter content has a greater potential to accumulate pesticides than sediment dominated by sand. However, concentrations of all pesticides were very weakly correlated to the mud, total organic content and total organic carbon fractions of sediment, including at the system specific level.

From an overall perspective, pesticides and/or their metabolites were most frequently detected at station MNG19, in a tributary of the uMngeni River estuary, and at station ISI8 in the Isipingo River (Figure 2.18). The high frequency of pesticide detection at station MNG19 is interesting considering it was situated in a channel draining runoff from a relatively low income residential suburb. At least one pesticide or metabolite was detected in sediment at each station in Durban Bay and at the majority of stations in the Amanzimnyama River, Island View Canal and Bayhead Canal (Figure 2.18). In Durban Bay, the most frequent occurrence of pesticides was in sediment at station DBAY5, situated off a canal (Moore Road Culvert) that drains surface runoff from a densely urbanised and industrialised area to the Bay. This and the detection of pesticides in the Amanzimnyama River, Island View Canal and Bayhead Canal suggests that riverine inflows and surface runoff are important sources of pesticides to Durban Bay. However, no pesticides were detected in sediment in the Umbilo and Umhlatuzana Rivers, which are the most significant sources of freshwater inflow to the Bay. In the 2011 survey, in contrast, pesticides were sporadically

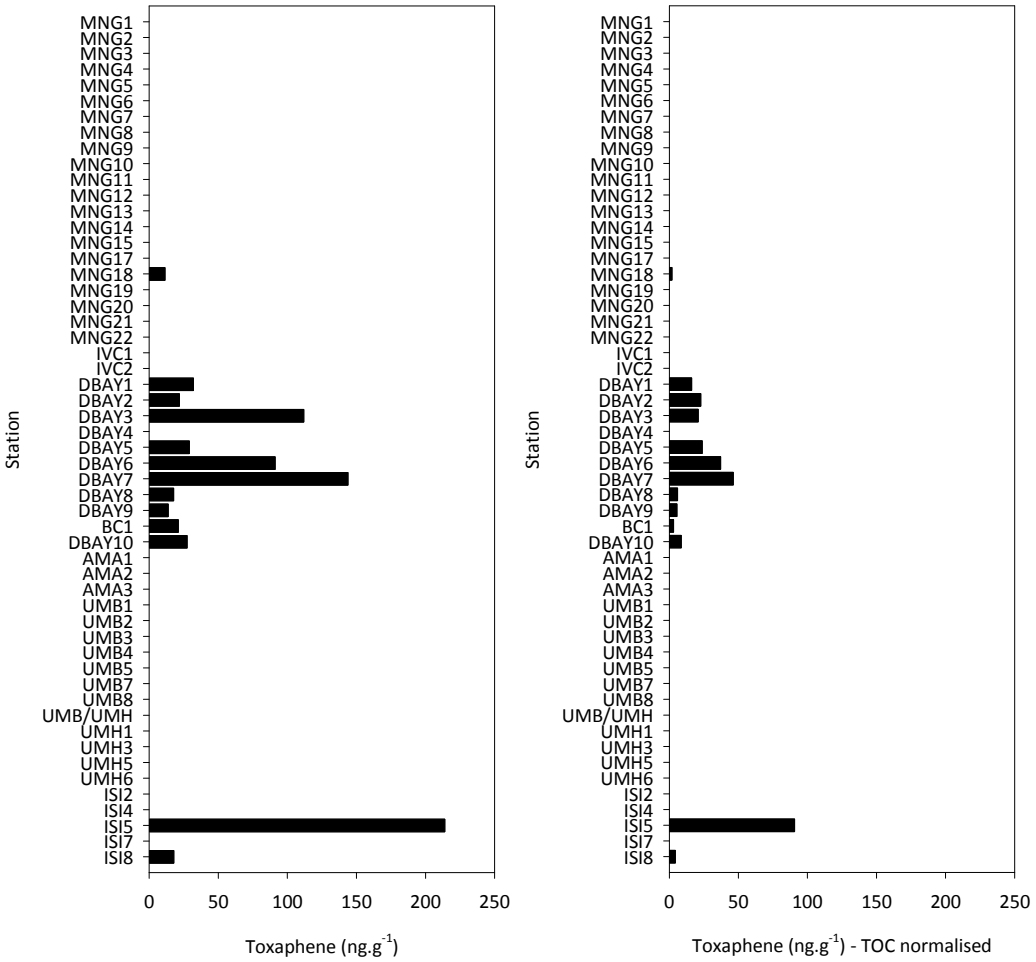

Figure 2.17. Toxaphene concentrations not normalised (left) and normalised (right) to total organic carbon (TOC) in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2012.

detected in the latter rivers, with the highest DDX concentration in fact detected in a tributary of the Umhlatuzana River. There were clear sources of pesticides to one 'arm' of the Isipingo River (stations ISI5 and ISI8), presumably due to pesticide application at surrounding industrial sites. Pesticides were sporadically detected and at variable frequencies in sediment in the uMngeni River, its estuary and tributaries of the estuary (Figure 2.18).

By far the highest total pesticide concentrations (*i.e.* sum of all pesticide concentrations) were for sediment at two stations in the Amanzimnyama River, due mainly to the very high DDX concentrations detected at these stations, followed by station ISI5 in the Isipingo River estuary, due to the high toxaphene concentration detected at the latter station (Figure 2.19).

In the survey discussed in Chapter 1 only two organochlorine pesticides were detected in sediment at concentrations exceeding the method detection limit, namely DDT and metabolites and chlordanes. This was essentially identical to the survey discussed in this chapter, with the obvious difference that endosulfans were detected at two stations in the 2012 survey. Toxaphene was not analysed in the 2011 survey. In the 2011 survey, DDX was detected in sediment at 79% of the stations sampled, with concentrations ranging from below the method detection limit to 54.5 ng.g^{-1}. The latter concentration was considerably lower than the highest concentrations detected in the 2012 survey (373.9 and 364.5 ng.g^{-1}). However, apart from these high concentrations and a concentration of 104.9 ng.g^{-1} at station IVC1 in Island View Canal, DDX concentrations were broadly comparable between the surveys (Figure 2.20). The frequency of DDX detection was, however, considerably higher in the 2011 survey, as DDX was detected in sediment at only 18.5% of stations in the 2012 survey. Although more rivers, estuaries and canals were

sampled in the 2011 survey and the method detection limit was lower, even if the same systems are compared and the method detection limit for the 2012 survey is considered then DDX was detected in sediment at 49% of stations in the 2011 survey, or about two and a half times more frequently than for the 2012 survey. The most pronounced difference between surveys in terms of the frequency of DDX detection was for the uMngeni River catchment (Figure 2.20). A further dissimilarity was that while the bulk of the DDX was present as technical DDT in the 2011 survey, in the 2012 survey DDE was the predominant form (8 samples) followed by DDD (5 samples). Technical DDT was present at a concentration exceeding the method detection limit in only two sediment samples in the 2012 survey. The implication was thus for recent sources of DDT over a large part of the study area in 2011 but not in 2012, which is difficult to explain. Nevertheless, both surveys demonstrated that DDX is a frequent and at times significant contaminant of sediment in freshwater and estuarine ecosystems in the eThekwini area of KwaZulu-Natal.

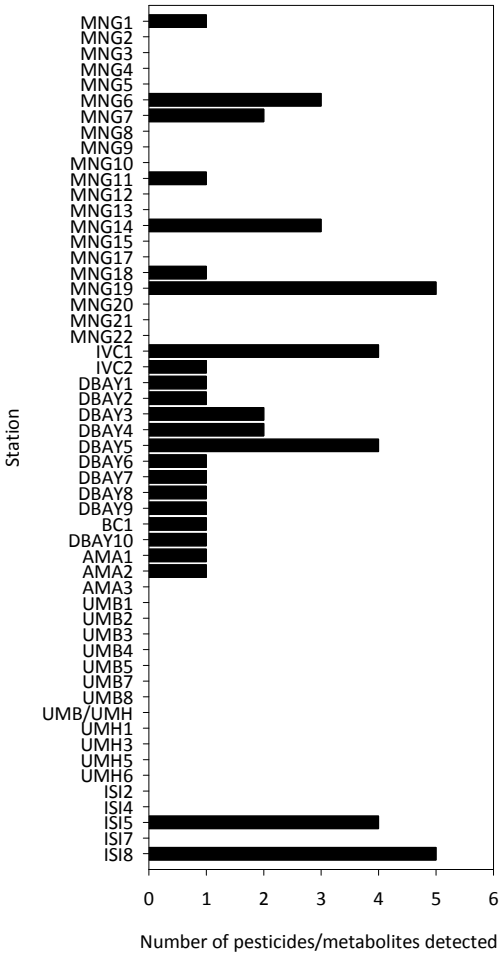

Figure 2.18. Number of pesticides and/or metabolites detected in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2012.

Metabolites of chlordane were detected at concentrations exceeding the method detection limit in sediment at a single station in the 2011 survey compared to nine stations in the 2012 survey. Although toxaphene was not analysed in the 2011 survey, Parlar 26, 50 and 62, which are congeners of toxaphene, were analysed but were not detected at concentrations exceeding the method detection limit. This contrasts with the 2012 survey, when toxaphene was detected in sediment at each station in Durban Bay and at three stations in other systems.

As stated previously, organophosphorous pesticides were not detected in sediment at concentrations exceeding the method detection limit. The only organophosphorous pesticide analysed in 2011 was chlorpyrifos, which was detected at a concentration exceeding the method detection limit in sediment at four stations.

Although the presence of DDX in sediment in rivers, estuaries and canals in the eThekwini area may outwardly appear surprising considering DDT was deregistered for agricultural use in 1976 and banned in 1983 (Bouwman *et al*., 1990), DDT is still used for the control of malaria-bearing mosquitoes in South Africa (Bouwman *et al*., 2006). The eThekwini area does not fall within a malaria control area, which in KwaZulu-Natal is situated in the north of the province. Batterman *et al*. (2008) reported the widespread presence of DDX in air samples collected in the Durban area and suggested an important source of the DDX is long-range atmospheric transport from malaria control areas. This might partly explain the frequent detection of DDX in sediment in rivers, estuaries and canals in the eThekwini area, but it seems unlikely diffuse atmospheric transport can account for the very high DDX concentrations detected at some stations. Batterman *et al*. (2008) also detected chlordane and toxaphene in air samples. DDX and hexachlorocyclohexane were detected on plastic packing pellets collected at one location on the Durban shoreline (Ogata *et al*., 2009), although many of the pesticides detected in air samples by Batterman *et al*.

(2008) and in sediment were not detected on the pellets. Schlenk *et al*. (2005) detected DDX, hexachlorocyclohexane, lindane and heptachlor expoxide in the tissue of three great white sharks (*Carcharodon carcharias*) caught off the eThekwini coastline. Although these sharks move over large areas and there is thus no certainty as to where the pesticides were accumulated, this does at least suggest the presence of these pesticides in east coast waters. This confirms sources of these pesticides in the eThekwini area. This said, recent analysis (2013) of the tissue of mussels collected along the eThekwini shoreline (CSIR, unpublished data), and the tissue of fish and mussels collected for this study (see Chapter 3) only revealed the presence of two pesticides, namely DDX and dieldrin.

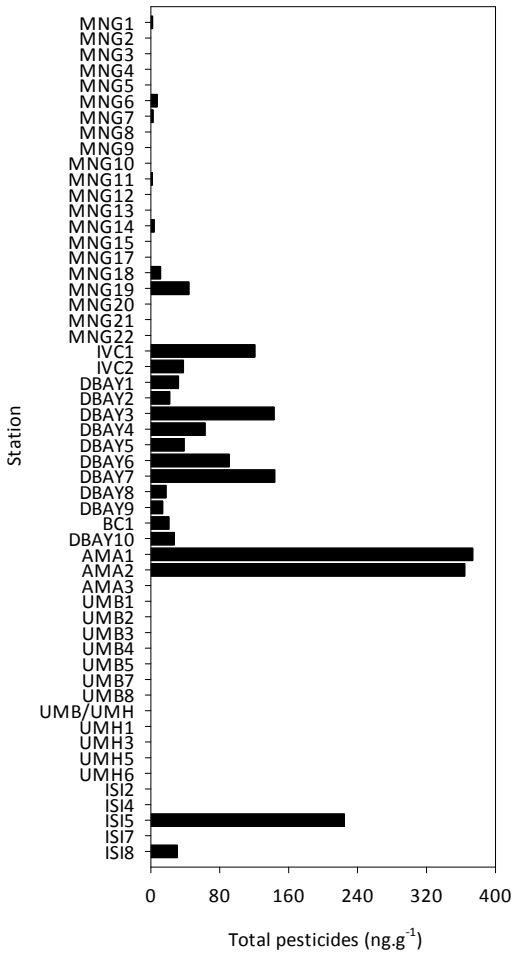

Figure 2.19. Total pesticide concentrations in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2012.

Of the various chemicals analysed in this study, by far the most research performed in South Africa has been on pesticides, particularly organochlorine pesticides. However, few of the studies were performed in coastal ecosystems. Bollmohr *et al*. (2007, 2009) detected endosulfan, DDE and several organophosphorous pesticides on suspended particulate matter entering the Lourens and Rooiels River estuaries in the Western Cape. Quinn *et al*. (2009) measured DDX concentrations between 0.27-4.62 ng.g^{-1} (mean of 3.53 ng.g^{-1}) in sediment collected in industrial, urban and agricultural areas in the Vaal Triangle. Quinn *et al*. (2009) also detected hexacyclochlorohexane, endosulfan and hexachlorobenzene at concentrations exceeding the method detection limit. Roos *et al*. (2011) measured organochlorine pesticide concentrations in 27 sediment samples collected at numerous locations in South Africa, including at one station near the mouth of the uMngeni River estuary. Hexachlorobenzene, hexacyclochlorohexane, heptachlor, mirex and DDX were detected in numerous of the samples analysed by Roos *et al*. (2011). Interestingly, in sediment collected in the uMngeni River estuary all pesticides were present at concentrations exceeding the method detection limit, which is in contrast to this study. At the single station sampled by Roos *et al*. (2011) in the uMngeni River estuary, the DDX concentration was 23.30 ng.g^{-1}, which was the highest concentration measured at any site sampled in South Africa by these workers. Humphries (2013) reported DDX concentrations between 0.8-123 ng.g^{-1} in sediment in Lake Sibaya in northern KwaZulu-Natal. Figure 2.21 compares DDX concentrations reported for sediment in the abovementioned South African studies to concentrations in sediment collected for the surveys discussed in this study. As is evident, DDX concentrations in sediment collected in rivers, estuaries and canals in the eThekwini area in 2011 and 2012 were generally comparable to concentrations reported for other areas of South Africa a. Numerous concentrations reported by Humphries (2013) were slightly higher than concentrations measured in the eThekwini area with the obvious exception of the very high concentrations in sediment collected at two stations in the Amanzimnyama River (Figure 2.21).

For further comparative purposes, total chlordane, DDX, total endosulfan and toxaphene concentrations measured in sediment collected in rivers, estuaries and canals in the eThekwini area in 2011 and 2012 are

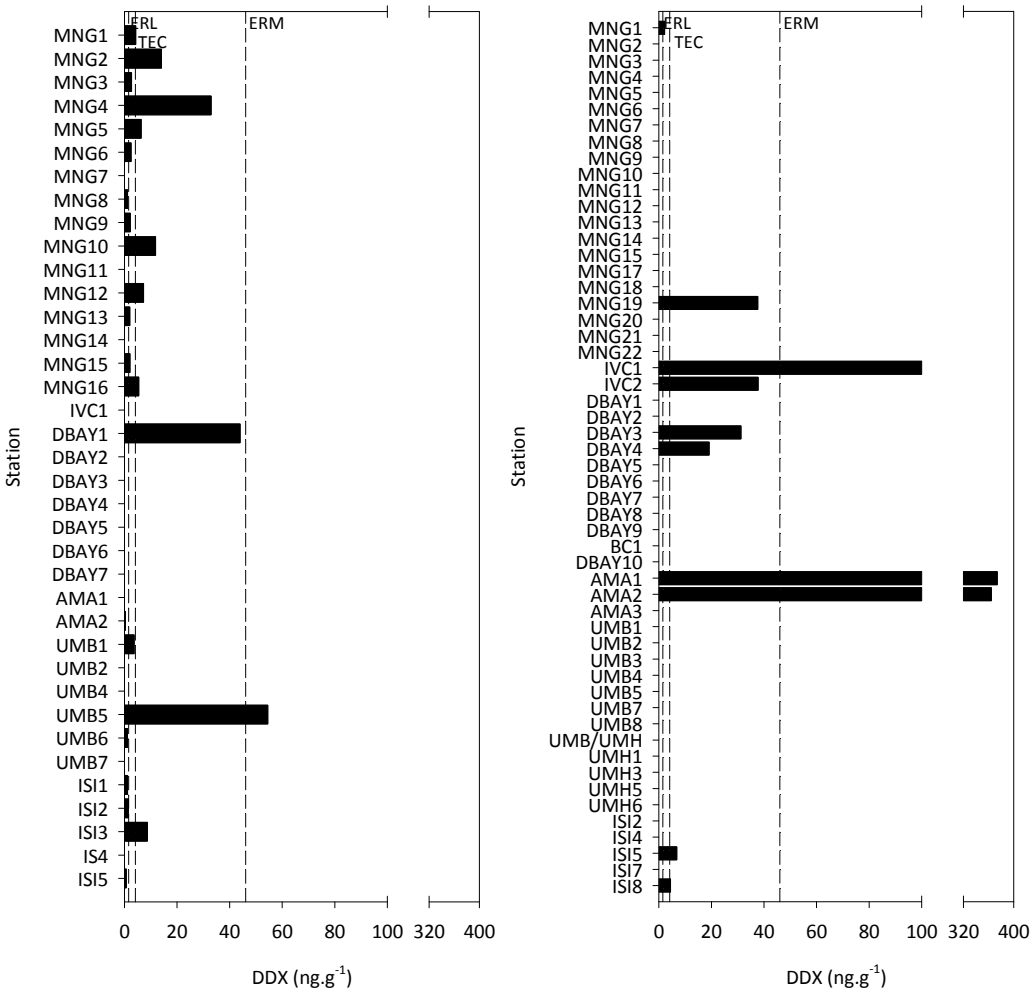

Figure 2.20. Comparison of DDX concentrations in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2011 (left) and 2012 (right). The dashed lines denote the Threshold Effect Concentration (TEC) of the consensus-based sediment quality guidelines derived by MacDonald *et al*. (2000) and the Effects Range Low (ERL) and Effects Range Median (ERM) of the sediment quality guidelines derived by Long *et al*. (1995).

compared to concentrations reported for studies performed in other parts of the world in Figures 2.22-2.25. Although chlordanes were sporadically detected in sediment collected in the eThekwini area, where detected the concentrations were high compared to concentrations reported for many studies in other parts of the world, with many of the concentrations falling within the 90th percentile of the concentration distribution (Figure 2.22). Numerous DDX concentrations fall in the upper part of the range reported for studies in other parts of the world, with the concentrations in sediment at two stations in the Amanzimnyama River being the 7th and 8th highest (Figure 2.23). Although endosulfans were only detected in sediment at one station in the 2012 survey, the concentration was the second highest reported for any comparative study in other parts of the world (Figure 2.24). Toxaphene concentrations at four stations far exceed the highest concentration reported for studies in other parts of the world, while concentrations at several other stations fall near the upper part of the range for these studies (Figure 2.25). It should, however, be noted that toxaphene is rarely the focus of attention in studies in other parts of the world. Thus, while pesticides were sporadic contaminants of sediment in the catchments studied in the eThekwini area of KwaZulu-Natal, when detected they were often at concentrations that are amongst the highest reported for studies anywhere in the world.

3.3.5 Polychlorinated biphenyls

Background information on the sources and significance of polychlorinated biphenyls as contaminants of sediment was provided in Chapter 1. Polychlorinated biphenyls were detected at concentrations exceeding

the method detection limit in sediment at 26 of the 54 stations sampled. Total polychlorinated biphenyl concentrations varied widely, from below the method detection limit at 52% of stations to 113.8 $ng.g^{-1}$ at station DBAY3 in Durban Bay (Figure 2.26). The mean concentration was 11.3 $ng.g^{-1}$, with a standard deviation of 24.2 $ng.g^{-1}$. The 25th, 50th and 75th percentiles of the concentration distribution was 0.0. 0.0 and 9.6 $ng.g^{-1}$ respectively. Thus, concentrations at the majority of stations were low. Polychlorinated biphenyls were detected in sediment at all stations in Durban Bay and at all or the majority of stations in the Amanzimnyama River, Island View Canal and Bayhead Canal. As stated above, the highest total polychlorinated biphenyl concentration was detected at station DBAY3 in Durban Bay, which was situated off a stormwater outfall that drains surface runoff into the Bay from part of the central business district of Durban. In the 2011 survey (Chapter 1), the total polychlorinated biphenyl concentration detected in this part of the Bay was amongst the highest for any station sampled. The second highest total polychlorinated biphenyl concentration was detected at station DBAY7, in that part of the Bay where vessel maintenance and construction facilities are concentrated. This also agrees with the 2011 survey, when the second highest total polychlorinated biphenyl concentration was also detected in this part of the Bay. In the 2011 survey, the highest total polychlorinated biphenyl concentration was detected in sediment off the inflow of the Amanzimnyama River. In the 2012 survey, the concentration at this station was the fifth highest concentration detected. There thus seem to be clear and significant sources of polychlorinated biphenyls in Durban Bay and in surrounding areas that are entering the Bay via riverine flow and surface runoff. Relatively high polychlorinated biphenyl concentrations were also detected in sediment at two stations in the Isipingo River. Polychlorinated biphenyls were infrequently detected at low concentrations in the uMngeni River, its estuary and tributaries of the estuary, and in the Umhlatuzana and Umbilo Rivers. This agrees with the findings of the 2011 survey.

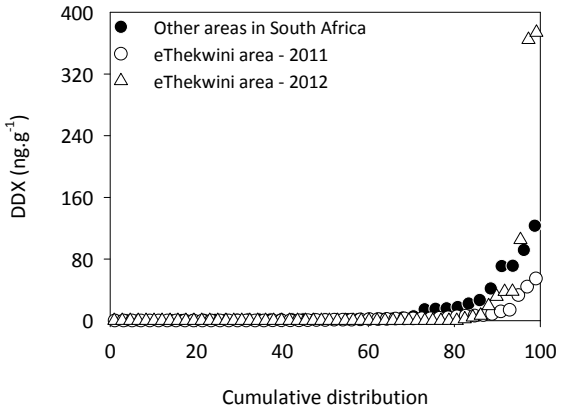

Figure 2.21. Comparison of DDX concentrations in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2012 and in other areas in South Africa (data from Humphries, 2013; Roos *et al*., 2011).

As was the situation for polycyclic aromatic hydrocarbons and pesticides, total polychlorinated biphenyl concentrations for all stations combined were very weakly correlated to the mud, total organic and total organic carbon fractions of sediment. There was no improvement in the strength of the relationships at the system specific level.

Total polychlorinated biphenyl concentrations in sediment at three stations, two in Durban Bay and one in the Isipingo River exceeded the Threshold Effect Concentration but not the Probable Effect Concentration of the sediment quality guidelines derived by MacDonald *et al*. (2000) (Figure 2.26). In comparison, total polychlorinated biphenyl concentrations at the latter stations, five other stations in Durban Bay and one other station in the Isipingo River exceeded the Effects Range Low of the Long *et al*. (1995) sediment quality guidelines. No concentrations exceeded the Effects Range Median of the latter guidelines (Figure 2.26). This difference in guideline exceedance is again attributable to the fact that the sediment quality guidelines derived by MacDonald *et al*. (2000) and Long *et al*. (1995) provide different guidelines for total polychlorinated biphenyls. Based on the Long *et al*. (1995) sediment quality guidelines the highest likelihood that total polychlorinated biphenyl concentrations were adversely affecting sediment-dwelling organisms was at stations DBAY3 and DBAY7 in Durban Bay and stations ISI4 and ISI8 in the Isipingo River. Thus, despite a ban on the production and the phasing out of the use of polychlorinated biphenyls these chemicals are still entering aquatic ecosystems in the greater Durban area and are accumulating in sediment in some systems to concentrations that pose a potentially significant toxicological risk to

sediment-dwelling organisms. This discussion of sediment quality guideline exceedances is, however, misleading in that only 22 of the possible 209 congeners were analysed for the 2012 survey. The 'total' polychlorinated biphenyl concentration calculated from the 22 congeners is thus probably a substantial underestimate of the total concentration and the degree and frequency of sediment quality guideline exceedance would thus likely to have been higher if a wider suite of congeners was analysed. The sum of 18 so-called National Oceanic and Atmospheric Administration congeners, namely PCB 8, 18, 28, 44, 52, 66, 101, 105, 118, 128, 138, 153, 170, 180, 187, 195, 206, 209, is often multiplied by a factor of 2 to estimate the total polychlorinated biphenyl concentration when a small set of congeners is analysed (Lauenstein and Cantillo, 1993). Howell *et al*. (2008) found that this approach provided a slight underestimate of the total polychlorinated biphenyl concentration. Fikslin and Santoro (2003) reported an overestimate (ratio 2.77) in one study and an underestimate in another study (ratio 1.48) when the sum of these 18 congeners multiplied by a factor of two was compared to the total polychlorinated biphenyl concentration estimated from 81 congeners analysed in sediment. If this approach was followed, the frequency of sediment quality guideline exceedance would obviously have been higher.

Organic carbon normalisation of total polychlorinated biphenyl concentrations substantially reduced concentration variability between systems and resulted in only a single concentration exceeding the Effects Range Low of the sediment quality guidelines derived by Long *et al.* (1995) (Figure 2.26). No normalised concentrations exceeded other sediment quality guidelines.

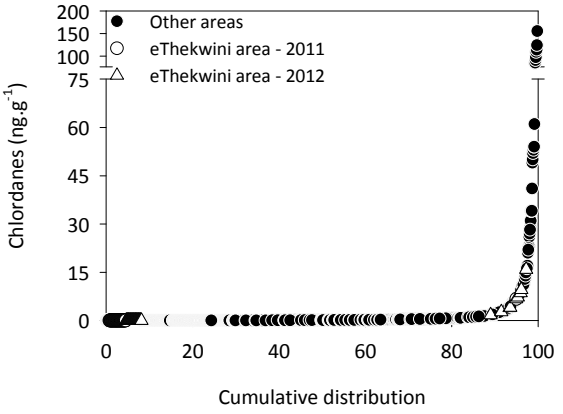

Figure 2.22. Comparison of total chlordane concentrations in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2012 and in other areas in South Africa (data from Daum *et al*., 2007; EMAP Delaware and Maryland Coastal Bays, 1993; EMAP Carolinian Province, 1995-1997; EMAP Texas, 1993-1994; EMAP Mid-Atlantic Integrated Assessment Estuaries, 1996-1998; Pait *et al*., 2007; Wang *et al*., 2008; Hu *et al*., 2009).

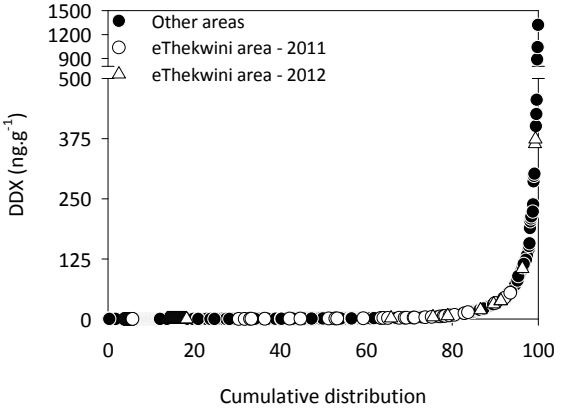

Figure 2.23. Comparison of DDX concentrations in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2012 and in other areas of the world (data from EMAP Mid-Atlantic Integrated Assessment Estuaries, 1996-1998; Barakat *et al*., 2002; Daum *et al*., 2007; Pait *et al*., 2007; Wade *et al*., 2008; Wang *et al*., 2008; Hu *et al*., 2009; Shim *et al*., 2010; Choi *et al*., 2011; Kanzari *et al*., 2012; Syakti *et al*., 2012; Pan *et al*., 2014).

Figure 2.27 compares polychlorinated biphenyl concentrations measured in sediment for the surveys discussed in this study to concentrations reported for sediment in other parts of South Africa. Note that for this comparison the total polychlorinated biphenyl concentrations for the 2011 survey were calculated as the same suite of 22 congeners analysed for the 2012 survey. Pieters (2007) reported polychlorinated biphenyl concentrations (sum of 12 congeners) in sediment collected at 22 sites across South Africa, including at the mouths of the Mlazi and uMngeni Rivers in Durban. Polychlorinated biphenyls were detected in all samples, at concentrations between 0.02-24.94 ng.g^{-1}. Concentrations in sediment collected at the mouths of the Mlazi and uMngeni Rivers in Durban were 0.64 and 0.55 ng.g^{-1} respectively, the seventh and eight highest concentrations for all sites investigated by Pieters (2007). Few of the congeners analysed by Pieters (2007) were analysed in this study, making direct comparison of the data impossible.

Nieuwoudt *et al*. (2009) reported polychlorinated biphenyl concentrations (sum of 12 congeners) in sediment collected at five sites near Sasolburg, Vanderbijlpark and Vereeniging in the Vaal Triangle area and at two reference sites near Balfour. Polychlorinated biphenyls were detected in all sediment samples, at concentrations between 0.1-1.8 ng.g^{-1}. Few of the congeners analysed by Nieuwoudt *et al*. (2009) were analysed in this study, again making direct comparison of the data impossible.

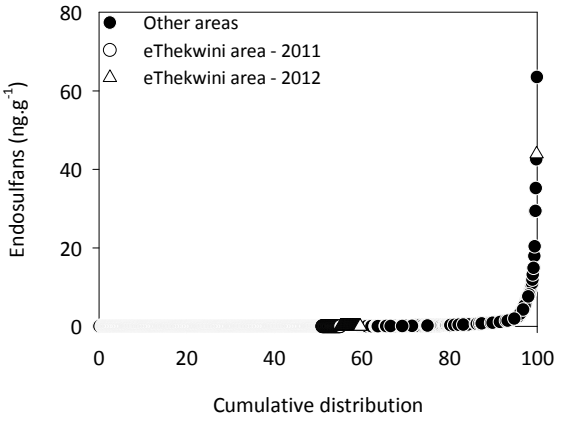

Figure 2.24. Comparison of total endosulfan concentrations in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2012 and in other areas in South Africa (data from EMAP Delaware and Maryland Coastal Bays, 1993; EMAP Carolinian Province, 1995-1997; EMAP Texas, 1993-1994; EMAP Mid-Atlantic Integrated Assessment Estuaries, 1996-1998; Pait *et al*., 2007; Wang *et al*., 2008; Hu *et al*., 2009).

Nevertheless, it is evident that the highest concentrations measured by Nieuwoudt *et al*. (2009) were low in comparison to this study. Roos *et al*. (2011) measured polychlorinated biphenyl concentrations (sum of seven congeners) in 27 sediment samples collected at numerous sites in South Africa, including at near the mouth of the uMngeni River estuary. Polychlorinated biphenyls were detected in all samples, at concentrations between 0.6-57.3 ng.g^{-1}. The concentration at the station near the mouth of the uMngeni River estuary was 46.18 ng.g^{-1}, which was the third highest concentration measured by Roos *et al*. (2011). Polychlorinated biphenyl concentrations (sum of seven congeners) were recently measured in 62 sediment samples collected in the Orange-Senqu River Basin (ORASECOM, 2013). Concentrations exceeded the method detection limit in nine samples, with the highest concentration at 2.83 ng.g^{-1}. As is evident in Figure 2.28, with the exception of four high concentrations the total polychlorinated biphenyl concentrations in sediment collected in rivers, estuaries and canals in the eThekwini area in 2011 and 2012 were generally comparable to concentrations reported for other areas of South Africa. It is, however, necessary to reiterate that fewer congeners were analysed in the comparator studies, with the result that total concentrations reported might have been as high or higher than for the surveys discussed in this study had the same number of congeners been analysed.

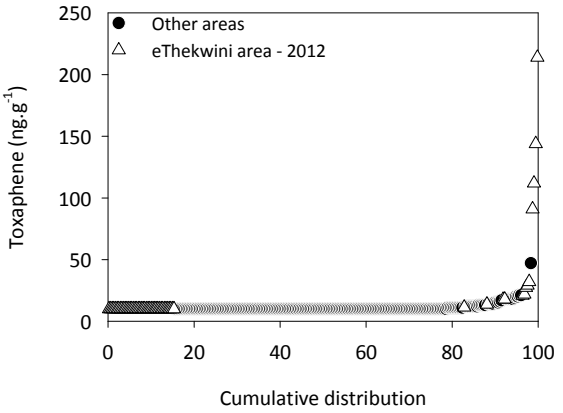

Figure 2.25. Comparison of toxaphene concentrations in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2012 and in other areas of the world (data from EMAP Louisianan Province, 1994; EMAP Texas, 1993-1994; WSDE, 2012).

For further comparative purposes, polychlorinated biphenyl concentrations measured in sediment collected in rivers, estuaries and canals in the eThekwini area in 2011 and 2012 are compared to concentrations reported for studies performed in other parts of the world in Figure 2.29. The number of congeners analysed in the comparator studies varied widely, from 7-209. Although concentrations in sediment in the eThekwini area do not appear especially high compared to other parts of the world, extremely high concentrations reported for some comparator studies skew the data. These high concentrations were generally for sediment collected in industrialised parts of the United States of America and Europe (*e.g*. Daum *et al*., 2000; Gunther *et al*., 2001; Pait *et al*., 2007). Of the 1083 concentrations

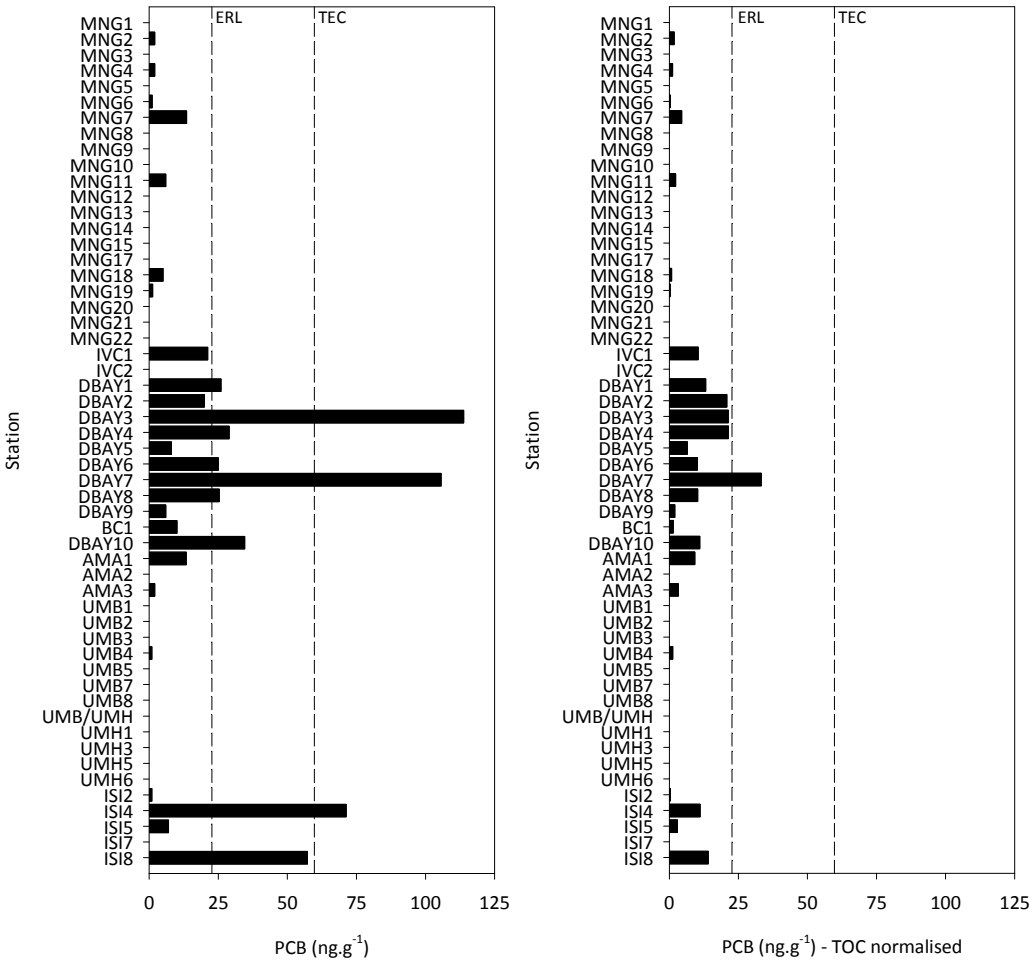

Figure 2.26. Total polychlorinated biphenyl (PCB) concentrations not normalised (left) and normalised (right) to total organic carbon (TOC) in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2012. The dashed lines denote the Threshold Effect Concentration (TEC) of the consensus-based sediment quality guidelines derived by MacDonald *et al*. (2000) and the Effects Range Low (ERL) and Effects Range Median (ERM) of the sediment quality guidelines derived by Long *et al*. (1995).

included in Figure 2.29, the highest concentration for the eThekwini area was in position 1059, for sediment collected at station DBAY3 in Durban Bay in 2011. In fact, two additional concentrations for the latter survey (station DBAY5 in Durban Bay and station AMA2 in the Amanzimnyama River) and three concentrations for the 2012 survey (stations DBAY3 and DBAY7 in Durban Bay and station ISI4 in the Isipingo River) are within the 90th percentile of the concentration distribution. In other words, these and several other concentrations were 'high' by international standards, although they are still well below the extremely high concentrations reported in some studies.

3.3.6 Metals

The need for and use of baseline metal concentration models for interpreting metal concentrations in sediment and for calculating metal Enrichment Factors was discussed in Chapter 1. In Figure 2.30, metal concentrations in sediment collected in the rivers, estuaries and canals sampled in the eThekwini area in 2012 are superimposed on aluminium normalised baseline models for metals in sediment in Durban Bay. As is evident, metal concentrations in sediment at a large proportion of the stations fall within baseline model upper and lower prediction limits, that is, within the concentration range expected for granulometrically equivalent but uncontaminated sediment. Numerous metal concentrations do, however, exceed the baseline model upper prediction limits, that is, reflect metal enriched/contaminated sediment. As discussed in Chapter 1, Enrichment Factors provide a more effective tool for comparing the magnitude of metal enrichment/contamination between samples (stations). Figure 2.31 presents Enrichment Factors for each

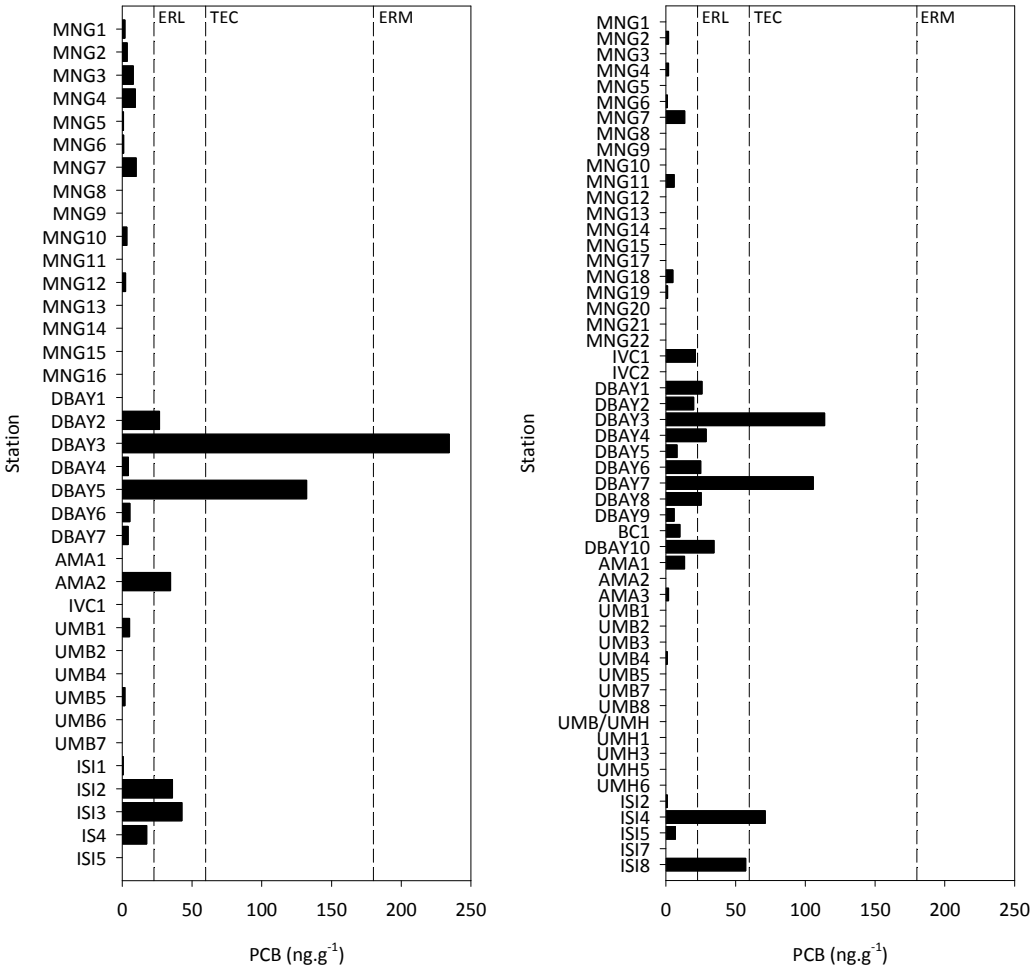

Figure 2.27. Comparison of polychlorinated biphenyl (PCB) concentrations (same congeners analysed) in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2011 (left) and 2012 (right). The dashed lines denote the Threshold Effect Concentration (TEC) of the consensus-based sediment quality guidelines derived by MacDonald *et al*. (2000) and the Effects Range Low (ERL) and Effects Range Median (ERM) of the sediment quality guidelines derived by Long *et al*. (1995).Note that although the same station identifiers were used between years these were often not coincident in the field and the data are thus not directly comparable between similarly named stations.

metal concentration in sediment collected in the rivers, estuaries and canals sampled. The most frequently enriched metal was copper (at 29% of stations), followed by cadmium, manganese and nickel (at 26% of stations each). From a cumulative enrichment perspective the most severely metal contaminated sediment was at station IVC1 in Island View Canal, followed by stations MNG18 and MNG19 in a tributary of the uMngeni River estuary and station DBAY3 in Durban Bay (Figure 2.32). The most frequently metal enriched/contaminated sediment was in Durban Bay and in the Amanzimnyama River, Island View Canal and Bayhead Canal (Figure 2.32). Some metal concentrations and associated Enrichment Factors were extremely high. For example, the Enrichment Factor for zinc in sediment at station MNG18 in a tributary of the uMngeni River estuary was 23.58, that is, 23.58 times higher than the highest zinc concentration expected for granulometrically equivalent but uncontaminated sediment. Similarly pronounced contamination was evident for some metals at station IVC1 in one arm of Island View Canal and station MNG19 in a tributary of the uMngeni River estuary. It is beyond the scope of this study to speculate on the anthropogenic sources of metals at stations where sediment was contaminated save to state there are numerous anthropogenic sources of metals to aquatic ecosystems in urbanised and industrialised areas. In Durban Bay this includes port associated activities.

Trends in metal enrichment/contamination of sediment in the survey discussed in this chapter were generally comparable to trends evident for the survey discussed in Chapter 1. One important difference,

however, was that in the 2011 survey beryllium was enriched in sediment across much of Durban Bay and in the Amanzimnyama River, Island View Canal, Isipingo River and estuary. In 2012, in contrast, there was no evidence for beryllium enrichment of sediment in these or any other systems. This suggests the enrichment in 2011 was possibly not real but rather due to the over extraction of this metal in three sediment batches in the laboratory (see Table 1.2). As was the case for the 2011 survey, cobalt contamination of sediment in Island View Canal and at one station in the Amanzimnyama River was evident in the 2012 survey (Figure 2.31). Sediment at the single station sampled in Bayhead Canal, which discharges surface runoff into Durban Bay, was also contaminated with cobalt, albeit that the magnitude of contamination was low. In 2012, however, sediment off the inflow of the Amanzimnyama River was not enriched/contaminated with cobalt. As discussed in Chapter 1 the cobalt contamination is interesting since this metal is rarely enriched in sediment in South African coastal ecosystems. Similar to the 2011 survey, widespread manganese enrichment of sediment in the uMngeni River estuary and its tributaries was evident in 2012. In contrast, only five sediment samples in other systems were enriched by this metal (Figure 2.31). As discussed in Chapter 1 it is difficult to determine whether the enrichment represents contamination since manganese is highly mobile in sediment under certain conditions, leading to its natural enrichment at the sediment-water interface.

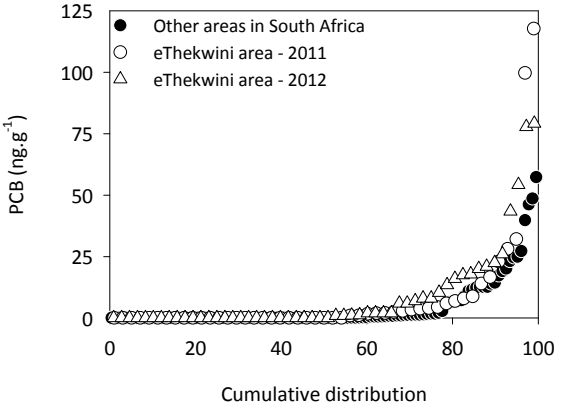

Figure 2.28. Comparison of total polychlorinated biphenyl (PCB) concentrations in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2012 and in other areas in South Africa (data from Pieters, 2007; Nieuwoudt *et al*., 2009; Roos *et al.*, 2011; ORASECOM, 2013).

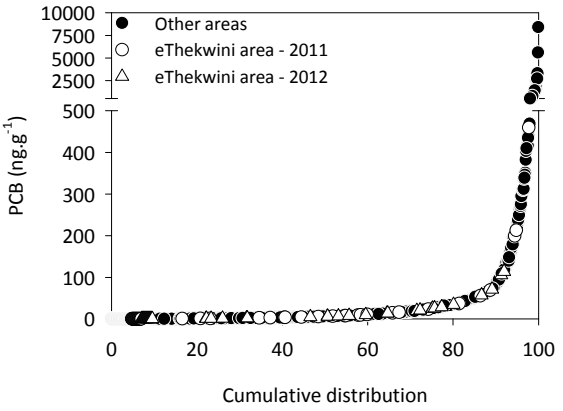

Figure 2.29. Comparison of total polychlorinated biphenyl (PCB) concentrations in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2011 and 2012 and in other areas of the world (data from EMAP, 1998; Daum *et al*., 2000; Gunther *et al*., 2001; Denton *et al*., 2006; Pait *et al*., 2007; Vane, 2007; Wade *et al*., 2008; Antizar-Ladislao, 2009; Ben Ameur *et al*., 2011; Choi *et al*., 2011; ; Shim *et al*., 2011; Kanzari *et al*., 2012; MDEP/MDMF, 2012; Ridgway *et al*., 2012; Syakti *et al*., 2012; Zhou *et al*., 2012; Pan *et al*., 2014).

Figure 2.33 presents the number of metal concentrations in sediment at each station that exceeded the Warning Level, Level I and Level II of the sediment quality guidelines used to regulate the disposal of dredged sediment in South African coastal waters. The concentrations of numerous metals in sediment exceeded the Warning Level, with the most frequent exceedance in Durban Bay and systems flowing into the Bay. Fewer metal concentrations exceeded the Level I, while exceedances of the Level II were restricted to stations MNG18 and MNG19 in a tributary of the uMngeni River estuary, station IVC1 in one arm of the Island View Canal, station AMA2 in the Amanzimnyama River, and station DBAY10 in Durban Bay off the inflow of the Amanzimnyama River (Figure 2.33).

3.3.7 Sediment quality guideline quotients

As discussed previously, to account for the fact that sediment is frequently contaminated by a mixture of chemicals yet sediment quality guidelines cater for individual chemicals, the mean sediment quality guideline quotient approach has been advocated. Mean sediment quality guideline quotients calculated

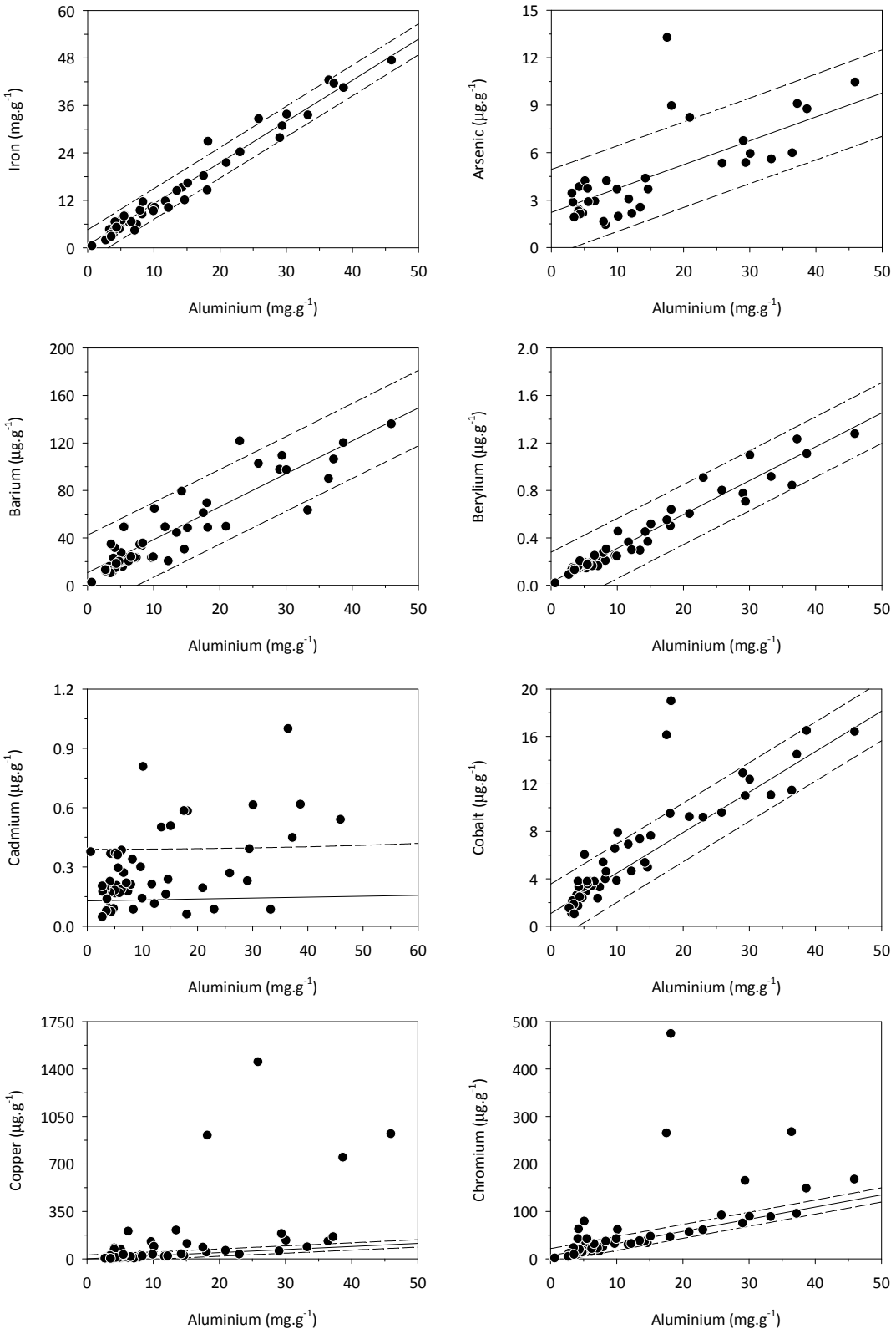

Figure 2.30. Aluminium normalised baseline models for metals in sediment from Durban Bay with metal concentrations in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2012 superimposed.

using the Probable Effect Concentration of the sediment quality guidelines derived by MacDonald *et al*. (2000) and the Effects Range Median of the sediment quality guidelines derived by Long *et al*. (1995) are presented in Figure 2.34. Although the trends in mean sediment quality guideline quotients are similar, the values of the quotients are different. The quotients are generally higher when the Effects Range Median of the Long *et al*. (1995) sediment quality guidelines is used for quotient calculation, because there are fewer

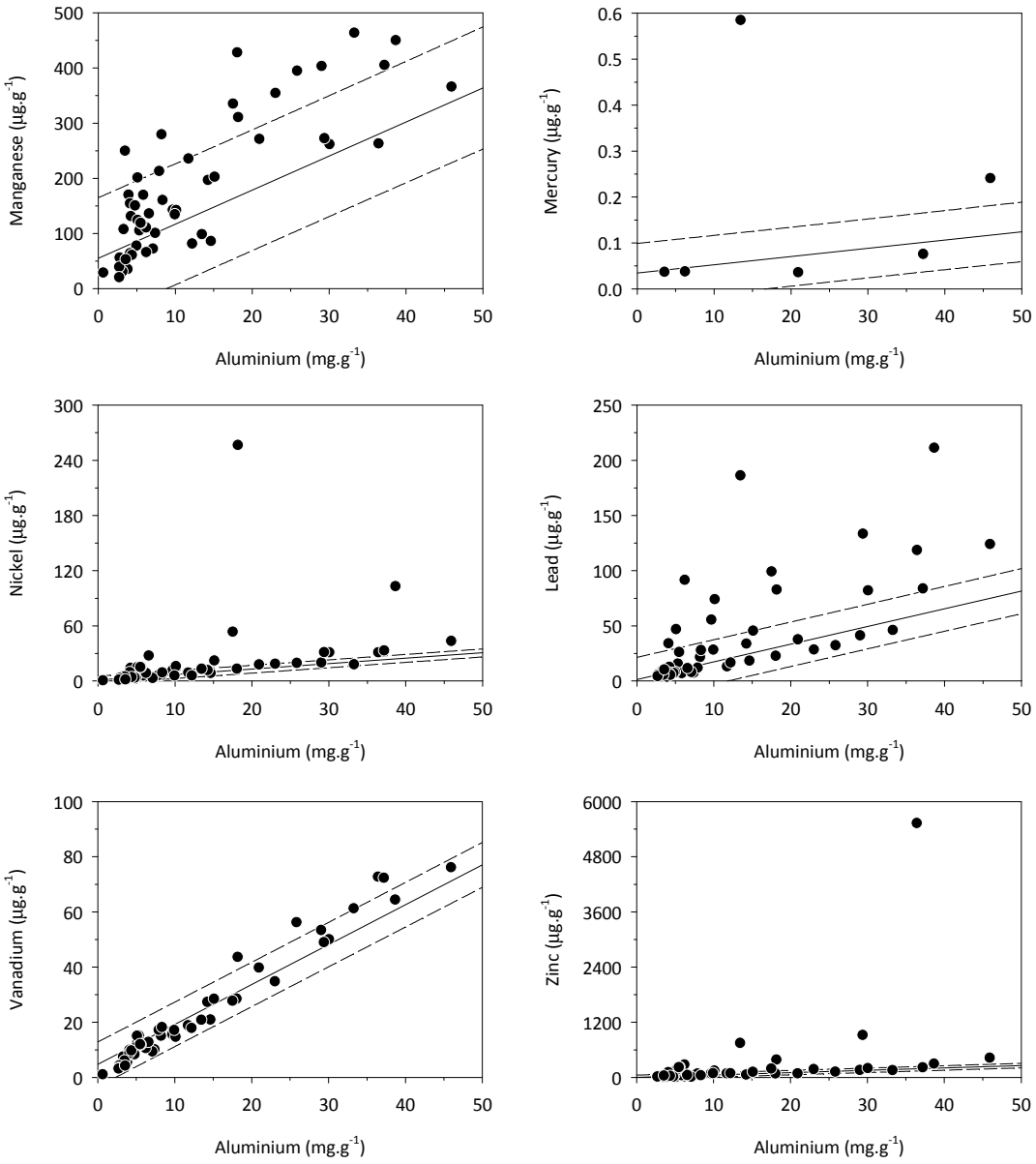

Figure 2.30 continued. Aluminium normalised baseline models for metals in sediment from Durban Bay with metal concentrations in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2012 superimposed.

guidelines for different chemicals compared to the sediment quality guidelines derived by MacDonald *et al*. (2000). Regardless of the sediment quality guideline used the mean sediment quality guideline quotients were highest for the Amanzimnyama River, Island View Canal, Bayhead Canal, and some parts of Durban Bay (Figure 2.34). Mean sediment quality guideline quotients were lower for the uMngeni River, its estuary and tributaries of the estuary, and for the Isipingo River and estuary, although relatively high quotients were evident at four stations in the former and two stations in the latter systems. The lowest mean sediment quality guideline quotients were for sediment in the Umbilo and Umhlatuzana Rivers.

Mean Probable Effect Concentration quotients have been related to the probability for toxicity based on the analysis of matching chemical and toxicity data from a large database for rivers in North America (Crane *et al*., 2002). The proportion of samples in mean Probable Effect Concentration quotient ranges of <0.1, 0.11-0.5, 0.51-1.0, 1.1-5.0 and >5 were determined to coincide with incidences of acute toxicity of ≤10%, 16%, 27%, 36%, and 100%. Mean Probable Effect Concentration quotients for sediment in the rivers, estuaries and canals studied were below 0.1 at all but 12 stations, with the highest quotient having a value of 0.78 (Figure 2.34).

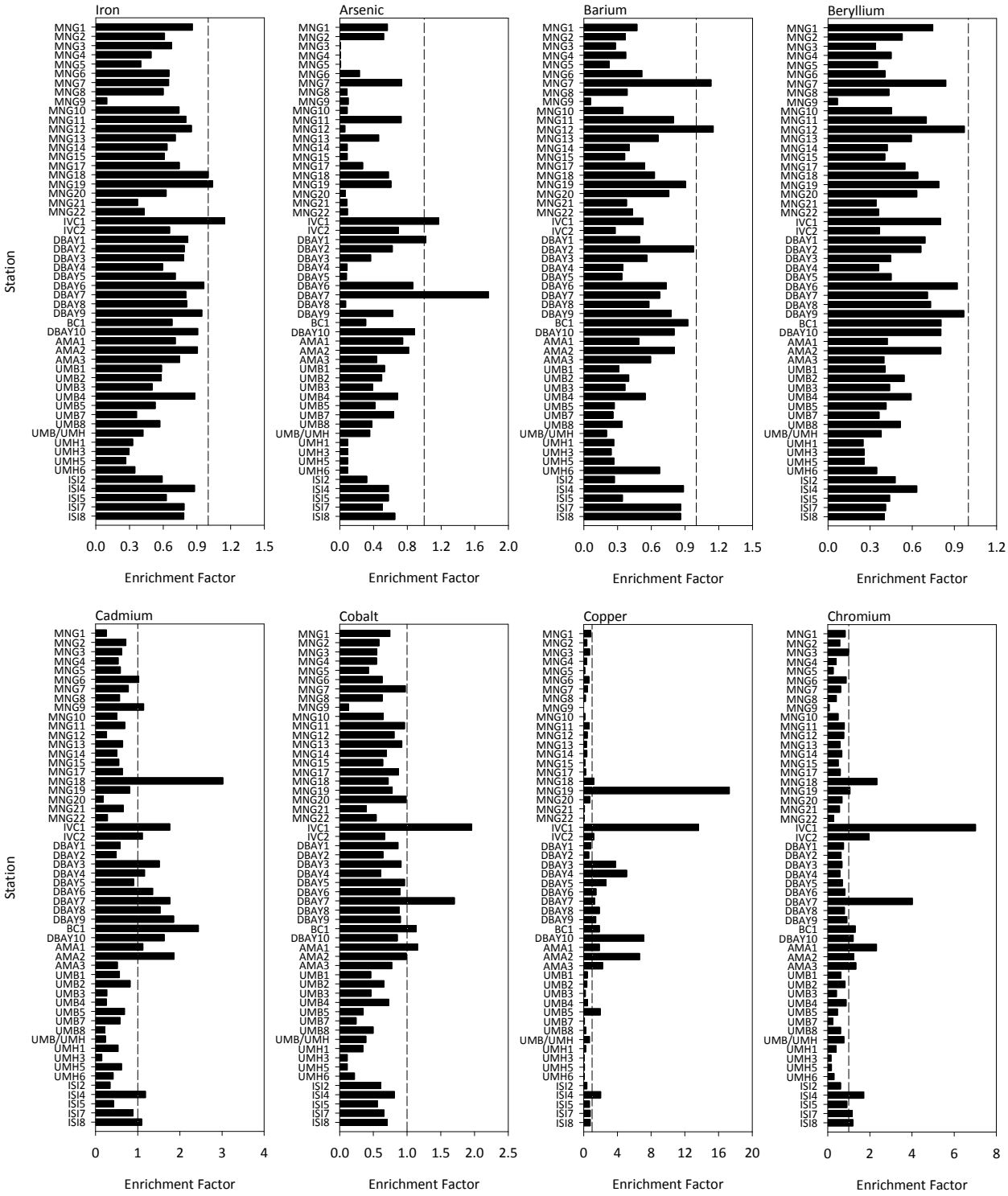

Figure 2.31. Enrichment Factors for metals in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2012. The dashed lines represent an Enrichment Factor of one.

Mean Effects Range Median quotients have been related to the probability for toxicity based on the analysis of matching chemical and toxicity data from a large database for estuaries in North America (Long *et al*., 2000). The proportion of samples in mean Effects Range Median quotient ranges of <0.1, 0.11-0.5, 0.51-1.5, and >1.5 were determined to coincide with incidences of acute toxicity of ≤10%, 25-30%, 50%, and ≥75%. Mean Effects Range Median quotients for sediment in the rivers, estuaries and canals studied were below 0.1 at all but eight stations, with the highest quotient having a value of 1.22 (Figure 2.34).

The mean sediment quality guideline quotients thus suggest there was a relatively low likelihood that organic chemicals in sediment from the rivers, estuaries and canals sampled were causing adverse effects

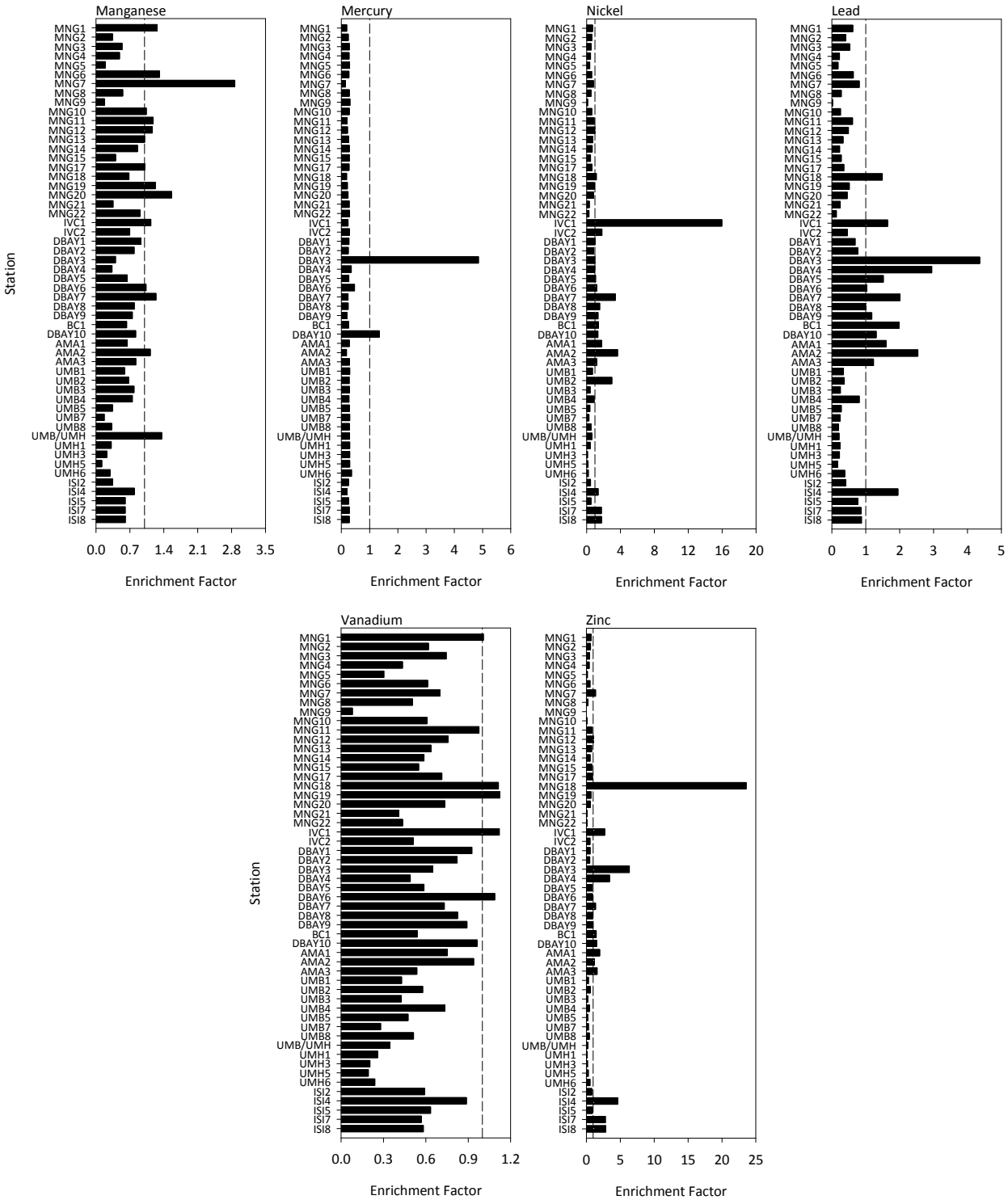

Figure 2.31 continued. Enrichment Factors for metals in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2012. The dashed lines represent an Enrichment Factor of one.

to sediment-dwelling organisms. The greatest risk was in the Amanzimnyama River, Island View Canal and Bayhead Canal, and some parts of Durban Bay. The quotients in some systems were considerably higher than quotients for the survey discussed in Chapter 1. For example, the highest mean Probable Effect Concentration quotient for the 2011 survey was 0.27, compared to 0.77 for the 2012 survey. The difference was as pronounced for the mean Effects Range Median quotient, with the highest quotient of 0.30 for the 2011 survey compared to 1.22 for the 2012 survey. The high quotients for the 2012 survey were largely driven by the very high DDX concentrations in sediment at two stations in the Amanzimnyama River. If the latter stations are not considered then the quotients were generally comparable between surveys.

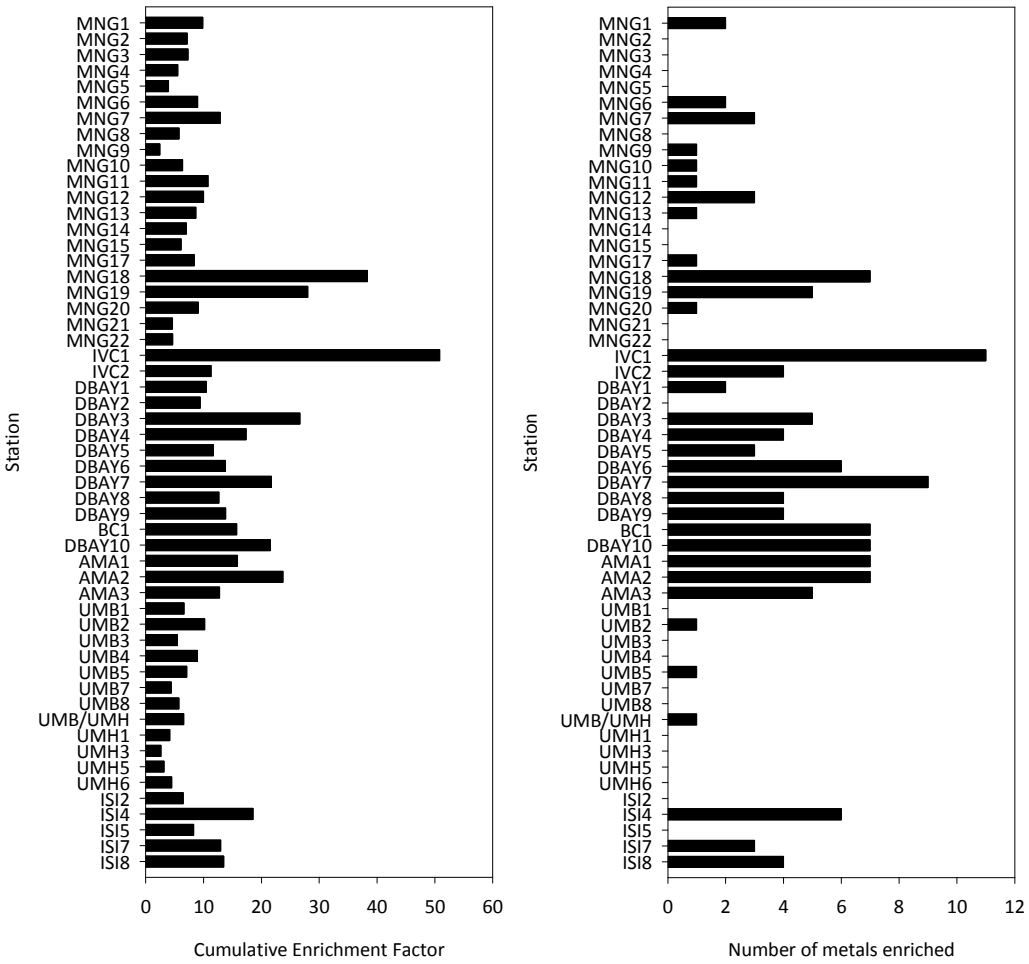

Figure 2.32. Cumulative Enrichment Factors (left) and number of metals at enriched concentrations (right) in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2012.

3.3.8 Toxicity testing

3.3.8.1 Validation of viability methods

Two methods were used to measure cell viability, namely the MTT-assay, and the Cell Index as provided by the xCELLigence apparatus. However, after completion of cell exposures in the xCELLigence apparatus the cells were used in another MTT-assay. This made it possible to compare the Cell Index to MTT-assay results within the same population of cells. Cell viability is provided in Table 2.3. The data were normalised using Box-Cox transformations. Because the data was heterogeneous, Welch's F test was used to perform an analysis of variance ($F = 8.78$, $p < 0.05$). A Tukey-b post-hoc test was performed to identify treatments that differed. There was a statistically significant difference between viability determined using the xCELLigence and MTT, and between MTT and MTT on the xCELLigence apparatus ($p < 0.05$). However, the means of the viabilities determined by MTT after Cell Index determination on the xCELLigence apparatus did not differ statistically significantly from viability determined with the Cell Index of the xCELLigence apparatus ($p > 0.05$). Any one of the latter assays was thus deemed suitable for viability estimation, but the xCELLigence apparatus data was chosen for further analysis because the results are less prone to human error than the MTT-assay.

3.3.8.2 Bioluminescence results

The luminescence bioassays are based on the ability of compounds in non-acid washed (polycyclic aromatic hydrocarbon) and acid washed (polychlorinated biphenyl) extracts to bind to the AhR of genetically modified rat hepatoma cells (H4IIE-*luc*). The binding elicits a light response that is quantified relative to the

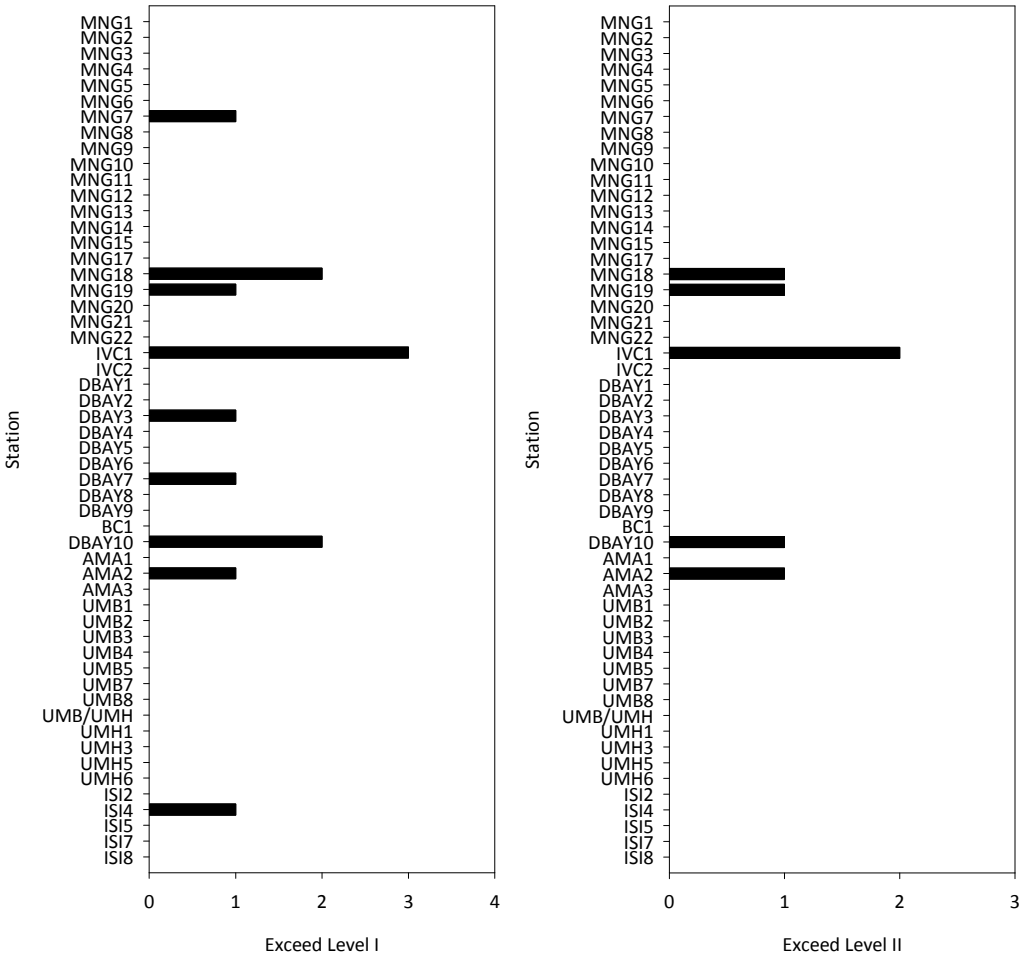

Figure 2.33. Number of metal concentrations in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2012 that exceeded the Level I and Level II of sediment quality guidelines used to regulate the disposal of dredged material in South African coastal waters.

response created by a known concentration of the reference compound TCDD, and is referred to as the %TCDD-max. Dose-response curves were generated for both the reference compound and sample extracts. The Effective Concentration (EC) at which the reference compound and samples elicited a 20, 50 and 80% response were calculated from the dose-response curves. The relative potency (REP) for a sample extract, at 20, 50, 80%, was determined by dividing the Effective Concentration of the reference compound by the Effective Concentration of the sample, creating a REP 20, REP 50 and REP 80. The relative potency values were back-calculated to the mass of sediment initially extracted. Not all samples elicited a sufficiently high response that an EC 50 or EC 80 was reached and these are thus mostly extrapolated values. In some instances the response elicited was too low and a relative potency value could not be quantified (Table 2.4). However, the EC 20 and consequent REP 20 were generally measurable for each sample (Table 2.4). Because this was the most accurate measurement, the REP 20 is used for further discussion and is termed the bioassay equivalent (BEQ).

Acid washed (containing mostly polychlorinated biphenyls) exposure responses were low, providing a REP 50 in only one instance (station UMB4), where multiple non-acid washed (containing PAHs) extracts elicited a REP 50 and in some cases a REP 80 (Table 2.4). Many acid washed extracts had a very low response. This indicates a low concentration of polychlorinated biphenyls available to elicit a response, but needs to be confirmed by the viability assay as this could be a result of cytotoxicity. Polycyclic aromatic hydrocarbon exposure responses were higher, with many of the stations having a REP 80 (Table 2.4). As with the relative potency values, the %TCDD-max values for polychlorinated biphenyl exposure responses (1.53-54.69 %TCDD-max) were usually much lower than those for the polycyclic aromatic hydrocarbon exposure

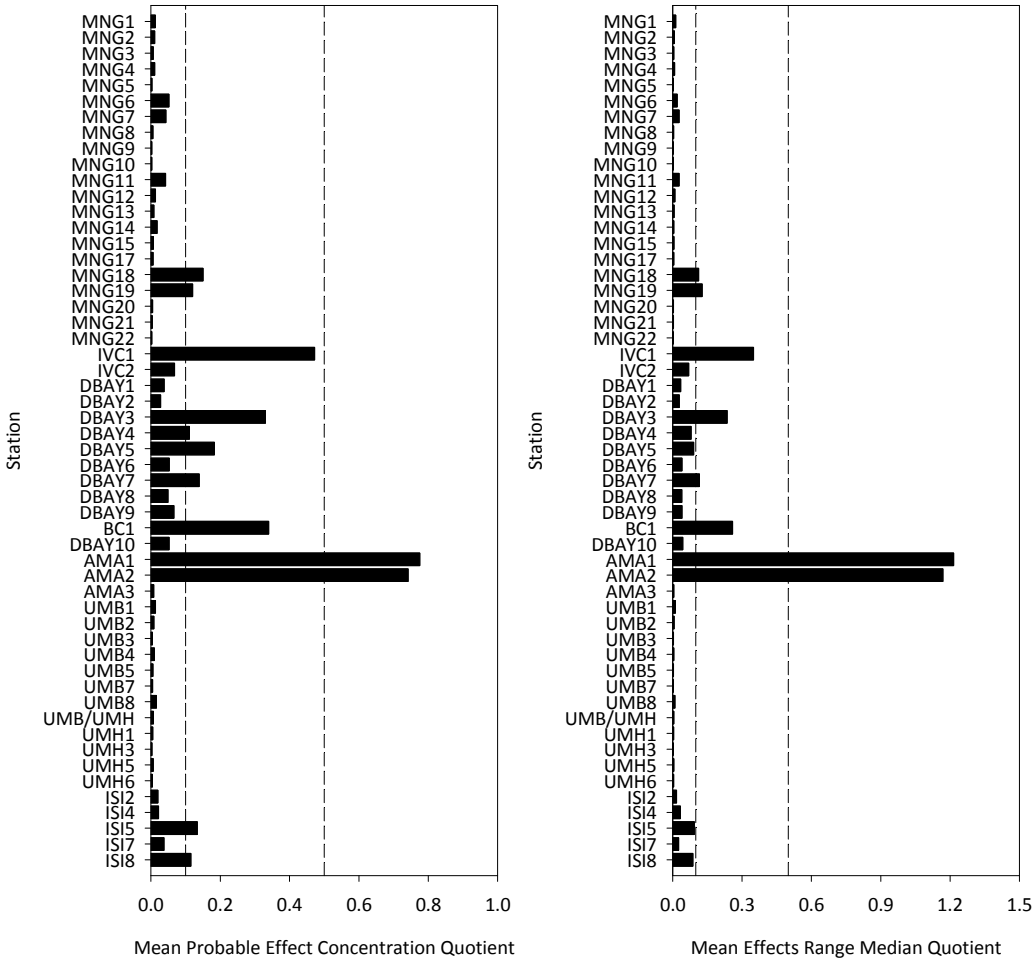

Figure 2.34. Mean Probable Effect Concentration (PEC) and Effects Range Median (ERM) quotients for sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2012. The dashed lines denote quotient ranges that coincide with incidences of acute toxicity provided in the text.

responses (1.68-150.56 %TCDD-max). The polycyclic aromatic hydrocarbon %TCDD-max was significantly greater ($p < 0.05$) than the %TCDD-max generated from the polychlorinated biphenyl extracts. The polycyclic aromatic hydrocarbon bioassay equivalents were also significantly larger than the polychlorinated biphenyl bioassay equivalents ($p < 0.05$). This indicates there were significantly more AhR agonists within the non-acid washed (polycyclic aromatic hydrocarbon) extracts compared to the acid washed (polychlorinated biphenyl) extracts. This was expected considering the non-acid washed extracts might have contained other persistent compounds other than polychlorinated biphenyls (*e.g.* PCDD/Fs), in addition to all other AhR agonists that may have been present. The clean-up methods, however, aimed to target only the compounds of interest. Super-induction is the ability of an extract to elicit a %TCDD-max that exceeds the maximum induction caused by TCDD, which is the most potent AhR agonist (Larsson *et al.*, 2012). This phenomenon was observed in 11 non-acid washed samples (Table 2.4). A possible explanation is that there were other chemicals in the extract capable of enhancing induction of the AhR response. However, these chemicals were not analysed in the samples and so it is unknown whether this was the case. It has been speculated that proteolysis of the AhR is inhibited and hence intracellular levels of ligand bound AhR is increased, which in turn increases the magnitude of the AhR dependent gene expression. Additionally, an unstable repressor protein has been suspected. When this repressor protein is inhibited of expression or is degraded it would be unable to cause repression of the AhR, which would result in an enhanced functionality of the AhR and enhanced transcription. However, it is thought a more likely explanation is that agonists present may co-activate the AhR and extracts may contain chemicals that influence other cellular signal transduction pathways, amplifying the induction response (Baston and Denison, 2011).

3.3.8.3 Viability

The analysis of real-time cell growth obtained from the xCELLigence apparatus showed the same general trend for almost all samples. For samples that had normal cell viability the Cell Index, which is dependent on the number of cells in each well and their morphology (Limame *et al.*, 2012), increased exponentially during the growth phase after seeding into the plate (time 0-24 hours; Figure 2.35). Upon dosing at 24 hours there was an initial increase of the Cell Index, possibly due to the change in ion concentration, followed by a decrease to roughly the same Cell Index as before the addition of the extract (indicated by black rectangle in Figure 2.35, time 24-28 hours). The Cell Index increased from approximately 28-42 hours and then gradually decreased (Figure 2.35). There were exceptions for some samples, where the Cell Index decreased steadily after dosing. These were samples that had decreased cell viability or increased cytotoxicity and are marked in bold text in Table 2.5. However, the decrease in Cell Index for the polycyclic aromatic hydrocarbon extract from station ISI8 was more rapid and began at the 30th hour, resulting in a very low Cell Index (Table 2.5). Therefore, the non-acid washed (polycyclic aromatic hydrocarbon) extract from station ISI8 in the Isipingo River was the most toxic. The implication of the extracts causing cytotoxicity is that they had components that inhibited cell growth and health. It is evident from Table 2.5

Table 2.3. Viability (%) of cells after exposure to extracts of sediment collected in 2012 from rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal.

	Polychlorinated biphenyls (acid washed)			**Polycyclic aromatic hydrocarbons (non-acid washed)**		
	xCELLigence	**MTT**		**xCELLigence**	**MTT**	
Station	**Cell Index**	**xCELLigence**	**MTT**	**Cell Index**	**xCELLigence**	**MTT**
AMA1	119	118	97	123	102	69
AMA2	131	120	97	109	82	110
AMA3	127	132	122	120	98	101
BC1	130	103	90	97	84	115
DBAY1	95	102	87	108	101	95
DBAY2	84	96	93	102	91	94
DBAY3	101	106	93	110	97	101
DBAY4	102	111	89	124	98	97
DBAY5	92	90	88	121	101	100
DBAY6	70	90	95	140	108	91
DBAY7	71	94	63	93	107	87
DBAY8	92	107	63	89	107	96
DBAY9	93	91	61	83	110	125
DBAY10	73	89	96	98	78	107
ISI2	68	91	90	101	102	116
ISI4	101	88	63	73	70	109
ISI5	87	105	97	71	102	112
ISI7	65	89	69	82	115	115
ISI8	72	94	73	8	55	39
IVC1	101	105	92	108	110	72
IVC2	92	105	96	65	84	122
UMB1	111	104	102	88	114	76
UMB2	128	94	78	91	78	90
UMB3	125	120	72	68	82	88
UMB4	136	110	119	72	62	113
UMB5	137	103	87	105	110	112
UMB7	142	107	105	79	91	128
UMB8	140	125	99	73	90	96
UMB/UMH	117	107	98	71	92	106
UMH1	117	95	97	95	106	101
UMH3	107	103	97	91	104	95
UMH5	119	106	89	101	108	101
UMH6	106	89	69	99	112	94

that where a sample caused reduced viability the resulting bioassay equivalent was generally lower compared to bioassay equivalents for cells that had normal viability. There were exceptions, where the cells showed reduced viability and yet the bioassay equivalent was high and similar to bioassay equivalents for cells that did not have increased cytotoxicity; these included station IVC2 in Island View Canal for polycyclic aromatic hydrocarbons and station ISI8 in the Isipingo River for polychlorinated biphenyls. This indicates there were many AhR ligands present, and although these cells experienced reduced health they were still able to elicit a high response from the ligands, or it could be that the ligands caused super induction of the few cells that survived. Therefore, the bioassay equivalent results reported for stations with cytotoxicity are likely an underestimate of the quantity of ligands available to bind to the AhR, and ultimately the bioassay equivalent reported might have been higher had the cells not suffered from reduced viability.

3.3.8.4 Toxicity testing

Comparison is made below between the toxicity estimated by chemical analysis of sediment, in the form of a toxic equivalent, and the corresponding bioassay toxicity, or bioassay equivalent. This was done to determine if these approaches provide similar results, because bioassay equivalents are directly related to toxic equivalents (Jaikanlaya *et al.*, 2009). The toxic equivalent concentration was calculated by multiplying polycyclic aromatic hydrocarbon isomer and polychlorinated biphenyl congeners by a Toxic Equivalent Factor (where available) and then summing the values. The toxic equivalent concentration for polychlorinated biphenyls is expressed relative to the dioxin 2,3,7,8-TCDD, one of the most toxic compounds known. The toxic equivalent concentration is thus roughly the amount of 2,3,7,8-TCDD that would give the same overall effect.

The polychlorinated biphenyl toxic equivalent was calculated using Toxic Equivalent Factors for fish from Van den Berg *et al.* (1998) (Table 2.6). This was because of the three animal categories for which Toxic Equivalent Factors have been derived, fish are the organisms most likely to be exposed to contaminants in sediment at the stations investigated in this study. Polycyclic aromatic hydrocarbons were expressed as having both a toxic equivalent-TCDD (Villeneuve *et al.*, 2000) and a toxic equivalent-BaP (Nisbet and LaGoy, 1992) (Table 2.6). The toxic equivalent-TCDD was compared to the bioassay equivalents generated from the bioassays. The toxic equivalent-BaP, which relates polycyclic aromatic hydrocarbon concentrations to the toxicity expected due to the isomer benzo(a)pyrene, was used to determine whether polycyclic aromatic hydrocarbons, once isomers were converted to their toxic equivalent-BaP, would exceed the sediment quality guidelines derived by Long *et al.* (1995) and MacDonald *et al.* (2000).

The toxic equivalent-BaP concentration at stations DBAY3, DBAY5, DBAY7, DBAY9 in Durban Bay, station IVC1 in one arm of Island View Canal, station BC1 in Bayhead Canal, and stations ISI5 and ISI8 in the Isipingo River exceeded the benzo(a)pyrene Threshold Effect Concentration of the sediment quality guidelines derived by MacDonald *et al*. (2000) (Figure 2.36). Only the concentration at station BC1 exceeded the benzo(a)pyrene Effects Range Low of the sediment quality guidelines derived by Long *et al*. (1995) (Figure 2.36). The total polycyclic aromatic hydrocarbon concentration at each of these stations exceeded the above mentioned guidelines (Figure 2.5). In contrast, while the total polycyclic aromatic hydrocarbon concentration at station MNG18 in a tributary of the uMngeni River estuary exceeded the Threshold Effect Concentration (Figure 2.7), the toxic equivalent-BaP concentration did not exceed the benzo(a)pyrene Threshold Effect Concentration (Figure 2.36). None of the toxic equivalent-BaP concentrations exceeded the Threshold Effect concentration of the sediment quality guidelines derived by MacDonald *et al*. (2000) or the Effects Range Median of the sediment quality guidelines derived by Long *et al*. (1995). Thus, a similar conclusion on the potential toxicity of polycyclic aromatic hydrocarbon concentrations to sediment-dwelling organisms was reached if the total polycyclic aromatic hydrocarbon concentration or toxic equivalent-BaP concentration was used for assessment purposes.

Table 2.4. %TCDD-max and relative potencies (REP; ± standard deviation) for polychlorinated biphenyl and polycyclic aromatic hydrocarbon fractions from the luminescence bioassay. - = response could not be quantified. Values in bold represent bioassay equivalents (BEQ) that were extrapolated.

	Polychlorinated biphenyls (acid washed)				Polycyclic aromatic hydrocarbons (non-acid washed)			
Station	**%TCDD-max**	**REP 20 (pg TCDDeq.g^{-1})**	**REP 50 (pg TCDDeq.g^{-1})**	**REP 80 (pg TCDDeq.g^{-1})**	**%TCDD-max**	**REP 20 (pg TCDDeq.g^{-1})**	**REP 50 (pg TCDDeq.g^{-1})**	**REP 80 (pg TCDDeq.g^{-1})**
AMA1	31.44	6.22 ± 1.62	**0.05 ± 0.05**	**1.99 ± 2.07**	150.56	217.76 ± 3.23	481.64 ± 54.98	1106.60 ± 79.71
AMA2	28.73	5.76 ± 1.46	**7.32 ± 5.68**	**1.53 ± 1.55**	84.38	171.15 ± 10.30	259.71 ± 17.56	396.12 ± 58.14
AMA3	20.64	10.89 ± 3.08	**0.51 ± 0.63**	**0.04 ± 0.05**	70.70	269.28 ± 4.34	136.15 ± 10.48	**35.03 ± 49.15**
BC1	17.49	4.82 ± 1.19	-	-	126.68	304.68 ± 0.69	574.95 ± 152.30	1219.70 ± 159.72
DBAY1	1.65	-	-	-	95.12	165.24 ± 0.68	282.64 ± 48.25	490.84 ± 167.10
DBAY2	1.65	-	-	-	73.92	85.04 ± 6.12	121.66 ± 21.02	**4.33 ± 0.11**
DBAY3	25.21	18.57 ± 5.98	**1.30 ± 1.67**	**0.09 ± 0.16**	139.20	528.49 ± 8.64	1023.60 ± 201.26	1985.60 ± 395.72
DBAY4	11.26	0.52 ± 0.29			127.94	165.79 ± 6.95	387.26 ± 40.12	952.43 ± 79.47
DBAY5	22.15	21.25 ± 7.63	**0.93 ± 1.03**	**0.01 ± 0.01**	149.19	634.21 ± 8.17	1104.50 ± 325.06	2105.80 ± 521.44
DBAY6	13.01	1.57 ± 1	-	-	110.09	230.79 ± 15.70	376.55 ± 68.99	597.51 ± 258.14
DBAY	18.85	9.69 ± 2.76	**0.12 ± 0.06**	**0.06 ± 0.01**	90.49	766.08 ± 3.47	461.16 ± 99.60	321.95 ± 164.77
DBAY8	13.34	0.22 ± 1.09	-	-	118.99	184.53 ± 1.12	386.44 ± 43.57	813.86 ± 177.56
DBAY9	15.12	1.58 ± 0.48	-	-	87.53	123.37 ± 5.66	185.96 ± 29.13	286.06 ± 100.94
DBAY10	23.03	10.56 ± 7.49	-	-	98.52	536.61 ± 2.86	884.18 ± 37.72	1483.90 ± 136.61
ISI2	19.26	1.84 ± 0.74	**0.93 ± 0.97**	**0.02 ± 0.02**	103.28	85.39 ± 3.66	173.67 ± 24.33	322.05 ± 111.25
ISI4	26.42	6.54 ± 0.5	-	-	129.62	160.70 ± 7.66	330.02 ± 59.91	541.23 ± 340.23
ISI5	38.76	35.26 ± 10.9	**20.41 ± 11.20**	**9.83 ± 7.55**	127.78	162.73 ± 7.99	382.88 ± 83.23	902.09 ± 237.36
ISI7	17.7	1.26 ± 0.36	**0.20 ± 0.01**	-	72.57	108.48 ± 3.76	171.82 ± 43.02	**260.99 ± 117.66**
ISI8	30.37	5.85 ± 1.35	**2.19 ± 1.18**	**0.11 ± 0.10**	1.68	-	-	-
IVC1	22.84	55.12 ± 9.77	**15.90 ± 9.89**	**3.82 ± 3.71**	4.27	69.01 ± 6.65	**411.97 - 92.52**	**282.47 120.89**
IVC2	13.73	12.68 ± 17.3	**0.94 ± 1.62**	**0.08 ± 0.14**	84.56	154.57 ± 5.84	232.64 ± 36.51	354.13 ± 104.08
UMB1	24.18	34.14 ± 31.35	**9.96 ± 17.25**	**4.28 ± 6.06**	58.19	67.72 ± 6.23	64.59 ± 28.13	**50.79 ± 35.29**
UMB2	11.63	0.41 ± 0.39	-	-	37.64	45.07 ± 2.20	**16.53 ± 1.65**	**5.03 ± 1.46**
UMB3	9.87	0.02 ± 0.03	-	-	36.54	33.55 ± 1.87	**10.16 ± 9.42**	**1.06 ± 1.44**
UMB4	54.69	93.54 ± 17.5	66.60 ± 8.32	**76.50 ± 4.24**	15.54	7.73 ± 8.04	**0.03 ± 0.05**	-
UMB5	11.51	0.12 ± 0.11	-	-	39.12	55.16 ± 6.11	**27.68 ± 15.83**	**16.69 ± 18.54**
UMB7	11.05	0.29 ± 0.21	-	-	29.99	29.46 ± 3.39	**6.44 ± 4.52**	**1.53 ± 1.53**
UMB8	17.57	4.93 ± 1.69	**0.03 ± 0.04**	-	46.82	55.55 ± 5.96	**41.39 ± 8.74**	**29.13 ± 13.15**
UMB/UMH	15.09	0.41 ± 0.15	-	-	39.00	5.53 ± 0.95	**2.55 ± 0.15**	**1.07 ± 0.30**
UMH1	3.23	-	-	-	19.88	9.07 ± 2.01	**0.23 ± 0.23**	**0.01 ± 0.01**
UMH3	9.87	-	-	-	26.95	25.43 ± 2.16	**2.64 ± 0.80**	**0.23 ± 0.16**
UMH5	5.99	-	-	-	42.36	53.92 ± 2.13	**31.86 ± 9.01**	**13.05 ± 6.34**
UMH6	10.07	0.33 ± 0.47	-	-	17.25	4.26 ± 3.18	**0.02 ± 0.03**	-

When the toxic equivalent-TCDD is compared to the bioassay equivalents for polycyclic aromatic hydrocarbons (Table 2.7), the bioassay equivalents were at least an order of magnitude greater than the toxic equivalents. The polychlorinated biphenyl toxic equivalents were two to three magnitudes smaller than the bioassay equivalents (Table 2.7). Even when the extract caused reduced viability of the cells, reducing their ability to elicit a response, the bioassay equivalents were still greater than the toxic equivalent-TCDD values. Polychlorinated biphenyl bioassay equivalents may be slightly over estimated because the acid-wash clean-up step did not remove other persistent organic pollutants (*e.g.* PCDD/Fs) that are also AhR agonists and which might have eluted with the same fraction during the gel permeation chromatography clean-up. If PCDD/Fs were present in the extract they would have contributed to the bioassay equivalent. This might explain the higher bioassay equivalents than the calculated toxic equivalents. Polycyclic aromatic hydrocarbon bioassay equivalents were also greater than the toxic equivalents, due to not having had an acid clean-up. Hence, persistent organic compounds and any other AhR agonists could bind to the AhR, although this would be a limited portion due to the targeted fraction collection during gel permeation chromatography clean-up.

Polychlorinated biphenyl toxic equivalents are an under-calculation of what was potentially present in the sediment because not all the polychlorinated biphenyl congeners with a Toxic Equivalent Factor were

Table 2.5. xCELLigence viability data and %TCDD-max values for polychlorinated biphenyl and polycyclic aromatic hydrocarbon extracts. Values highlighted in bold indicate that cell viability was reduced to below 75%.

	Polychlorinated biphenyls (acid washed)		**Polycyclic aromatic hydrocarbons (non-acid washed)**	
Station	**xCELLigence viability (%)**	**%TCDD-max**	**xCELLigence viability (%)**	**%TCDD-max**
AMA1	119	31.44	123	150.56
AMA2	131	28.73	109	84.38
AMA3	127	20.64	120	70.70
BC1	130	17.49	97	126.68
DBAY1	95	1.65	108	95.12
DBAY2	84	1.65	102	73.92
DBAY3	101	25.21	110	139.20
DBAY4	102	11.26	124	127.94
DBAY5	92	22.15	121	149.19
DBAY6	**70**	**13.01**	140	110.09
DBAY7	**71**	**18.85**	93	90.49
DBAY8	92	13.34	89	118.99
DBAY9	93	15.12	83	87.53
DBAY10	**73**	**23.03**	98	98.52
ISI2	**68**	**19.26**	101	103.28
ISI4	101	26.42	**73**	**129.62**
ISI5	87	38.76	**71**	**127.78**
ISI7	**65**	**17.70**	82	72.57
ISI8	**72**	**30.37**	**8**	**1.68**
IVC1	101	22.84	108	4.27
IVC2	92	13.73	**65**	**84.56**
UMB1	111	24.18	88	58.19
UMB3	125	9.87	**68**	**36.54**
UMB4	136	54.69	**72**	**15.54**
UMB5	137	11.51	105	39.12
UMB7	142	11.05	79	29.99
UMB8	140	17.57	**73**	**46.82**
UMB/UMH	117	15.09	**71**	**39.00**
UMH1	117	3.23	95	19.88
UMH3	107	9.87	91	26.95
UMH5	119	11.51	101	42.36
UMH6	106	10.07	99	17.25

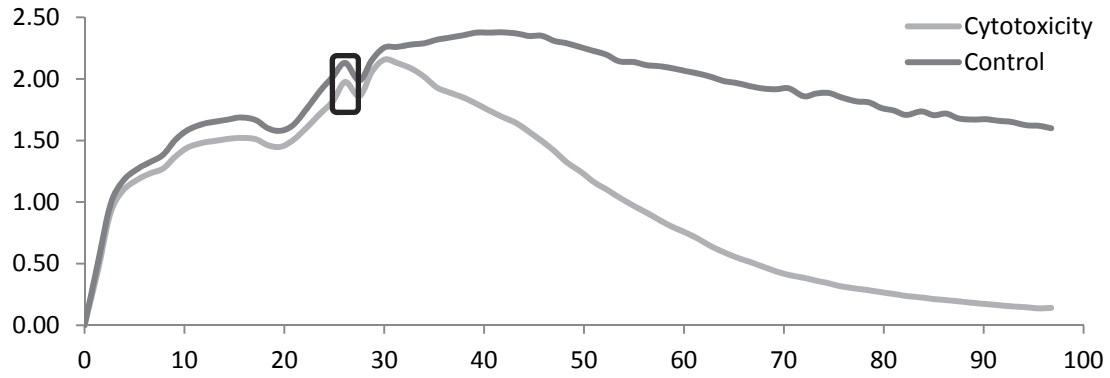

Figure 2.35. Example of an xCELLigence plot representing the change of the Cell Index over time from the moment the cells were put into the wells (time 0 hr). The time of dosing is indicated by the black rectangle.

analysed, and there were multiple instances of congeners present at a concentration below the method detection limit and which were thus assumed to not be present. For polycyclic aromatic hydrocarbons, in contrast, concentrations below the method detection limit were replaced with a value equivalent to one half the method detection limit. Cell bioassays often yield bioassay equivalents that are significantly higher than calculated toxic equivalents (Behnisch *et al.*, 2001; Denison *et al.*, 2004). It has been suggested that this difference may be a result of inequalities in the Toxic Equivalent Factor values used and the bioassay based relative potency, along with additional agonists present in the extract that were not chemically analysed.

Although there was some congruence between polychlorinated biphenyl and polycyclic aromatic hydrocarbon toxic equivalents and bioassay equivalents, more often than not there was little similarity (Figure 2.37). A toxic equivalent could not be calculated for many stations, but the bioassay equivalent at these stations was often similarly low. This was most evident for stations in the Umbilo and Umhlatuzana Rivers with the exception of stations UMB1, UMB4 and UMB8, where the bioassay equivalent was higher than the toxic equivalent. Five other stations also had bioassay equivalents higher than the toxic equivalent. The higher bioassay equivalent could be due to other AhR ligands eliciting an effect.

The bioassay equivalents and toxic equivalents for polychlorinated biphenyls and polycyclic aromatic hydrocarbons are compared to sediment quality guidelines that prescribe a toxic equivalent-TCDD guideline in Figures 2.38-2.40. The guidelines were derived for dioxins, but are used here because the mode of action for polychlorinated biphenyls and polycyclic aromatic hydrocarbons is also via the AhR. Since South Africa does not have guidelines for polychlorinated biphenyls and polycyclic aromatic hydrocarbons and the Long *et al*. (1995) and MacDonald *et al*. (2000) sediment quality guidelines do not provide toxic equivalent-TCDD guidelines, toxic equivalent-TCDD guidelines for Canada, Japan, the Netherlands and the United Kingdom are used.

The polychlorinated biphenyl toxic equivalents were so low they are not visible when included with bioassay equivalents in the same graph (Figure 2.38). No toxic equivalents exceeded the guideline for the Netherlands. However, it should again be noted that the toxic equivalents could be higher than those reported because not all of the compounds with toxic equivalency factors were analysed in the sediment samples. For example, several of the dioxin-like polychlorinated biphenyl congeners were not analysed. The bioassay equivalent at nine stations exceeded the guideline for the Netherlands (Figure 2.38).

For polycyclic aromatic hydrocarbons the toxic equivalents were much lower than bioassay equivalents (Figure 2.39). Toxic equivalents at numerous stations exceeded toxic equivalent-TCDD guidelines for the Netherlands, Japan and the United Kingdom (Figure 2.39). The guidelines for these countries vary widely, however, with the result that the frequency of exceedance varied widely.

The bioassay equivalent and toxic equivalent data needed to be normalised to 1% total organic carbon for comparison to the Canadian sediment quality guidelines (Figure 2.40). Neither the polycyclic aromatic hydrocarbon nor polychlorinated biphenyl toxic equivalents were high enough to be included with bioassay equivalents in the same graph. Stations AMA1, AMA3, DBAY2, DBAY4, DBAY5, DBAY6, DBAY9, UMB1, UMB5, UMB7 and UMH3 had polycyclic aromatic hydrocarbon bioassay equivalents that exceeded the guideline. Polychlorinated biphenyl bioassay equivalents exceeded the guideline only for stations UMB1 and UMB4.

Thus, polycyclic aromatic hydrocarbon and polychlorinated biphenyl concentrations in sediment collected at numerous stations in rivers, estuaries and canals in the eThekwini area in 2012 were high enough to suspect they were posing a potential toxicological risk to sediment-dwelling organisms. To identify stations where adverse effects were most likely based on comparison to sediment quality guidelines, the stations where total polycyclic aromatic hydrocarbon and polychlorinated biphenyl concentrations exceeded the Long *et al.* (1995) and MacDonald *et al.* (2000) sediment quality guidelines are compared to the stations where the toxic equivalent and/or bioassay equivalent exceeded the Canadian sediment quality guidelines. The Canadian sediment quality guidelines were used as the point for comparison since they are the most sensitive. For polychlorinated biphenyls, no toxic equivalents exceeded the Canadian Threshold Effect Concentration and were thus not used in the comparison. Data for the uMngeni River, its estuary and tributaries of the estuary are excluded from the comparison since no bioassay equivalents were calculated for this system. Also, no total polychlorinated biphenyl concentrations in sediment in the latter catchment exceeded sediment quality guidelines.

Table 2.6. Polycyclic aromatic hydrocarbon toxic equivalents (TEQ) calculated based on TEF values of TCDD and benzo(a)pyrene (BaP) as the reference compound.

Station	Polycyclic aromatic hydrocarbons TEQ_{TCDD} ($ng.g^{-1}$)	Polycyclic aromatic hydrocarbons TEQ_{BaP} ($ng.g^{-1}$)	Station	Polycyclic aromatic hydrocarbons TEQ_{TCDD} ($ng.g^{-1}$)	Polycyclic aromatic hydrocarbons TEQ_{BaP} ($ng.g^{-1}$)
AMA1	3.56×10^{-3}	43.21	MNG7	2.09×10^{-3}	80.21
AMA2	1.78×10^{-3}	26.86	MNG8	3.71×10^{-4}	11
AMA3	8.26×10^{-4}	12.99	MNG9	1.83×10^{-4}	6.81
BC1	3.26×10^{-2}	612.55	MNG10	1.36×10^{-4}	6.5
DBAY1	2.63×10^{-3}	40.69	MNG11	2.65×10^{-3}	100.68
DBAY2	1.39×10^{-3}	21.62	MNG12	1.07×10^{-3}	27.61
DBAY3	2.04×10^{-2}	311.39	MNG13	5.48×10^{-4}	20.04
DBAY4	5.63×10^{-3}	83.55	MNG14	6.69×10^{-4}	24.4
DBAY5	1.49×10^{-2}	214.28	MNG15	2.57×10^{-4}	7.23
DBAY6	6.64×10^{-3}	90.96	MNG17	3.63×10^{-4}	10.89
DBAY7	1.7×10^{-2}	254.71	MNG18	3.32×10^{-3}	56.86
DBAY8	5.15×10^{-3}	78.58	MNG 19	1.72×10^{-3}	64.78
DBAY9	1.09×10^{-2}	153.09	MNG20	2.4×10^{-4}	8.82
DBAY10	3.31×10^{-3}	52.83	MNG21	3.42×10^{-4}	10.57
ISI2	1.24×10^{-3}	50.53	MNG22	1.35×10^{-4}	6.51
ISI4	1.29×10^{-3}	20.86	UMB1	6.01×10^{-4}	21.67
ISI5	1.13×10^{-2}	358.39	UMB2	7.08×10^{-4}	25.71
ISI7	4.22×10^{-3}	105.06	UMB3	2.22×10^{-4}	7.33
ISI8	8.52×10^{-3}	221.25	UMB4	1.44×10^{-3}	23.04
IVC1	2.08×10^{-2}	321.88	UMB5	6.55×10^{-4}	11.91
IVC2	1.2×10^{-3}	17.49	UMB7	6.98×10^{-4}	9.82
MNG1	5.5×10^{-4}	51.83	UMB8	1.18×10^{-3}	14.66
MNG2	9.56×10^{-4}	27.79	UMB/UMH	5.67×10^{-4}	10.41
MNG3	4.44×10^{-4}	18.25	UMH1	3.85×10^{-4}	7.87
MNG	8.36×10^{-4}	36.61	UMH3	2.12×10^{-4}	6.99
MNG5	1.43×10^{-4}	6.71	UMH5	3.98×10^{-4}	13.14
MNG6	2.54×10^{-3}	50.29	UMH6	1.72×10^{-4}	6.88

At 27% of the stations the total polychlorinated biphenyl concentration exceeded the Effects Range Low or Threshold Effect Concentration, while at only 5% of stations was the bioassay equivalent in excess of the Canadian Threshold Effect Concentration. When polychlorinated biphenyl concentration exceedances are compared to bioassay equivalent exceedances there were no stations where both sediment quality guidelines were exceeded (Figure 2.41). A possible reason for there being no stations in common is that four of the extracts (for stations DBAY6, DBAY7, DBAY10, ISI8) caused cytotoxicity within the assay. The two stations that had bioassay equivalent concentrations that exceeded the Canadian Threshold Effect Concentration may have had AhR ligands other than polychlorinated biphenyls, such as PCDD/Fs, which elicited the response. It could also be that the polychlorinated biphenyls contained a large proportion of non-dioxin like polychlorinated biphenyls, which are unable to bind to the AhR and therefore could not elicit a response.

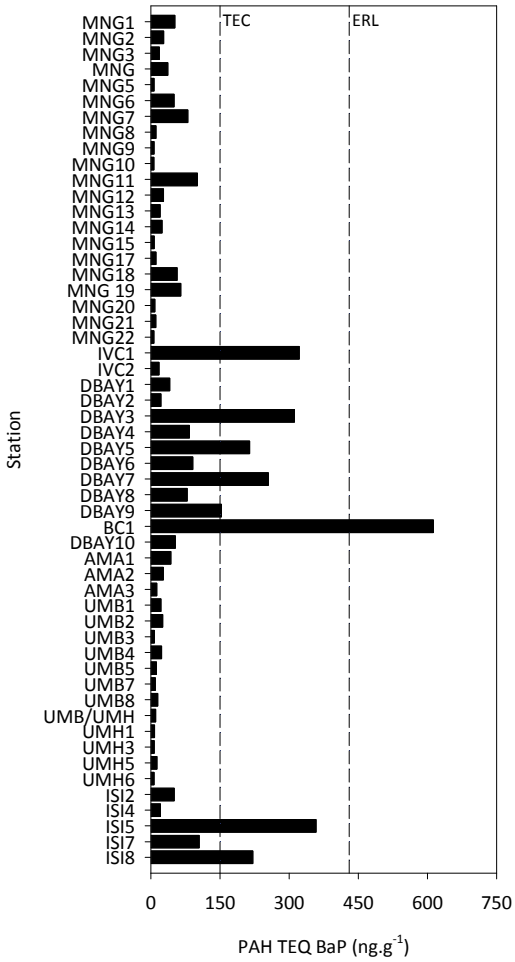

Figure 2.36. Benzo(a)pyrene toxic equivalents (TEQ), with the Threshold Effect Concentration (TEC) for benzo(a)pyrene for the sediment quality guidelines derived by MacDonald *et al*. (2000) and Effects Range Low (ERL) of the sediment quality guidelines derived by Long *et al*. (1995) superimposed.

For polycyclic aromatic hydrocarbons the bioassay equivalent, total polycyclic aromatic hydrocarbon concentration and benzo(a)pyrene equivalent are considered (Figure 2.42). No toxic equivalents exceeded the Canadian Threshold Effect Concentration. At 30% of stations the bioassay equivalent exceeded the Threshold Effect Concentration.

The benzo(a)pyrene equivalent at 19% of stations exceeded the Threshold Effect Concentration, and at station BC1 also the Effects Range Low of the Long *et al*. (1995) sediment quality guidelines. At 27% of stations concentrations exceeded the polycyclic aromatic hydrocarbon Threshold Effect Concentration of the sediment quality guidelines derived by Macdonald *et al*. (2000), and concentrations at five of these stations also exceeded the Effects Range Low of the sediment quality guidelines derived by Long *et al*. (1995). Concentrations at stations DBAY3, DBAY7, BC1, IVC1, ISI5 and ISI8 exceeded the Canadian Threshold Effect Concentration and benzo(a)pyrene equivalent Threshold Effect Concentration. At station AMA1, concentrations exceeded the bioassay equivalent and total polycyclic aromatic hydrocarbon concentration guidelines. DBAY5 was the only station where the Canadian Threshold Effect Concentration, polycyclic aromatic hydrocarbon Threshold Effect Concentration and benzo(a)pyrene equivalent Threshold Effect Concentration was exceeded.

The results show it is not possible to assess toxicity using a single method. Each method failed to identify sediment at some stations as cause for concern but that were shown by other methods to in fact be cause for concern. Estimating toxicity from the bioassays used in this study has limitations in that a non-acid-washed sample may elicit responses from all possible AhRs while the acid-washed extract may elicit a response from all persistent compounds. This can be remedied by not focussing solely on polycyclic aromatic hydrocarbons or polychlorinated biphenyls, but on all compounds that could bind to the AhR.

Table 2.7. Polychlorinated biphenyl (PCB) and polycyclic aromatic hydrocarbon (PAH) TEQ_{TCDD} and bioassay equivalents (BEQ). The data are also normalised to 1% total organic carbon (TOC). Values in bold indicate stations where low viability was recorded. - = stations for which bioassays were not performed.

Station	TOC (%)	PAH BEQ ($pg.g^{-1}$)	PAH TEQ ($pg.g^{-1}$)	PCB BEQ ($pg.g^{-1}$)	PCB TEQ ($pg.g^{-1}$)	Normalised to 1% TOC: PAH BEQ ($pg.g^{-1}$)	PAH TEQ ($ng.g^{-1}$)	PCB BEQ ($pg.g^{-1}$)	PCB TEQ ($pg.g^{-1}$)
AMA1	1.45	217.76	3.56	6.22	5.85×10^{-6}	1.50	2.46×10^{-2}	4.29×10^{-2}	4.03×10^{-8}
AMA2	2.34	171.15	1.78	5.76	0.00	7.31×10^{-1}	7.60×10^{-3}	2.46×10^{-2}	0.00
AMA3	0.6	269.28	0.83	10.89	0.00	4.49	1.38×10^{-2}	1.82×10^{-1}	0.00
BC1	6.84	304.68	32.64	4.82	6.65×10^{-6}	4.45×10^{-1}	4.77×10^{-2}	7.05×10^{-3}	9.72×10^{-9}
DBAY1	1.97	165.24	2.63	0.00	1.00×10^{-5}	8.39×10^{-1}	1.34×10^{-2}	0.00	5.08×10^{-8}
DBAY2	0.96	528.49	1.39	0.00	0.00	5.51	1.45×10^{-2}	0.00	0.00
DBAY3	5.33	165.79	20.40	18.57	1.76×10^{-4}	3.11×10^{-1}	3.83×10^{-2}	3.48×10^{-2}	3.31×10^{-7}
DBAY4	1.35	634.21	5.63	0.22	8.40×10^{-6}	4.70	4.17×10^{-2}	1.63×10^{-3}	6.22×10^{-8}
DBAY5	1.22	230.79	14.87	14.18	1.00×10^{-5}	1.89	1.22×10^{-1}	1.16×10^{-1}	8.20×10^{-8}
DBAY6	2.45	766.08	6.64	**13.01**	1.00×10^{-5}	3.13	2.71×10^{-2}	5.31×10^{-2}	4.08×10^{-8}
DBAY7	3.17	184.53	16.97	**9.69**	6.70×10^{-5}	5.82×10^{-1}	5.35×10^{-2}	3.06×10^{-2}	2.11×10^{-7}
DBAY8	2.46	123.37	5.15	1.35	2.18×10^{-5}	5.02×10^{-1}	2.10×10^{-2}	5.49×10^{-3}	8.86×10^{-8}
DBAY9	2.97	536.61	10.86	1.58	0.00	1.81	3.66×10^{-2}	5.32×10^{-3}	0.00
DBAY10	3.11	85.04	3.31	**10.56**	2.80×10^{-5}	2.73×10^{-1}	1.06×10^{-2}	3.40×10^{-2}	8.99×10^{-8}
ISI2	2.5	85.39	1.24	**1.84**	0.00	3.42×10^{-1}	4.96×10^{-3}	7.36×10^{-3}	0.00
ISI4	6.36	**160.70**	1.29	31.75	7.60×10^{-5}	2.53×10^{-1}	2.03×10^{-3}	4.99×10^{-2}	1.19×10^{-7}
ISI5	2.36	**162.73**	11.32	35.26	7.20×10^{-6}	6.90×10^{-1}	4.80×10^{-2}	1.49×10^{-1}	3.05×10^{-8}
ISI7	1.29	108.48	4.22	**17.70**	0.00	8.41×10^{-1}	3.27×10^{-2}	1.37×10^{-1}	0.00
ISI8	4.07	**0.00**	8.52	5.85	3.12×10^{-5}	0.00	2.09×10^{-2}	1.44×10^{-2}	7.65×10^{-8}
IVC1	7.07	61.72	20.81	36.74	1.13×10^{-5}	8.73×10^{-2}	2.94×10^{-2}	5.20×10^{-2}	1.60×10^{-8}
IVC2	2.03	**154.57**	1.20	8.70	0.00	7.61×10^{-1}	5.92×10^{-3}	4.29×10^{-2}	0.00
MNG1	1.95	-	0.55	-	0.00	0.00	2.82×10^{-3}	0.00	0.00
MNG2	1.13	-	0.96	-	0.00	0.00	8.46×10^{-3}	0.00	0.00
MNG3	0.4	-	0.44	-	0.00	0.00	1.11×10^{-2}	0.00	0.00
MNG4	1.71	-	0.84	-	0.00	0.00	4.89×10^{-3}	0.00	0.00
MNG5	0.25	-	0.14	-	0.00	0.00	5.72×10^{-3}	0.00	0.00
MNG6	2.75	-	2.54	-	0.00	0.00	9.23×10^{-3}	0.00	0.00
MNG7	2.99	-	2.09	-	0.00	0.00	6.98×10^{-3}	0.00	0.00
MNG8	0.32	-	0.37	-	0.00	0.00	1.16×10^{-2}	0.00	0.00
MNG9	0.16	-	0.18	-	0.00	0.00	1.14×10^{-2}	0.00	0.00
MNG10	0.19	-	0.14	-	0.00	0.00	7.14×10^{-3}	0.00	0.00
MNG11	2.6	-	2.65	-	0.00	0.00	1.02×10^{-2}	0.00	0.00
MNG12	1.84	-	1.07	-	0.00	0.00	5.82×10^{-3}	0.00	0.00
MNG13	0.91	-	0.55	-	0.00	0.00	6.03×10^{-3}	0.00	0.00
MNG14	0.38	-	0.67	-	0.00	0.00	1.76×10^{-2}	0.00	0.00
MNG15	0.37	-	0.26	-	0.00	0.00	6.94×10^{-3}	0.00	0.00
MNG17	0.4	-	0.36	-	0.00	0.00	9.08×10^{-3}	0.00	0.00
MNG18	5.89	-	3.32	-	3.00×10^{-4}	0.00	5.63×10^{-3}	0.00	5.09×10^{-7}
MNG19	3.76	-	1.72	-	0.00	0.00	4.58×10^{-3}	0.00	0.00
MNG20	0.76	-	0.24	-	0.00	0.00	3.15×10^{-3}	0.00	0.00
MNG21	1.01	-	0.34	-	0.00	0.00	3.39×10^{-3}	0.00	0.00
MNG22	0.11	-	0.14	-	0.00	0.00	1.23×10^{-2}	0.00	0.00
UMB1	0.34	67.72	0.60	34.14	0.00	1.99	1.77×10^{-2}	1.00	0.00
UMB2	0.67	45.07	0.71	0.16	0.00	6.73×10^{-1}	1.06×10^{-2}	2.39×10^{-3}	0.00
UMB3	0.61	**33.55**	0.22	9.87	0.00	5.50×10^{-1}	3.64×10^{-3}	1.62×10^{-1}	0.00
UMB4	0.79	**6.84**	1.44	93.54	0.00	8.66×10^{-2}	1.82×10^{-2}	1.18	0.00
UMB5	0.33	55.16	0.65	11.51	0.00	1.67	1.98×10^{-2}	3.49×10^{-1}	0.00
UMB7	0.18	29.46	0.70	11.05	0.00	1.64	3.88×10^{-2}	6.14×10^{-1}	0.00
UMB8	1.41	**55.55**	1.18	4.93	0.00	3.94×10^{-1}	8.38×10^{-3}	3.50×10^{-2}	0.00
UMB/UMH	0.54	**5.53**	0.57	15.09	0.00	1.02×10^{-1}	1.05×10^{-2}	2.79×10^{-1}	0.00
UMH1	0.22	9.07	0.38	3.27	0.00	4.12×10^{-1}	1.75×10^{-2}	1.49×10^{-1}	0.00
UMH3	0.28	25.43	0.21	9.87	0.00	9.08×10^{-1}	7.58×10^{-3}	3.53×10^{-1}	0.00
UMH5	1.03	53.92	0.40	11.51	0.00	5.23×10^{-1}	3.86×10^{-3}	1.12×10^{-1}	0.00
UMH6	0.27	3.76	0.17	10.07	0.00	1.39×10^{-1}	6.38×10^{-3}	3.73×10^{-1}	0.00

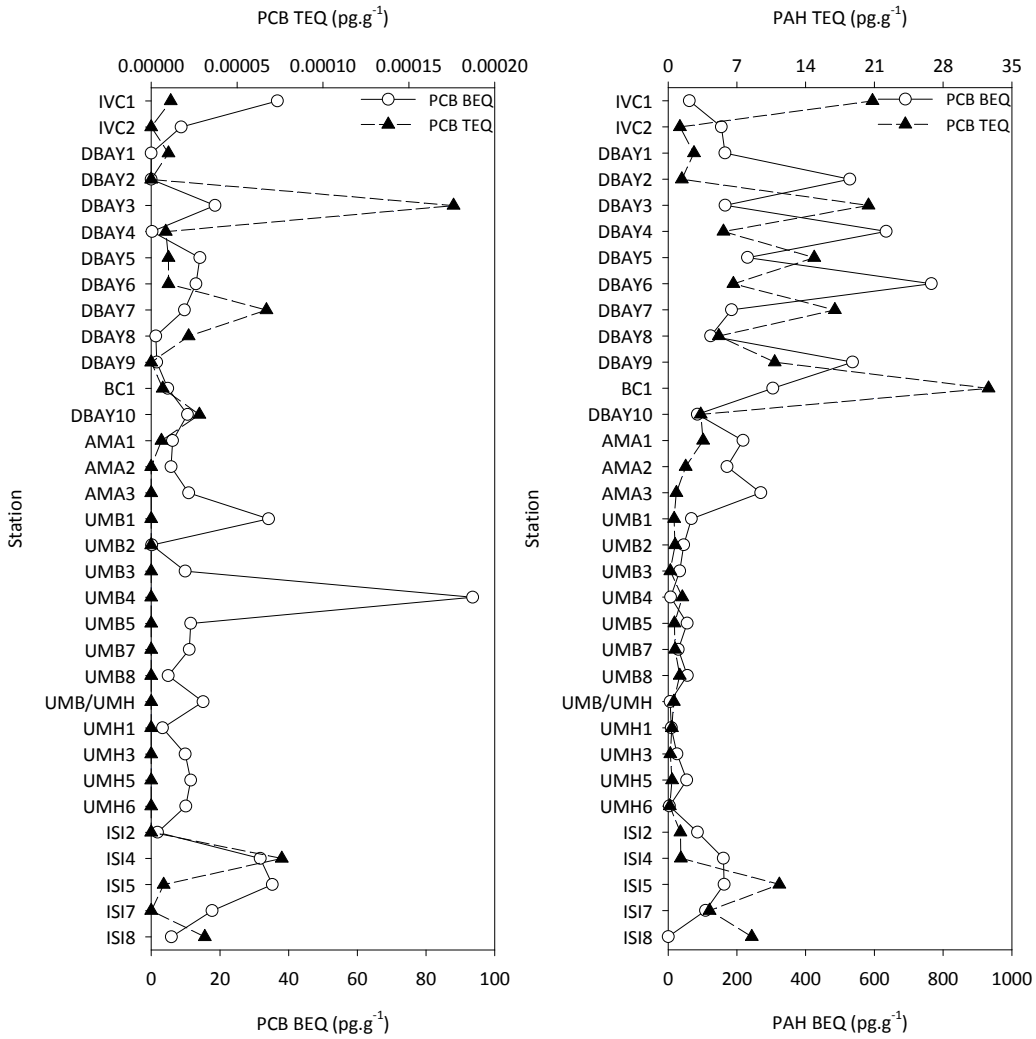

Figure 2.37. Comparisons of bioassay equivalents (BEQ) to TEQ_{TCDD} for polychlorinated biphenyls (PCB) and polycyclic aromatic hydrocarbons (PAH) in sediment at each station.

Additionally, the cells may experience cytotoxicity and the true response cannot be determined. It is usually impossible, due mainly to financial constraints, to analyse for a sufficiently wide suite of chemicals, whether these be polycyclic aromatic hydrocarbons, polychlorinated biphenyls or dioxins. It would be more efficient to analyse for priority polycyclic aromatic hydrocarbons and dioxin-like compounds (*i.e.* dioxin like polychlorinated biphenyls and dioxins), which are more likely to pose toxicological risks and also have toxic equivalency factor values. This should be done in conjunction with bioassays, which can estimate the concentration of additional components that may have been present in the sample but that were not analysed in the laboratory. One drawback of these approaches is that when the sediment samples were extracted, compounds were 'forced' into solution by the extraction method, yet the entire concentration of the chemicals might not have been bioavailable form in sediment in the collection environment.

3.4 CONCLUSIONS

- Polycyclic aromatic hydrocarbons, some organochlorine pesticides, polychlorinated biphenyls, and certain metals were frequent and in some cases significant contaminants of sediment sampled in Durban Bay, the uMngeni River, its estuary and tributaries of the estuary, and in the Isipingo River and its estuary in May 2012. Organophosphorous pesticides were not detected at concentrations exceeding the method detection limit.
- As was the case for the study discussed in Chapter 1, polycyclic aromatic hydrocarbons were ubiquitous in sediment. It is likely that polycyclic aromatic hydrocarbons in sediment at the majority of stations had

a predominantly anthropogenic source considering that the major land-use in the catchments of each system studied is urban and industrial (albeit to varying degrees). The highest total polycyclic aromatic hydrocarbon concentrations were generally detected in sediment in Durban Bay and in rivers and canals that discharge surface runoff into the Bay, namely Island View Canal, Bayhead Canal and the Amanzimnyama River. Total polycyclic aromatic hydrocarbon concentrations in the uMngeni River catchment, and especially in the Umbilo and Umhlatuzana Rivers in the Durban Bay catchment were generally low. This said, one of the highest total polycyclic aromatic hydrocarbon concentrations was detected at a station situated in a tributary of the uMngeni River estuary, adjacent to an industrial park.

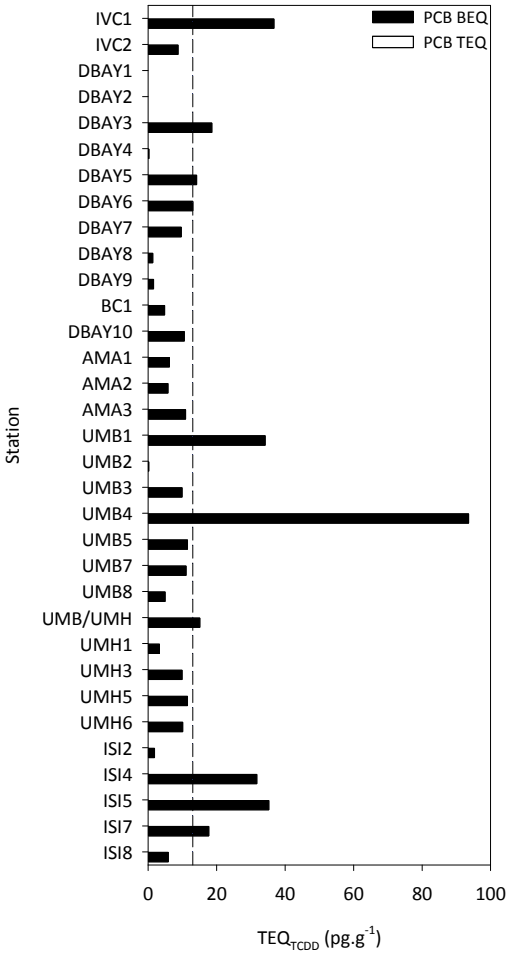

Figure 2.38. Polychlorinated biphenyl (PCB) bioassay equivalents (BEQ) and toxic equivalents (TEQ) compared to the TEQ_{TCDD} sediment quality guideline for the Netherlands.

- Based on the ratio between various isomers, polycyclic aromatic hydrocarbons in sediment in the rivers, estuaries and canals sampled were diagnosed as being derived predominantly from combustion (pyrogenic) sources. Only at a few stations was there evidence for a strong or dominant petroleum or oil (petrogenic) contribution.
- Based on the comparison of polycyclic aromatic hydrocarbon concentrations to sediment quality guidelines derived to be protective of sediment-dwelling organisms in North American freshwater and coastal ecosystems there seems a likelihood that concentrations in sediment at some stations were posing an acute toxic risk to sediment-dwelling organisms. The greatest risk was for sediment in Durban Bay, Island View Canal and Bayhead Canal.
- Seventeen organochlorine pesticides and/or metabolites were detected in sediment at concentrations exceeding the method detection limit. Toxaphene was the most frequently detected pesticide, at 13 of the 54 stations sampled. However, the majority of stations where this pesticide was detected were situated in Durban Bay, alluding to a source in or near the Bay.
- Chlordane and DDX concentrations at numerous stations exceeded sediment quality guidelines derived to be protective of sediment-dwelling organisms in North American freshwater and coastal ecosystems, with the highest potential risk for DDX at two stations in the Amanzimnyama River.
- Polychlorinated biphenyls were detected in sediment collected at 24 of the 54 stations sampled. Polychlorinated biphenyls were detected in all sediment samples collected in Durban Bay and in all or the majority of samples collected in the Amanzimnyama River, Island View Canal and Bayhead Canal. The highest total polychlorinated biphenyl concentration was detected at a station in Durban Bay, situated off a stormwater outfall, closely followed by the concentration at another station in Durban Bay situated near vessel maintenance and construction facilities. Polychlorinated biphenyls were sporadically detected at low concentrations in the uMngeni River, its estuary and tributaries of the estuary, and in the Umhlatuzana and Umbilo Rivers.
- Based on the comparison of total polychlorinated biphenyl concentrations to sediment quality guidelines derived to be protective of sediment-dwelling organisms in North American freshwater and

coastal ecosystems there seems a likelihood that concentrations in sediment at some stations were posing an acute toxic risk to sediment-dwelling organisms. The highest potential risk was for sediment in Durban Bay, particularly at the stations mentioned above, and in some parts of the Isipingo River.

- The most frequent and severe metal contamination of sediment was in Island View Canal, at numerous stations in Durban Bay, at one station in the Amanzimnyama River, and at two stations in a tributary of the uMngeni River estuary. Based on a comparison of metal concentrations to sediment quality guidelines used to regulate the disposal of dredged material in South African coastal waters there seems a likelihood that concentrations in sediment in parts of the latter systems and at isolated locations in other systems were posing an acute toxic risk to sediment-dwelling organisms.
- The mean sediment quality guideline quotient approach to estimating the potential toxicological significance of multiple chemicals in sediment suggested that the greatest likelihood for adverse effects posed by organic chemicals to sediment-dwelling organisms was for sediment in some parts of Durban Bay, Island View Canal, Bayhead Canal and the Amanzimnyama River.

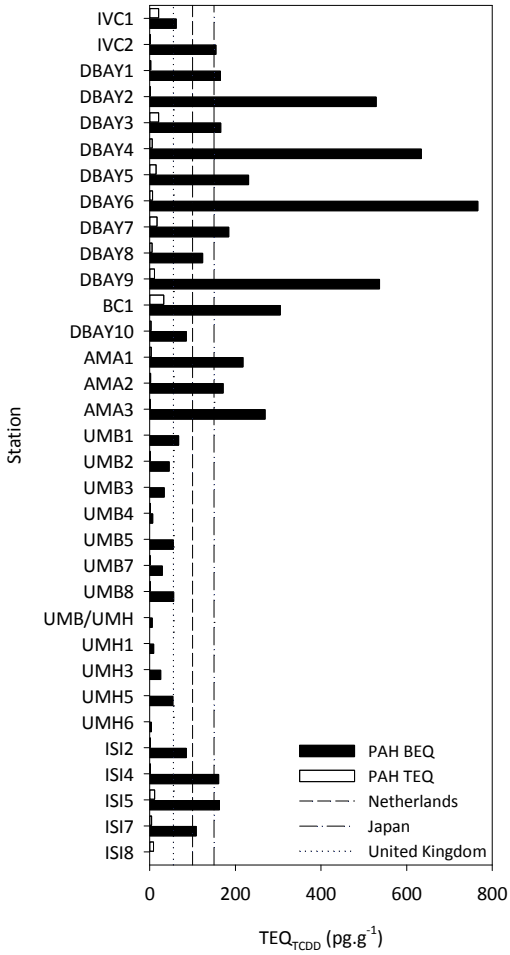

Figure 2.39. Polycyclic aromatic hydrocarbon (PAH) bioassay equivalents (BEQ) and toxic equivalents (TEQ) compared to TEQ_{TCDD} sediment quality guidelines for various countries.

- As mentioned previously, polycyclic aromatic hydrocarbons were ubiquitous in sediment in both surveys, although the concentrations differed slightly between surveys. The trend in polychlorinated biphenyl contamination of sediment was also comparable between surveys. Although DDT and its metabolites were widespread and significant contaminants of sediment in both surveys, there was a relatively large difference in the frequency of detection between surveys and, importantly, the contribution of technical DDT to the DDX concentration differed. Chlordane was more frequently detected in the survey performed in 2012. The general consistency of trends in contamination of sediment by these chemicals implies it is not necessary to monitor for these chemicals in sediment annually, but surveys could be performed every three to four years to determine whether there is any change in the magnitude and frequency of contamination.
- Polycyclic aromatic hydrocarbon concentrations in sediment collected in rivers, estuaries and canals in the eThekwini area in 2011 and 2012 were generally higher compared to concentrations reported for other areas of South Africa. DDX concentrations in sediment were generally comparable to concentrations reported for other areas of South Africa, with the exception of very high concentrations in sediment collected at two stations in the Amanzimnyama River. Total polychlorinated biphenyl concentrations in sediment were generally comparable to concentrations reported for other areas of South Africa. However, more congeners were analysed than in comparator studies, making direct comparison of the data difficult.
- A relatively small proportion of polycyclic aromatic hydrocarbon concentrations in sediment collected in rivers, estuaries and canals in the eThekwini area in 2011 and 2012 were ‘high’ by international

standards. However, a large proportion of the concentrations exceeded the median concentration reported in international studies.

- Although chlordanes were sporadically detected in sediment collected in rivers, estuaries and canals in the eThekwini area in 2011 and 2012, the concentrations were high compared to concentrations reported for many studies in other parts of the world, with many of the concentrations falling within the 90th percentile of the concentration distribution. Numerous DDX concentrations fall in the upper part of the range reported for studies in reported in international studies, with the concentrations in sediment at two stations in the Amanzimnyama River being the 7th and 8th highest. Although endosulfans were only detected in sediment at one station in the 2012 survey, the concentration was the second highest reported for any comparative international study. Toxaphene concentrations at four stations far exceed the highest concentration reported for comparative international studies, while concentrations at several other stations fall near the upper part of the range for comparator studies.
- Polychlorinated biphenyl concentrations in some sediment samples collected in rivers, estuaries and canals in the eThekwini area in 2011 and 2012 were 'high' by international standards, albeit that these are well below the extremely high concentrations reported in some comparator studies.

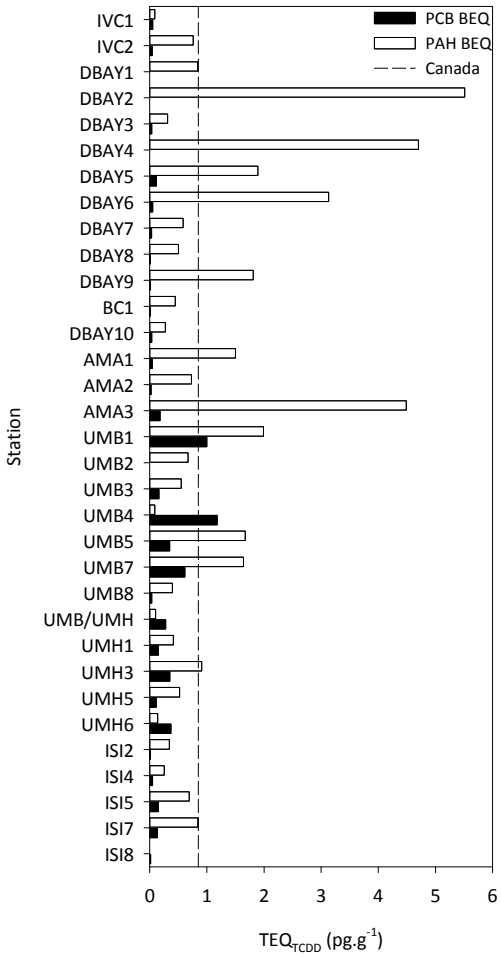

Figure 2.40. Polycyclic aromatic hydrocarbon (PAH) and polychlorinated biphenyl (PCB) bioassay equivalents (BEQ) (expressed as 1% TOC) compared to the Canadian TEQ_{TCDD} sediment quality guidelines.

- Although the comparison of chemical concentrations to sediment quality guidelines suggests the likelihood that polycyclic aromatic hydrocarbons, DDX, chlordanes, polychlorinated biphenyls and metals in sediment at some stations in rivers, estuaries and canals were likely posing an acute toxic risk to sediment-dwelling organisms, the magnitude and probability of the risk differed depending on which the sediment quality guidelines used to interpret the data. This creates uncertainty on whether toxic effects were likely manifesting and identifies the need for the toxicity testing or some other form of biological assessment to resolve this uncertainty.
- Toxicity testing of sediment using the H4IIE cell bioassay suggested that polycyclic aromatic hydrocarbon and polychlorinated biphenyl concentrations in sediment at numerous stations sampled in rivers, estuaries and canals in the eThekwini area were high enough to suspect they were posing a toxicological risk to sediment-dwelling organisms. An important finding was that toxicity testing and estimates of risk posed by contaminants in sediment using sediment quality guidelines were weakly correlated.
- The methods used in this study to screen for toxicity (or loadings which could cause detrimental effects) did not correspond well. However, the activation of the AhR of the H4IIE cells signals the presence of a dioxin-like halogenated aromatic hydrocarbon, which are known for causing toxicity. It is likely that the cells were activated by the dioxin-like halogenated aromatic hydrocarbon that had not been instrumentally analysed.
- Therefore, in utilising this as a screening tool it is possible to determine if there is toxicological risk at

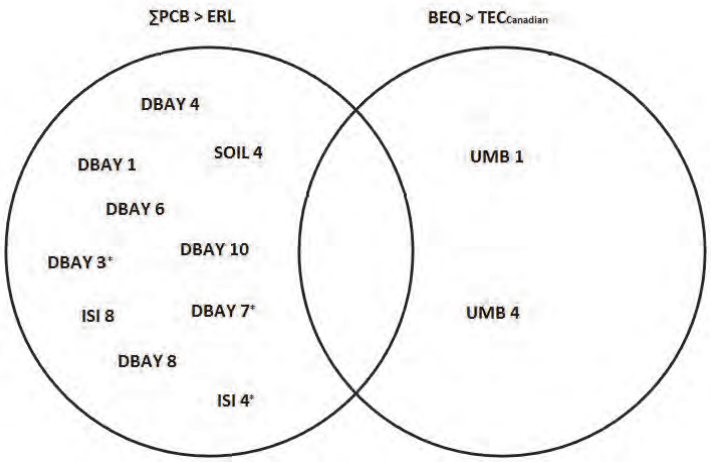

Figure 2.41. Comparison of the sites where total polychlorinated biphenyl (ΣPCB) concentrations exceeded the Threshold Effect Concentration (TEC) and Effects Range Low (ERL) (marked with *), and the bioassay equivalent (BEQ) exceeded the Threshold Effect Concentration (TEC) of the Canadian sediment quality guidelines.

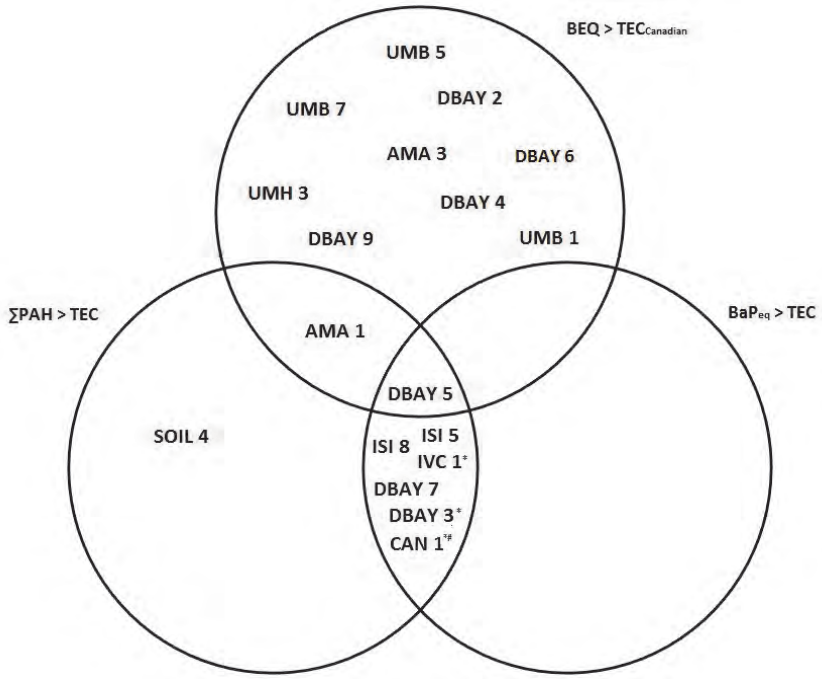

Figure 2.42. Comparison of stations where the total polycyclic aromatic hydrocarbon (ΣPAH) concentration exceeded the Threshold Effect Concentration (TEC) and Effects Range Low (ERL) (marked with *), the Threshold Effect Concentration (TEC) of the Canadian sediment quality guidelines, and BaP equivalent concentrations exceeded the Threshold Effect Concentration (TEC) and Effects Range Low (ERL).

sampling sites, caused by the mixture of dioxin-like compounds. Sites that have high responses can be further chemically analysed. In doing so the costs involved in analysing samples that have low compound concentrations, could be reduced. The instrumental analyses should focus on the dioxin-like compounds, as these are most likely to cause adverse effects.

CHAPTER 4: POLYCYCLIC AROMATIC HYDROCARBON, PESTICIDE, POLYCHLORINATED BIPHENYL AND METAL CONCENTRATIONS IN FISH AND MUSSELS IN THREE ESTUARIES IN THE ETHEKWINI AREA OF KWAZULU-NATAL AND POTENTIAL RISKS TO HUMAN CONSUMERS

4.1 INTRODUCTION

Many organic chemicals, including polychlorinated biphenyls and organochlorine pesticides, have a high bioaccumulation and biomagnification potential in estuarine and marine fish and shellfish (*e.g.* Zaranko *et al*., 1997). Some fish and shellfish, for example, have been shown to accumulate organic chemicals to concentrations in their tissue that are up to one million times higher than in the surrounding water column. The high bioaccumulation and biomagnification potential is because many of these chemicals are resistant to breakdown and rates of metabolism and elimination are slow. A significant route of human exposure to many of these contaminants is dietary, primarily through the consumption of fish and shellfish (*e.g.* Adams *et al*., 1994; Kannan *et al*., 1997; Dougherty *et al*., 2000; Tsutsumi *et al*., 2001; Smith and Gangolli, 2002; Borak and Hosgood, 2007; Domingo and Bocio, 2007). Whether the consumption of marine and estuarine fish and shellfish is a significant route of exposure to contaminants for the South African population is essentially unknown. This is because almost no attention has been directed at identifying whether marine and estuarine fish and shellfish are accumulating contaminants in their tissue to the extent these pose a risk to the health of human consumers. One objective of this study was thus to improve our understanding in this context, by assessing the concentrations of organic chemicals and metals in the tissue of fish and shellfish in Durban Bay and the uMngeni and Isipingo River estuaries and using the concentrations to perform a screening level assessment of potential health risks to human consumers. The focus on Durban Bay and the uMngeni and Isipingo River estuaries was based on the fact that sediment in these catchments was identified as being the most contaminated by organic chemicals and metals through the research discussed in Chapters 1 and 2.

Fish and shellfish have proved to be useful sentinels for contaminant monitoring in aquatic ecosystems because, as stated above, they are often able to accumulate contaminants in their tissue to concentrations orders of magnitude higher than in the surrounding water column. Not only does this accumulation provide an indicator of contaminants in the aquatic ecosystem of interest but importantly also the bioavailability of the contaminants. Thus, while the chemical analysis of sediment provides important information on the degree and extent of contamination of this matrix, a significant limitation is that is unknown what proportion, if any, of the contaminants in sediment are in a bioavailable form and are thus able to enter the foodweb. This is important since contaminants can only be bioaccumulated and biomagnified, and thus exert a toxic effect if they are in a bioavailable form. An additional objective of this study was thus to determine the efficacy of using fish and shellfish as sentinels for organic contaminant monitoring in coastal ecosystems, by determining whether the same chemicals identified as significant and widespread contaminants of sediment in Durban Bay and the uMngeni and Isipingo River estuaries and their catchments were being accumulated by fish and shellfish in these systems.

4.2 A NOTE ON BIOACCUMULATION AND BIOMAGNIFICATION

Aquatic organisms accumulate and retain certain chemicals when exposed to the chemicals through water, their diet, and other sources. The magnitude of accumulation can vary widely depending on the chemical and its properties. The term bioaccumulation refers to the net accumulation of a chemical by an aquatic organism as a result of uptake from all environmental sources (*e.g*. water, food, sediment). Bioaccumulation can be viewed as the result of competing rates of chemical uptake and elimination (chemical loss) by aquatic organisms. When the rates of chemical uptake and elimination achieve balance

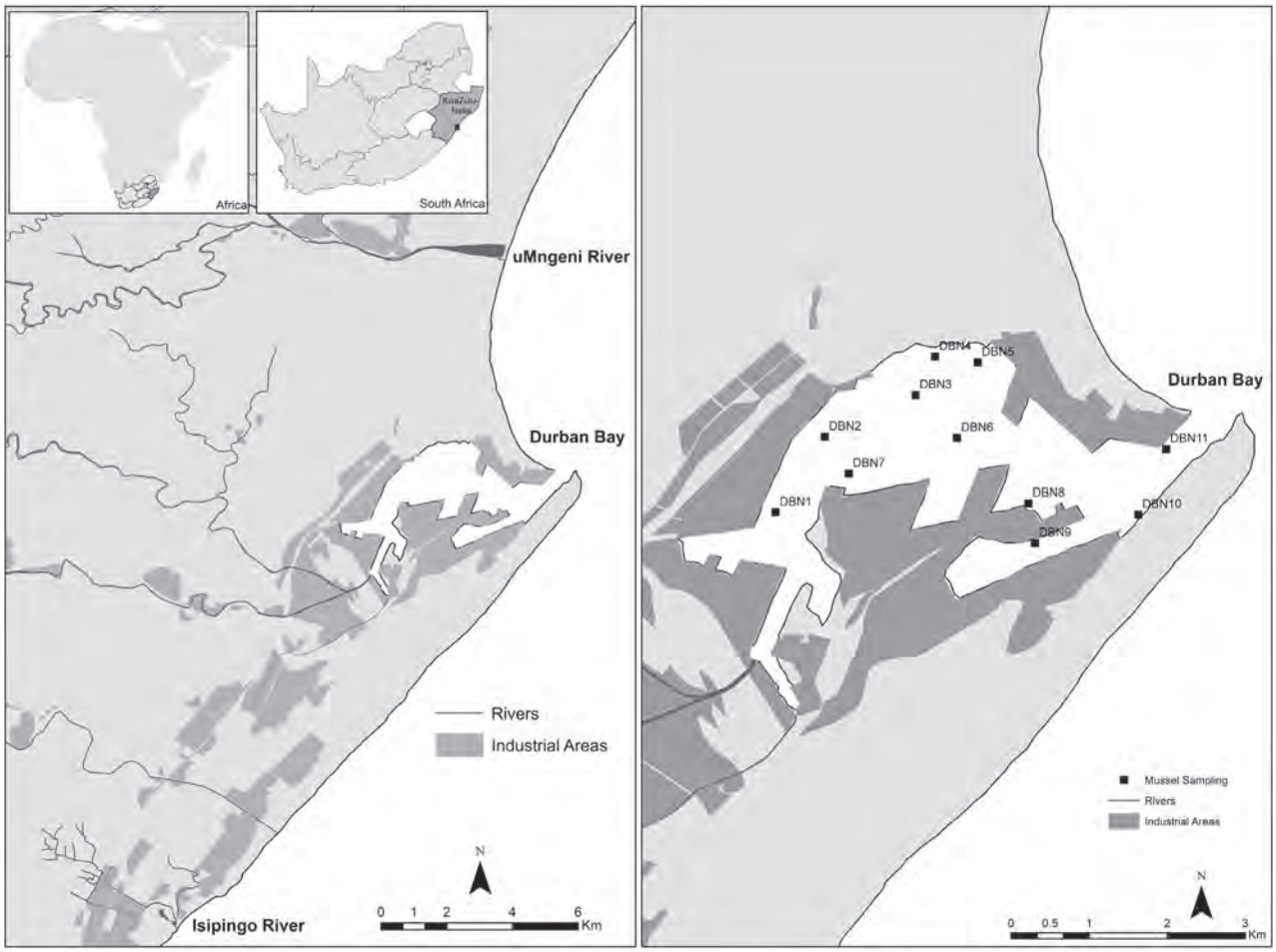

Figure 3.1. Maps showing the positions of the uMngeni River estuary, Durban Bay and Isipingo River estuary, where fish were caught (right), and the positions where mussel samples were collected in Durban Bay (right) in 2013.

the distribution of the chemical between the organism and its source(s) is said to be at steady-state. For chemicals that are persistent (*i.e.* resistant to metabolism) and hydrophobic, chemical concentrations in some aquatic organisms may be several orders of magnitude higher than their concentrations in water. These chemicals may also biomagnify in aquatic food webs, a process whereby chemical concentrations increase in aquatic organisms of each successive trophic level due to increasing dietary exposures (*e.g.* increasing concentrations from algae to zooplankton to forage fish to predator fish) (USEPA, 2003).

4.3 EXPERIMENTAL

4.3.1 Sampling design

As discussed in Chapters 1 and 2, the most significant contamination of sediment by organic chemicals and metals was evident in Durban Bay and uMngeni and Isipingo River catchments. The estuarine reaches of these catchments were the logical focus for assessing contaminant accumulation by fish and shellfish since estuaries are depositional environments and thus sinks for contaminants introduced into upstream waters. Fish and shellfish in estuaries are thus exposed to contaminants introduced into the freshwater and estuarine reaches of catchments. Estuaries are also important sites for recreational and subsistence fishing. In fact, Durban Bay and uMngeni and Isipingo River estuaries are important fishing sites in the Durban area. From a logistical perspective, the collection of fish and shellfish in the estuarine reaches of catchments is also easier than in the freshwater reaches.

The objective of this study was not to analyse contaminant concentrations in all fish species in each system studied, nor to perform a detailed human health risk assessment, since this would have been logistically

and financially too challenging. As stated above, the human health risk assessment component of the study was designed to be of a screening type, to identify whether a more detailed risk assessment is required. A screening assessment as a prelude to a detailed risk assessment is the approach recommended by the United States Environmental protection Agency (USEPA, 2000a,b), based on logistical and financial considerations. Thus, while the human health risk assessment component of this study relied on the collection of fish and shellfish that are consumed by recreational and subsistence fishers (see Table 3.2 for fish catch statistics for Durban Bay and the uMngeni River estuary), a range of fish occupying different habitats and trophic positions, and of different sizes (Table 3.1) were analysed to satisfy other objectives of the study.

Although the predominant focus was on fish, the brown mussel (*Perna perna*) as a shellfish representative was analysed for comparative purposes. Bivalve shellfish (*e.g.* mussels, oysters) are widely used to monitor the status and trends of contaminants in coastal waters through so-called Mussel Watch programmes. Bivalves possess a number of characteristics that make them useful in this context, including that they usually have a wide geographical range, which allows for comparisons between different geographical areas, are sessile and thus reflect local trends in contaminant exposure in contrast to mobile organisms such as fish that may have accumulated contaminants in water distant to where they were caught, and they effectively concentrate a wide range of chemicals (contaminants) in their food and in water in their tissue with little metabolic transformation (Roesijadi *et al*., 1984; S Phillips, 1988; Sericano *et al*., 1995; Baudrimont *et al*., 2005; Kimbrough *et al*., 2008). One limitation of mussels, however, is that they are restricted to saline environments as they do not tolerate low salinities. They are not, therefore, residents of the vast majority of estuaries along the South African coastline.

4.3.2 Fieldwork

Mussels were collected by hand from navigation markers and other floating structures at eleven locations in Durban Bay (Figure 3.1). Since mussels are sedentary they provided an opportunity to identify possible spatial trends in contaminant exposure/bioaccumulation in the Bay. Mussels are not present in the Silt Canal part of Durban Bay, where the water and sediment quality is poorest (CSIR, unpublished data). Although the precise reason for their absence in this part of the Bay is unknown, this may due to the low salinity of surface waters in this part of Bay as a result of freshwater inflow from the Amanzimnyama, Umbilo and Umhlatuzana Rivers. Mussels are not resident in the Isipingo and uMngeni River estuaries, also presumably because of low salinities that characterise estuarine environments, in addition to the lack of suitable rock and other solid substrata for colonisation.

Table 3.1. Fish and shellfish caught and collected for this study.

Type	Species	Common name
Finfish	*Ambassis gymnocephalus*	Bald glassy
Finfish	*Ambassis natalensis*	Slender glassy
Finfish	*Gerres methueni*	Pursemouth
Finfish	*Liza dumerilii*	Grooved mullet
Finfish	*Liza macrolepis*	Bigscale mullet
Finfish	*Liza tricuspidens*	Striped mullet
Finfish	*Mugil cephalus*	Striped mullet, flathead mullet
Finfish	*Myxus capensis*	Freshwater mullet
Finfish	*Oreochromus mossambicus*	Mozambique tilapia
Finfish	*Pomadasys commersonii*	Spotted grunter
Finfish	*Pseudorhombus arsius*	Largetooth flounder, sole
Finfish	*Sillago sihama*	Silver sillago, whiting
Finfish	*Sphyraena jello*	Barracuda, pick-handle
Finfish	*Valamugil buchanani*	Bluetail mullet
Finfish	*Valamugil cunnesius*	Longarm mullet, roundhead mullet
Shellfish	*Perna perna*	Brown mussel

Table 3.2. Species composition of recorded catches by shore- and boat-anglers in Durban Bay and shore-anglers in the uMngeni River estuary from January to December 2000. Results are presented in terms of total number of fish recorded (Total no.), total number of fish retained (No. kept), and total mass of fish retained (Mass) (from Pradervand *et al.*, 2003). Fish highlighted in grey were analysed for this study.

			Durban Bay shoreline			Durban Bay boat			Mngeni River estuary shoreline		
Family	**Species**	**Common name**	**Total no.**	**No. kept**	**Mass (kg)**	**Total no.**	**No. kept**	**Mass (kg)**	**Total no.**	**No. kept**	**Mass (kg)**
Rhinobatidae	*Rhinobatos annulatus*	Lesser sandshark				1	0		7	2	1
Dasyatidae	*Himanturac gerrardi*	Brown stingray				1	1	1.5			
Elopidae	*Elops machnata*	Ladyfish	4	2	6.5	15	15	55			
Albulidae	*Albula vulpes*	Bonefish	2	2	0.4						
Muraenidae	*Thyrsoidea macrura*	Slender giant moray	6	1	2	7	1	2	2	1	2
Clupeidae	*Hilsa kelee*	Kelee shad	0	9	2.5						
Synodontidae	*Synodus indicus*	Indian lizardfish	1	0		2	0		1	0	
Belonidae	Unidentified	Needlefish	1	0							
Platycephalidae	*Platycephalus indicus*	Bartail flathead	48	0		40	17	16.5	2	1	0.3
Ambassidae	*Ambassis* spp	Glassy	2	0					6	0	
Kuhliidae	*Kuhlia mugil*	Barred flagtail				1	0				
Serranidae	*Epinephelus andersoni*	Catface rockcod	2	0		15	3	3.4			
	Epinephelus coioides	Orangespotted rockcod	1	0		9	5	2.9			
	Epinephelus marginatus	Yellowbelly rockcod	1	0							
	Epinephelus spp	Unspecified rockcod				54	0		1	0	
Teraponidae	*Terapon jarbua*	Thornfish	2	0		3	0		26	0	
Pomatomidae	*Pomatomus saltatrix*	Elf	7	7	3.4	11	1	0.6	1	1	0.6
Haemulidae	*Pomadasys commersonii*	Spotted grunter	134	34	29.5	551	185	233.6	34	6	2.7
	Pomadasys kaakan	Javelin grunter	11	9	0.9	96	7	3.9			
	Pomadasys maculatum	Saddle grunter	5	2	0.7	155	0				
	Pomadasys multimaculatum	Cock grunter	6	2	3.3	151	6	8.2			
	Pomadasys olivaceum	Piggy	23	4	0.1						
	Pomadasys spp	Unspecified grunter	17	0					7	0	
Lutjanidae	*Lutjanus* spp	Unspecified snapper	2	0							
Sparidae	*Acanthopagrus berda*	River bream	41	19	3.6	9	2	0.8	39	6	1.3
	Crenidens crenidens	White karanteen	73	49	8.9	2	2	0.1			
	Diplodus sargus capensis	Blacktail	34	5	1.1	5	1	0.8			
	Diplodus cervinus hottentotus	Zebra	8	0		2	0		6	0	
	Rhabdosargus holubi	Cape stumpnose	2	0					2	1	0.1
	Rhabdosargus sarba	Natal stumpnose	21	12	12	38	30	24.6	1	1	0.3
	Rhabdosargus spp	Unspecified stumpnose	8	0							

			Durban Bay shoreline			Durban Bay boat			Mngeni River estuary shoreline		
Family	**Species**	**Common name**	**Total no.**	**No. kept**	**Mass (kg)**	**Total no.**	**No. kept**	**Mass (kg)**	**Total no.**	**No. kept**	**Mass (kg)**
	Sarpa salpa	Karanteen	2	0		1	0		1	0	
Monodactylidae	*Monodactylus falciformis*	Cape moony	26	3	0.4				1	0	
Gerreidae	*Gerres* spp	Pursemouth	16	14	3.6						
Ephippidae	*Platax pinnatus*	Dusky batfish				1	0				
Drepanidae	*Drepane longimanus*	Concertina fish				16	12	5.6			
Sillaginidae	*Sillago sihama*	Silver sillago	15	13	2.3	38	3	0.9			
Sciaenidae	*Argyrosomus japonicus*	Dusky kob	18	8	1.8	9	5	10.9			
	Argyrosomus thorpei	Squaretail kob	5	3	1.5	32	8	4.4			
	Johnius dussumieri	Small kob				2	0				
	Otolithes ruber	Snapper kob	26	5	2.6	47	25	14.2	11	2	0.6
	Unidentified	Unspecified kob	2	0		8	0				
Leiognathidae	*Leiognathus equula*	Slimy	145	6	1.1	39	0		37	5	0.9
Carangidae	*Alectis indicus*	Indian mirrorfish				4	4	5.6			
	Caranx ignobilis	Giant kingfish	4	4	3.2				1	0	
	Caranx sem	Blacktip kingfish	3	3	3.2	3	2	2.8			
	Caranx sexfasciatus	Bigeye kingfish	3	3	7.3	8	8	33.6			
	Caranx spp	Unspecified kingfish	2	0		13	7	6.6			
	Trachinotus botla	Largespot pompano							3	0	
	Megalaspis cordyla	Torpedo scad	3	1	0.9	81	29	20.9			
	Scomberoides tol	Needlescaled queenfish	4	1	0.3	4	0				
	Scomberoides	Largemouth queenfish				49	44	106.8			
Pomacentridae	*Abudefduf* spp.	Damsel	2	2	0.6						
Labridae	Unidentified Wrasse					2	0				
Mugilidae	*Mugil cephalus*	Flathead mullet	2	82	36.6	7	5	2.4	64	64	13.2
	Liza alata	Diamond mullet	13	13	11.5				1	1	1
	Liza tricuspidens	Striped mullet	4	4	1.2				7	0	
	Unidentified	Unspecified mullet	56	0					23	0	
Acanthuridae	*Acanthurus* sp	Surgeon	1	1	0.3						
Trichiuridae	*Trichiurus lepturus*	Cutlassfish	3	2	0.8	36	4	1.2	1	0	
Soleidae	Unidentified	Unspecified sole	1	0		27	10	2.9	1	0	
Tetraodontidae	Unidentified	Toby				8	1	0.7	16	0	
Cichlidae	*Oreochromis mossambicus*	Moçambique tilapia							1	1	0.2
Claridae	*Clarius gariepinus*	Sharptooth catfish							3	2	8
Other	Unidentified	Unidentified fish				4	0		36	0	

The original intent was to target mussels of a total valve length between 60-80 mm, since mussels of this length are targeted for the eThekwini Mussel Watch programme. This would facilitate direct comparison of contaminant concentrations in the tissue of mussels collected in Durban Bay and along the eThekwini shoreline. However, navigation markers in Durban Bay are periodically removed for maintenance purposes and the length of mussels on any particular marker depends on the period that the marker has remained in the water. Thus, the average total length of mussels processed ranged between 57.7-104.2 mm. After collection the mussels were wrapped in aluminium foil, sealed in plastic bags, and kept cool on ice until return to the laboratory, where they were frozen pending further processing.

Fish were collected using a variety of gear, including seine, gill and throw nets, beam trawl, and rod and reel. The fish were rinsed on-site, and depending on their size were then wrapped individually or in batches in aluminium foil, sealed in plastic bags, and kept cool on ice in the field until return to the laboratory, where they were frozen pending further processing. Apart from various species of mullet and the grunter *Pomadasys commersonnii*, which were targeted as they are amongst the fish most commonly caught and consumed by recreational and subsistence fishers in two of the systems studied (see Table 3.2), and ambassids, which were targeted to determine if they can be used as sentinels for contaminant monitoring in estuaries, fish were collected on an 'as caught basis'. The decision on whether to retain a fish species was made in the field based on the size and/or number of individuals caught, to ensure there was sufficient tissue for chemical analysis and to avoid the unnecessary sacrifice of fish. Although the objective was to collect at least three but preferably nine similarly sized individuals of various mullet species and spotted grunter within each system, this was rarely achieved. A longer fishing period would have allowed collection of the targeted number of fish but a decision needed to be made on the financial implications of fishing for a longer period. A total of nine days was spent collecting the fish analysed for this study. The reader should thus note that numerous of the fish species that would have relevance to this study because they are caught and consumed by recreational and subsistence fishers, particularly in Durban Bay (Table 3.2), were not targeted because of logistical and financial considerations. Many of these fish species are difficult to catch and/or are transient visitors to Durban Bay and rarely enter the uMngeni and Isipingo River estuaries.

4.3.3 Laboratory analyses

4.3.3.1 Fish and mussel processing

Mussels were processed in a partially thawed state. The length of each mussel was measured to the nearest 0.1 mm using Vernier callipers before they were shucked. The wet tissue mass of each mussel was measured to the nearest 0.01 g. About 40-60 mussels from each collection location were processed in this manner and the tissue composited. The tissue was stored in pre-cleaned (acid and hexane rinsed) amber glass jars with an aluminium foil lining cleaned in the same manner as the jars. The samples were again frozen pending freeze drying and ball-milling.

Fish were also processed in a partially thawed state. The standard, fork and total length (as appropriate and to the nearest millimetre) and weight (to nearest 0.01 g) of each fish was measured. Where appropriate or possible the fish were scaled. The external surfaces of fish were then thoroughly rinsed in running distilled water to remove mucus and other adhering matter and patted dry with absorbent towelling. Skin-on fillets were removed, dissected into blocks and stored in pre-cleaned amber glass jars with an aluminium foil lining (jars and lining cleaned in same manner described above for mussels). The tissue was again frozen pending freeze drying and ball-milling. Certain fish were too small to obtain sufficient tissue for analysis from an individual and were composited, using the 75% rule. In other words, the total length for the smallest fish in the composite was 75% of the largest fish. Ambassids were too small to remove fillets and were processed whole. The external surface of about 50 individuals of these fish were cleaned in running distilled water to remove mucus and other adhering matter and patted dry with absorbent towelling, dissected into small pieces, and frozen pending freeze drying and ball-milling.

All apparatus used to clean and dissect mussels and fish was comprised of non-contaminating material (*e.g.* stainless steel knives) and was cleaned between the processing of batches of mussels or fish by sequentially rinsing in 10% HNO_3, hexane and deionised water. Dissection boards were also cleaned between dissections in the same manner.

The moisture content of fish and mussel tissue was determined by drying a known mass of wet tissue and re-weighing the dried tissue.

4.3.3.2 Chemical analysis of tissue

Mussel and fish tissue samples were analysed in laboratories at the CSIR and Australian Government National Measurement Institute. For metal analysis, weighed aliquots of freeze dried tissue were digested in concentrated nitric and hydrochloric acids using microwave assistance. Metals were detected and quantified using Inductively Coupled Plasma-Mass Spectrometry or Inductively Coupled Plasma-Atomic Emission Spectrometry, and for mercury using Cold Vapour Atomic Absorption Spectrometry. For each batch of 20 samples or less a procedural blank, duplicate, blank spike, matrix spike and laboratory control sample was analysed. The reader should note that although arsenic is technically a metalloid it is referred to as a metal in this report for the sake of simplicity.

For butyltin analysis, alkyl tins were extracted with acidified ethanol. The acidified ethanol was then derivatised using sodium tetraethylborate. The ethylated derivatives were extracted into hexane and analysed using Gas Chromatograph Inductively Coupled Plasma-Mass Spectrometry, where characteristic isotopes of tin were used for quantitation and identification. Tetrabutyltin was used as the internal standard. For each batch of 20 samples or less a procedural blank, duplicate and blank spike was analysed.

For organochlorine pesticides and polychlorinated biphenyls, weighed aliquots of freeze dried tissue were extracted using dichloromethane. The extract was cleaned up using Gel Permeation Chromatography or silica column clean up. The final extract was analysed using Gas Chromatograph-Electron Capture Detection (dual column). Confirmation was by Gas Chromatograph Tandem Mass Spectrometry. For each batch of 20 samples or less a procedural blank, duplicate and blank spike was analysed. Surrogates were added to all samples to determine recovery.

All chemical concentrations are reported on a wet weight basis unless otherwise stated.

4.3.4 Risk assessment

4.3.4.1 General

Risk assessment is a process through which the degree and nature of a risk is characterised. The outcome of a risk assessment determines whether there is a need for risk management, that is, whether prevention and control measures or options can and should be implemented to reduce the risk. In the context of fish and shellfish consumption, this may include a ban or an advisory on consumption for particular fish species in a waterbody. The risk assessment approach followed in this study is for all intents and purposes identical to that recommended by the United States Environmental Protection Agency (USEPA, 2000a,b) for evaluating human health risks arising from exposure to chemicals through the consumption of fish and shellfish (*i.e.* a dietary pathway). The risk assessment process comprises four stages, namely:

- Hazard identification,
- Dose-response assessment,
- Exposure assessment,
- Risk characterisation.

4.3.4.2 Hazard identification

Screening Values (sometimes called Action Levels), which represent concentrations of chemicals in fish and shellfish tissue that are of potential human health concern, were calculated for two components of the population, namely subsistence and recreational consumers (discussed further below). The concentrations of certain chemicals in fish and mussels caught or collected in Durban Bay and the Isipingo and uMngeni River estuaries exceeded Screening Values for carcinogenic and/or non-carcinogenic health effects and indicated the need for a more detailed assessment of the potential health risks posed to humans.

4.3.4.3 Dose-response assessment

The quantitative relationship between a chemical dose and the incidence of carcinogenic and non-carcinogenic health effects in humans was assessed using toxicity data from the United States Environmental Protection Agency Integrated Risk Information System (IRIS).

4.3.4.4 Exposure assessment

The goal of exposure assessment is to identify human populations that might be exposed to chemicals of concern and the pathway through which they may be exposed, and to identify variables for the exposure assessment that allow the chemical dose to be quantified. The degree to which a risk assessment represents an exposed population depends on assumptions made for the assessment. Unfortunately, many of the variables required to calculate exposure have not as far as the scientists that prepared this report could establish been quantified for the South African population. It was, therefore, necessary to make informed assumptions or rely on default values prescribed by the United States Environmental Protection Agency (USEPA, 2000a,b). Whether these assumptions are valid for recreational and subsistence consumers in the greater Durban area is uncertain and represents an uncertainty of the risk assessment.

4.3.4.5 Identification of exposed populations

As mentioned previously, two exposed populations were identified, namely subsistence and recreational consumers. These populations are distinguished by the amount of fish and shellfish they consume. Subsistence consumers, through socio-cultural practices or necessity (*e.g.* economic reasons), consume larger amounts of fish and shellfish compared to recreational consumers and are, therefore, potentially at greater risk of exposure to chemicals accumulated by fish and shellfish. Recreational consumers consume fish and shellfish at a lower rate, but which nevertheless is considered to exceed the rate for the general population.

The United States Environmental Protection Agency (USEPA, 2000a,b) recommends consideration of sensitive and insensitive segments of the exposed populations. Sensitive segments are defined as infants, children and females of childbearing age, while insensitive segments are adult males and adult females beyond their childbearing years. These different segments were not considered in this study since the ingestion rate was considered proportional to body weight. Assessing the risk posed to an average adult thus concurrently caters for the risk posed to females of childbearing age, children and infants.

4.3.4.6 Exposure pathway

Although several exposure pathways could conceivably result in human exposure to the chemicals of concern, for the purposes of this study the consumption of fish and shellfish was considered the only source of exposure. This is an obvious simplification of the real-world situation since many foodstuffs contain metals and polycyclic aromatic hydrocarbons amongst other chemicals. Other exposure pathways besides consumption, such as inhalation, may also result in exposure.

4.3.4.7 Quantification of exposure

An individual's exposure depends upon several factors, including the concentrations of contaminants in fish

and shellfish tissue, the amount of fish and shellfish tissue consumed, how often and how long fish and shellfish are consumed, and the consumers body weight. Because exposure occurs over time the total exposure is divided by a time period of interest to obtain an average exposure rate per unit time. When this is expressed as a function of body weight the exposure rate is referred to as the Chemical Specific Daily Intake (CDI). The Chemical Specific Daily Intake of chemicals in fish and mussels was calculated as:

$$CDI = (C \times CR \times EF \times ED)/(BW \times AT) \quad \text{Equation 1}$$

Where:
CDI = Daily intake of a specific chemical ($mg.kg^{-1}$-day),
C = Chemical concentration in fish or mussel tissue ($mg.kg^{-1}$),
CR = Consumption rate (kg per day),
EF = Exposure frequency (days per year),
ED = Exposure duration (years),
BW = Body weight (kg),
AT = Averaging time for exposure duration (EF $\times$ ED for non-carcinogens and 70 years x 365 days per year for carcinogens).

4.3.4.8 Chemical concentrations in fish and mussel tissue

The concentrations of chemicals in fish and mussel tissue (parameter C in Equation 1) are provided in Appendices 14-17. Laboratory methods and instruments do not allow for the accurate measurement of chemicals below a certain concentration known as the method detection limit. Concentrations reported as below the method detection limit are often referred to as non-detects. Because there is no certainty that a chemical reported as below the method detection limit was not present in the tissue of fish or shellfish a decision must be made on how to treat non-detects. The most conservative approach is to substitute non-detects with a concentration equivalent to one-half the method detection limit, rather than a value of zero. This is consistent with United States Environmental Protection Agency risk assessment guidance (USEPA, 2000a,b). However, there may be problems associated with this approach if the method detection limit is not sufficiently low. This is because total concentrations of some chemicals are used to assess risk, but these chemicals are comprised of 'chemical building blocks', or individual chemicals. For example, the total polychlorinated biphenyl concentration is the sum of 'chemical building blocks' called congeners. If the method detection limit is not sufficiently low then replacing the concentration of each 'chemical building block' with a concentration equivalent to one-half the method detection limit may result in the total concentration being identified as posing a risk to human consumers even though the concentrations of all congeners were below the method detection limit. To comprehensively evaluate the risk of exposure to chemicals through the consumption of fish and mussels for this study, the risk was assessed by substituting polycyclic aromatic hydrocarbon, polychlorinated biphenyl and DDT concentrations below the method detection with a concentration equivalent to one-half the method detection limit and with a concentration equivalent to zero. As mentioned previously, the bulk of the organochlorine pesticides and their metabolites were never detected at a concentration exceeding the method detection limit and were assumed not to be present in fish and mussel.

Inorganic arsenic and cadmium non-detects were not substituted with a equivalent to one-half the method detection limit since these are naturally occurring chemicals and will be present in the tissue of fish and mussels.

Mercury is present in fish and shellfish tissue in two predominant forms, namely elemental mercury and methylmercury. The most toxic form is methylmercury. Analysing for methylmercury is expensive and the approach followed in this study was to analyse for elemental mercury and assume that all of this mercury was present as methyl-mercury. This approach is valid in that the contribution of methylmercury to total

mercury in fish and shellfish typically exceeds 90% (>95% - Bloom, 1992; >96% - Kim, 1995; 90 to 100% - USEPA 2000, 2009 a; 98% - Hammerschmidt and Fitzgerald, 2006; >95% - Senn *et al*., 2010), although the contribution can be variable (45 to 124% - Kannan *et al*., 1988; 43 to 76% - Forsyth *et al*., 2004; 60 to 100% - Storelli *et al*., 2005). Assuming all mercury is present as methylmercury is thus a conservative approach.

A number of polycyclic aromatic hydrocarbon isomers were detected in fish and mussels. Of these only benzo(a)pyrene has a Cancer Slope Factor (latter term discussed below). To estimate the risk from exposure to polycyclic aromatic hydrocarbons in fish and mussels a Toxic Equivalency Factor approach was followed. This involved expressing the carcinogenic potency of six isomers relative to benzo(a)pyrene and then summing the potencies and that for benzo(a)pyrene to derive the Toxic Equivalency Factor (USEPA, 2000a,b).

DDX was determined as the sum of *p'p*' isomers of DDT, DDD and DDE.

Polychlorinated biphenyls were analysed as congeners. However, the Cancer Slope Factor for polychlorinated biphenyls used in risk assessment is for Aroclors. Two approaches were thus followed for this risk assessment. First, congeners were summed to determine a total polychlorinated biphenyl concentration, either with non-detects replaced with a value equivalent to one half the method detection limit or a value of zero. Second, an Aroclor equivalent polychlorinated biphenyl concentration was calculated by summing the concentrations of congeners 8, 18, 28, 44, 52, 66, 101, 105, 118, 128, 138, 153, 170, 180, 187, 195, 206, 209 and multiplying the sum by a factor of two. These congeners were designated by the National Oceanic and Atmospheric Administration as always or very often appearing in sediment and fish tissue and which also do not readily degrade, and typically represents about 45% of the total polychlorinated biphenyl concentration in fish and shellfish (Lauenstein and Cantillo*,* 1993). The factor of two was designed to account for the difference in concentrations estimated from this small number of congeners and all possible congeners in bivalves, but was nevertheless applied here also to fish. However, other studies have reported different factors. For example, Greenfield and Allen (2013) reported an exponential relationship between the sum of 40 congeners and the sum of 209 congeners, while Lefkovitz *et al*. (2001) reported that the sum of 107 congeners was 1.35, 1.37 and 1.45 times higher than the sum of the above 18 congeners for lobster hepatopancreas from three locations, and 1.47 for edible lobster tissue. Lefkovitz *et al*. (2001) also reported a slight difference in the factors depending on whether polychlorinated biphenyls were analysed by GC-MS or GC-ECD. Based on these findings, Lefkovitz *et al*. (2001) suggested that a more reasonable determination of 'total' polychlorinated biphenyls could be estimated by multiplying the eighteen National Oceanic and Atmospheric Administration congeners analysed by GC-MS by a factor of 1.4. Fikslin and Santoro (2003) showed that twice the sum of the eighteen National Oceanic and Atmospheric Administration congeners provided a similar estimate of the concentration of 81 congeners analysed in a species of fish (mean ratio of 1.95), but for other fish analysed either provided an over- or underestimate of the 'total' polychlorinated biphenyl concentration (mean ratios of 1.48-1.85 and 2.75-2.77). Howell *et al*. (2008) reported a slight overestimate of total polychlorinated biphenyl concentrations by the sum of eighteen National Oceanic and Atmospheric Administration congeners multiplied by a factor of two for fish, and a larger overestimate for crab tissue. In another approach, according to the Deutsche Industrie Norm the sum of congeners 28, 52, 101, 138, 153 and 180 is multiplied by a factor of five to estimate the total polychlorinated biphenyl concentration represented by 209 congeners (WHO, 1993; Cullen *et al*., 1996).

For the risk assessment, the concentrations of each chemical were averaged across individuals or composite samples of the same fish species within each system, since consumers are likely to consume a range of different sized fish with different chemical concentrations in their tissue. This approach was not followed for mussels since it was considered more likely that the bag limit of mussels would be satisfied by collection from one area, because of the comparative ease of collecting these organisms.

4.3.4.9 Consumption rate

The consumption rate (parameter CR in Equation 1) is critical for calculating the Daily Intake. As far as the scientists that prepared this report could establish a quantitative study of fish and shellfish consumption rates has not been performed for the eThekwini area of KwaZulu-Natal. Nel and Steyn (2002) provide average per capita fresh and canned fish consumption rates for South Africans of 1-5 years, 6-9 years, and 10 years and older, as 6.7, 7.2 and 11.77-15.13 g per day respectively (two approaches were used to define intake of fish for the 10 years and older category). However, only a low proportion of the study participants reported the consumption of fish. If only those participants consuming fish are considered then the consumption rates increased to 89.8, 85.1 and 113.8-125.28 g per day respectively (two approaches were used to define intake of fish for the 10 years and older category). For the purposes of this study, the ingestion rate for recreational consumers was taken as the 90th percentile of the average per capita consumption of fish and shellfish in the United States of America, at 17.5 g per day. This consumption rate slightly exceeds the average consumption rate for the South Africans of 10 years and older, and thus provides a conservative estimate of risk. Informal discussions with recreational fishers at some fishing clubs in Durban Bay intimated that they consume up to five or six meals of fish per month. Thus, the risk for a second group of recreational fishers was assessed at a consumption rate of six 227 g meals per month, or 45.4 g per day. A meal size of 227 g is the average size of a fish or shellfish meal for adults in the United States of America (USEPA 2000b). These consumption rates for recreational fishers are referred to as Scenario 1 and Scenario 2. The consumption rate for subsistence consumers was taken as the 99th percentile of the average per capita consumption of fish and shellfish in the United States of America, at 142.4 g per day. Again this slightly exceeds the average consumption rate for members of the South African population that reported they consume fish and shellfish in the survey by Nel and Steyn (2002) and thus also provides a conservative estimate of risk.

Since consumers usually find it difficult to assess their consumption rate in grams per day it is worthwhile placing the abovementioned consumption rates into context. The typical weight of (frozen) packaged fish fillets (*e.g.* hake) purchased in stores in South Africa is about 100 -120 g. A standard can of tuna purchased from retail outlets weighs 170 g including packing liquid (oil or water), and about 140 g after draining. A 'large' can of foodstuff typically weighs 410 g. In a South African restaurant, a 'fish serving is typically of the order of 180-280 g in wet weight. The United States Environmental Protection Agency (USEPA, 2000a,b) considers the average size of a fish or shellfish meal for adults of 70 kg weight in the United States of America to be 227 g before cooking. This equates to a meal of about two fish fillets purchased in South African stores and about the average fish meal size in a restaurant, and the same meal size has been assumed for this study. At a meal size of 227 g the ingestion rates equate to a little more than two meals a month and 28 meals a year for recreational consumers under Scenario 1, six meals a month and 72 meals a year for recreational consumers under Scenario 2, and about 19 meals a month and 229 meals a year for subsistence consumers.

4.3.4.10 Chemical absorption

It was assumed the entire concentration of chemicals in fish and mussel tissue ingested by humans is absorbed across the intestinal tract.

4.3.4.11 Exposure frequency

An exposure frequency of 365 days per year was assumed for the Chemical Specific Daily Intake calculation, a standard practice for human health risk assessment.

4.3.4.12 Exposure duration

The exposure duration is the period over which exposure occurs at the concentration and ingestion rate specified. As is the case for other parameters in Equation 1, the period that subsistence and recreational

consumers might consume fish and mussel caught and collected in Durban Bay and the Isipingo and uMngeni River estuaries is unknown. Bradshaw *et al*. (2011) estimated the average life expectancy at birth for males and females in South Africa in 2011 at 57.2 and 62.8 years respectively. This provides an average life expectancy for South Africans of 60 years. Since the general approach in risk assessment is to over- rather than underestimate risk by using conservative values for parameters in risk equations and a large proportion of South Africans can be expected to have a lifespan longer than 60 years, a life expectancy of 70 years was used in this study. This assumes an individual will live in the same area for a 70 year period and will consume fish contaminated at or above the level of concern during this period. Additional motivation for using this exposure period is that the United States Environmental Protection Agency's Integrated Risk Information System (IRIS) assumes a 70 year lifetime for the derivation of cancer slope factors. The use of a 70 year life expectancy thus avoids the need to adjust cancer slope factors to a shorter life expectancy.

An exposure period of thirty years was used to assess non-carcinogenic risk. This default value is recommended by the United States Environmental Protection Agency (USEPA, 2000a,b).

4.3.4.13 Averaging time

As discussed earlier, exposure to contaminants in fish or shellfish occurs over time. Therefore, the total exposure is divided by the time period of interest to obtain an average exposure rate per unit time. When this rate is expressed as a function of body weight the resulting exposure rate is referred to as the Daily Intake expressed in milligrams of a chemical taken into the body per kilogram body weight per day. The averaging time for estimating carcinogenic risk was 25 550 days, the number of days in a 70 year exposure period. The averaging time for assessing non-carcinogenic risk was 10 950 days, the number of days in a 30 year exposure period. This assumes that fishers will live in or at least consume mussels and fish for these periods.

4.3.4.14 Body weight

There is conflicting information on the average body weight of South Africans. The South African Demographic and Health Survey for 2003 (DOH, 2007) provides the average bodyweight for South African's of 15 years and older at 66 kg for males and 68 kg for females. The average body weight is thus 67 kg. The South African National Health and Nutrition Examination Survey (Shisana *et al*., 2013) provides the average bodyweight for South African's of 15 years and older at 67.3 kg for males and 72.2 kg for females. The average body weight is thus 69.8 kg. For the purposes of this study an average body weight of 67 kg was used as its use provides a conservative estimate of risk. The United States Environmental Protection Agency's Integrated Risk Information System (IRIS) assumes a 70 kg adult body weight for the derivation of Cancer Slope Factors.

4.3.4.15 Cooking loss of contaminants

Cooking can lead to the loss of certain chemicals from the tissue of fish and shellfish (*e.g.* Armbruster *et al*., 1987, Zabik *et al*., 1996; Salama *et al*., 1998), with a concomitant lowering of the risk profile. This is significant for organic chemicals, such as polychlorinated biphenyls, which are usually associated with lipids. Lipids are commonly lost during the cooking process, or if the skin of fish is removed then before cooking. This is because the most significant fat deposits in fish are situated immediately beneath the skin. Chemicals may also be volatised during the cooking process. However, cooking loss will not result if a stew-type is prepared, that is, the lost lipids are not allowed to 'escape'. The situation is slightly different for metals, which can become concentrated in mussel and fish tissue due to fluid loss, although their bioaccessibility may decrease. This is despite the fact that a significant proportion of the metal content in mussels and fish may be lost during the cooking process, although this is metal specific (Metian *et al*., 2009). However, several workers have reported no loss of contaminants during cooking of eels and fish

(*e.g.* Trotter *et al*., 1989; Moya *et al*., 1998).

Cooking loss was not incorporated into this risk assessment given the incomplete information on how each chemical is affected by cooking. This is the most conservative approach and is in agreement with United States Environmental Protection Agency (USEPA, 2000a,b) guidance on fish and shellfish consumption advisories, which recommends that cooking loss should only be considered if there is information on how methods of preparation influence chemical concentrations in fish and shellfish tissue. However, some agencies recommend reducing chemical concentrations by up to 50% for polychlorinated biphenyls and similar chemicals that have a high octanol/water partition coefficient (K_{ow} >3) and are thus concentrated in fatty tissue rather than muscle.

4.3.4.16 Risk Characterisation

Risk characterisation integrates the results of the exposure assessment with chemical toxicity information to derive estimates of risk. Non-carcinogenic and carcinogenic risk estimates are calculated separately because of fundamental differences in their critical toxicity values.

4.3.4.16.1 Non-carcinogenic risk

In general, humans that consume contaminated seafood are exposed to low concentrations of chemicals over an extended period. This type of exposure rarely results in acute toxicity, that is, exposure to a single, high dose of a chemical. However, long-term exposure may result in chronic toxicity. The potential for chronic, non-carcinogenic health effects was thus evaluated by calculating the ratio of chemical exposure to an Oral Reference Dose (RfD). This ratio of exposure to toxicity for an individual chemical, referred to as a Hazard Quotient (HQ), was calculated as:

$$HQ = CDI/RfD \qquad \text{Equation 2}$$

Where:
HQ = Chemical specific hazard quotient (unitless),
CDI = Chemical specific daily intake ($mg.kg^{-1}$-day),
RfD = Chemical specific reference dose ($mg.kg^{-1}$-day).

The oral reference dose is an estimate, with an uncertainty spanning perhaps an order of magnitude (an order of magnitude corresponds to a tenfold difference), of the daily oral exposure of a population, including sensitive subpopulations, to a potentially hazardous material that is likely to be without an appreciable risk of deleterious non-carcinogenic effects over a lifetime (USEPA, 2000b). The underlying assumption of a reference dose is that there is a threshold dose below which there is a negligible risk that certain toxic effects will occur.

Because of uncertainty associated with toxicity data 'safety factors' are included, resulting in a lower and more protective reference dose. If a Hazard Quotient exceeds a value of one (*i.e.* exceeds the Oral Reference Dose) then individuals may be at risk. The magnitude of the risk can be inferred from the degree to which the reference dose is exceeded. If the Hazard Quotient is only slightly above a value of one then the dose will likely fall below the toxic effect level because of the abovementioned safety factors. However, a Hazard Quotient is not linear, with the result that a Hazard Quotient of four does not imply a four times greater risk compared to a Hazard Quotient of one. Rather, the United States Environmental Protection Agency (USEPA, 2000b) suggests that a Hazard Quotient of less than one should be interpreted as 'no cause for concern' whereas a Hazard Quotient exceeding one should indicate some cause for concern.

To estimate the cumulative potential for non-carcinogenic effects due to simultaneous exposure to multiple chemicals in fish and mussel tissue, Hazard Quotients for all chemicals and health effects were

summed to derive a Hazard Index. The Hazard Index is interpreted in the same manner as the Hazard Quotient, that is, a Hazard Index less than one should be interpreted as no cause for concern whereas a Hazard Index exceeding one should indicate some cause for concern. Although many workers re-investigate Hazard Indices exceeding a value of one by then only considering groups of toxicologically similar chemicals (*i.e.* with similar health effects or that affect the same organ), this approach was not followed in this study.

4.3.4.16.2 Carcinogenic risk

The potential health risk posed by chemicals identified as (probable) carcinogens was estimated as the incremental probability of an individual developing cancer over a lifetime of exposure. The United States Environmental Protection Agency (USEPA, 2000b) assumes that a threshold dose does not exist for carcinogens and that any dose can contribute to carcinogenic health risk. In other words, there is never a zero probability of cancer risk when exposed to carcinogenic chemicals. Carcinogenic risk was calculated as an Excess Cancer Risk (ECR), as:

$$ECR = CDI \times CSF \qquad \text{Equation 3}$$

Where:
ECR = Excess Cancer Risk (unitless),
CDI = Chemical specific daily intake ($mg.kg^{-1}$-day),
CSF = Chemical specific cancer slope factor ($mg.kg^{-1}$-day)

The Cancer Slope Factor (CSF) is an upper-bound estimate, approximating 95% confidence limits, of the probability an individual will develop cancer over a lifetime as a consequence of exposure to a given dose of a specific carcinogen (USEPA, 2000b). Current regulatory practice suggests that there is no 'safe dose' of a carcinogen and that a very small dose of a carcinogen will give a very small cancer risk. Cancer risk estimates are, therefore, not yes/no answers but measures of probability. Such measures, however uncertain, are useful in determining the magnitude of a cancer threat because any level of a carcinogenic contaminant carries an associated risk. The interpretation of Excess Cancer Risk thus requires that an acceptable increase in cancer risk be defined. This is referred to as the acceptable risk level. There is no universally accepted acceptable risk level. The United States Environmental Protection Agency (USEPA, 2000b) considers risk levels between 10^{-4} (one excess case of cancer for every 10 000 persons) and 10^{-6} (one excess case of cancer for every 1 000 000 persons) to be acceptable for the purpose of issuing fish and shellfish consumption advisories. Acceptable risk levels of 1×10^{-5} or 1×10^{-6} are most commonly used. However, because of the well-documented health benefits of consuming fish and shellfish some jurisdictions consider a risk level of 1×10^{-4} as acceptable. Risks above 1×10^{-4} are nearly always considered unacceptable. For this risk assessment the acceptable risk level was defined as 1×10^{-5}. Where risks fall between 1×10^{-5} and 1×10^{-4} this is considered as warranting further investigation. Risks exceeding 1×10^{-4} are considered unacceptable and warranting some form of action or management to reduce the risk.

To estimate the cumulative cancer risk due to simultaneous exposure to multiple chemicals in fish and mussel tissue the Excess Cancer Risk for individual chemicals was summed to calculate a total Excess Cancer Risk.

4.3.4.17 Meal limits

As discussed below, Hazard Indices for numerous fish species in the different systems and for mussels at numerous locations in Durban Bay exceeded a value of one or the Excess Cancer Risk exceeded an acceptable risk level of 1×10^{-5}. This does not necessarily mean the fish and mussels cannot be consumed but rather that care should be taken in the number of meals consumed per defined period. Thus, the number of meals that can safely be consumed per month was calculated. For this purpose meal size was set at 227 g and the acceptable risk level was set at 1×10^{-5} for meal consumption limit calculation.

4.4 RESULTS AND DISCUSSION

4.4.1 Chemical concentrations in fish and mussel tissue

The concentrations of chemicals in the tissue of fish caught and mussels collected in Durban Bay and the uMngeni and Isipingo River estuaries are presented in Figures 3.2-3.5. Each metal, including inorganic arsenic, was detected at a concentration exceeding the method detection limit in the tissue of mussels at all locations in Durban Bay (Figure 3.2). The majority of metals were also detected at concentrations exceeding the method detection limit in the tissue of fish. The exceptions were inorganic arsenic, which was not detected in any fish, cadmium, which was detected in only four species (*Ambassis gymnocephalus* and *Pomadasys commersonnii* in Durban Bay (but in only three of the ten individuals analysed), *Ambassis natalensis* in the Isipingo River estuary, and *Ambassis natalensis* and *Liza dumerilii* in the uMngeni River estuary), and mercury, which was detected in all species apart from the mullet *Mugil cephalus* caught in Durban Bay (Figure 3.2). There was a pronounced difference in concentrations of the majority of metals between fish and mussels, with mussels usually having substantially higher metal concentrations in their tissue compared to fish (Figure 3.2). Tissue concentrations of selenium were broadly comparable between mussels and fish, while fish in Durban Bay generally had considerably higher concentrations of mercury in their tissue compared to mussels. These differences between fish and mussels should not at face value be taken as indicating that mussels had accumulated higher concentrations of metals in their tissue because of their more frequent or prolonged exposure to metal contaminated water and food. This is because mussels and fish naturally have a different propensity for accumulating certain metals in their tissue, even on exposure to similarly contaminated food, sediment and water. Bivalves, for example, typically accumulate higher concentrations of zinc in their tissue while many fish have a higher propensity for accumulating mercury in their tissue.

Metal concentrations in the tissue of the majority of fish caught in Durban Bay and the uMngeni and Isipingo River estuaries were generally comparable. There were exceptions for some fish, including the silver sillago *Sillago sihama* caught at two locations in Durban Bay, which had very high arsenic concentrations in their tissue, and the ambassid *Ambassis gymnocephalus* caught in Durban Bay, which had substantially higher concentrations of cadmium and zinc in their tissue compared to other fish. The majority of fish species caught in Durban Bay had considerably higher mercury concentrations and to a lesser degree nickel concentrations in their tissue compared to fish caught in the uMngeni and Isipingo River estuaries (Figure 3.2).
Metal concentrations in the tissue of mussels at stations DBN1-DBN5 in the upper part of Durban Bay were generally higher than in mussels at stations DBN6-DBN11 in the lower part of the Bay. Metal concentrations were poorly correlated to the average length and wet tissue mass of mussels, suggesting this trend reflects the different exposure to and accumulation of metals by mussels between the upper and lower parts of Durban Bay. This makes sense when it is considered that sediment in the upper part of Durban Bay is far more metal contaminated compared to the lower part of the Bay (CSIR, unpublished data).

As mentioned above, high arsenic concentrations were detected in the tissue of the silver sillago *Sillago sihama* caught at two locations in Durban Bay, but not at a third location (Figure 3.2). High cadmium concentrations were detected in the tissue of the ambassid *Ambassis gymnocephalus* caught at two locations in Durban Bay (Figure 3.2). Although cadmium concentrations in the tissue of *Ambassis natalensis* caught at single locations in the uMngeni and Isipingo River estuaries were substantially lower than for *Ambassis gymnocephalus* in Durban Bay, the cadmium concentration in these fish was nevertheless substantially higher than the concentrations in other fish caught in these estuaries. In fact, apart from the ambassids, cadmium was only detected at a concentration exceeding the method detection limit in the tissue of three individuals of the spotted grunter *Pomadasys commersonnii* caught in Durban Bay and in a composite sample of the mullet *Liza dumerilii* caught in the uMngeni River estuary, but at low

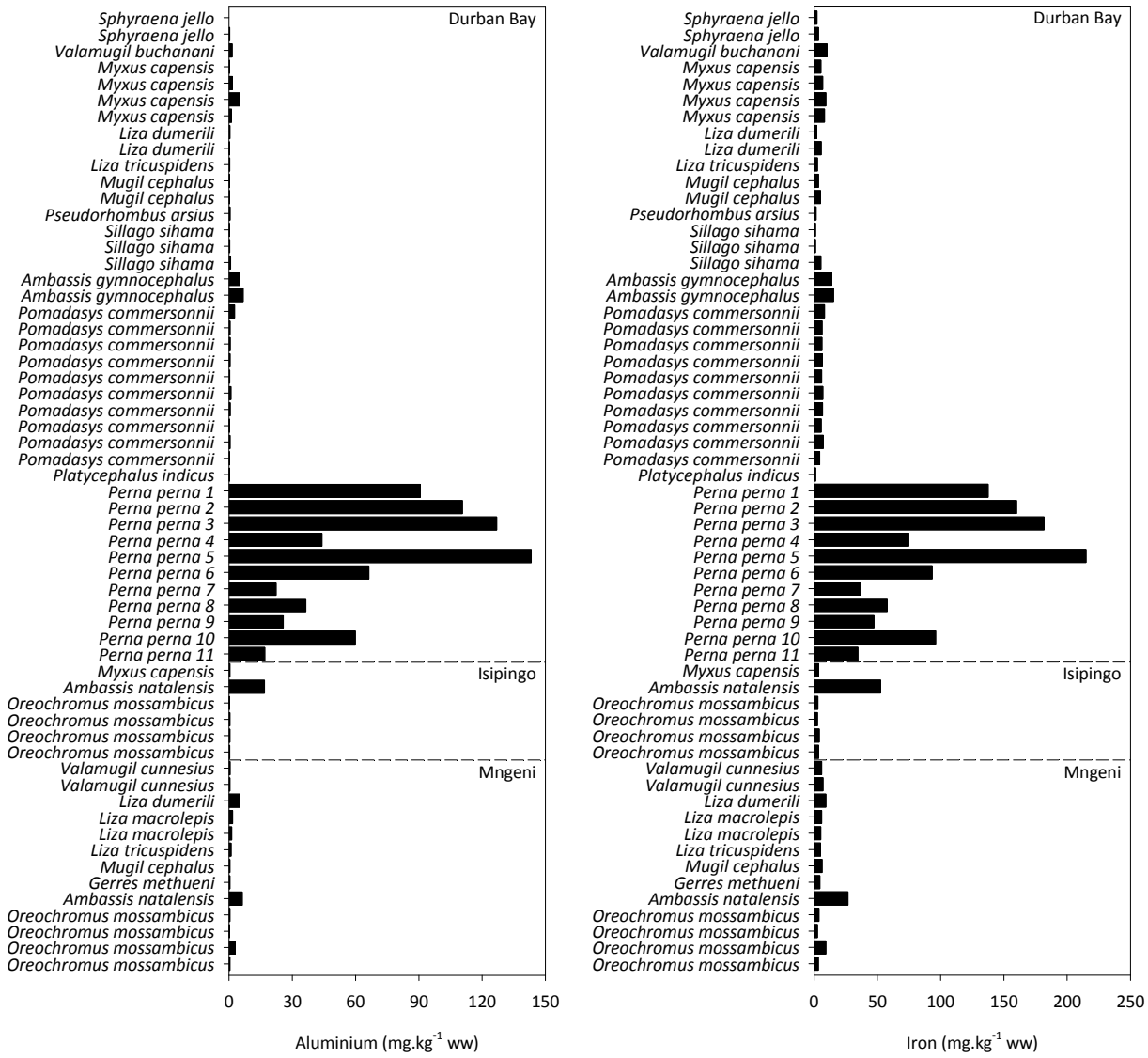

Figure 3.2. Metal concentrations in the tissue of fish caught and mussels collected in Durban Bay and the uMngeni and Isipingo River estuaries in 2013.

concentrations in both cases.

Arsenic is generally present in seafood at considerably higher concentrations compared to other foods (*e.g.* Schoof *et al.*, 1999), and seafood consequently contributes the major proportion of this metal in the human diet (*e.g.* ~90%, Adams *et al*., 1994; >80%, FSA, 2005). The inorganic arsenic concentration in fish and mussel tissue is of particular interest since many workers only analyse for total arsenic because of the technical and financial implications associated with inorganic arsenic analysis. However, inorganic arsenic is the most toxic form of arsenic and is the form used for risk assessment purposes. Inorganic arsenic is generally present in seafood at negligible concentrations and most workers consequently assume a proportion of the total arsenic concentration was of an inorganic form, based on the contribution of inorganic to total arsenic reported in the scientific literature. There is, however, no consistency in this regard, with the contribution assumed to be anywhere between about 1-10%. The approach recommended by the United States Food and Drug Administration for human health risk assessment purposes is, for example, to assume that inorganic arsenic comprises 10% of the total arsenic concentration (USFDA, 1993). In this study, the average (± standard deviation) proportion that inorganic arsenic comprised of total arsenic was 1.97% (± 1.48%) for fish (median = 1.52%) across all systems and 3.11% (± 1.36%) for mussels in Durban Bay (median = 3.23%). These proportions are within the ranges reported for other studies (*e.g.*

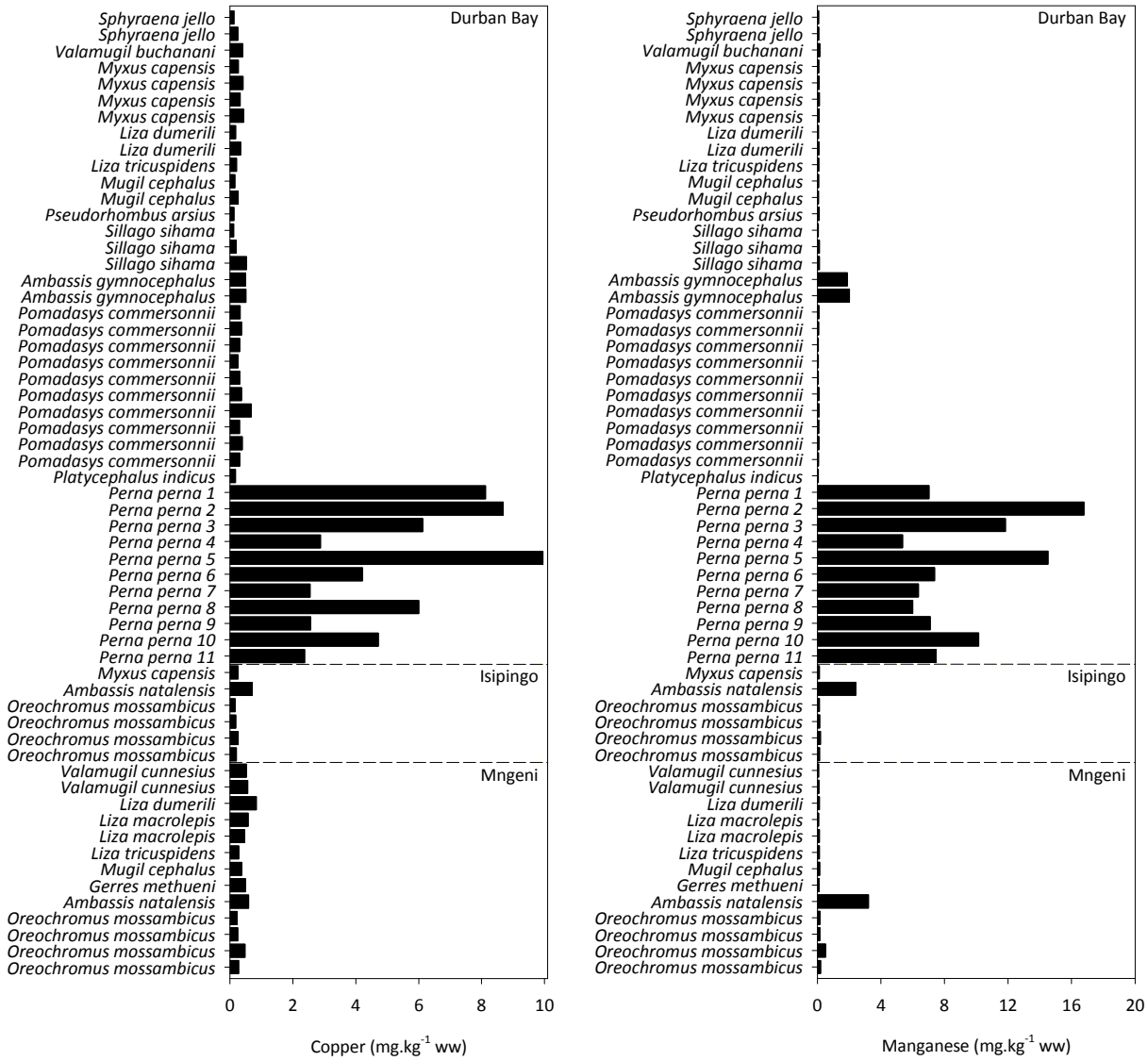

Figure 3.2 continued. Metal concentrations in the tissue of fish caught and mussels collected in Durban Bay and the uMngeni and Isipingo River estuaries in 2013.

Donohue and Abernathy, 1999; Li *et al*., 2003; see Lorenzana *et al*. (2009) for review).

As stated previously, inorganic arsenic was never detected in the tissue of fish at concentrations exceeding the method detection limit and the above statistics for fish were calculated by substituting inorganic arsenic non-detects with a concentration equivalent to one-half the method detection limit. The 'absence' of inorganic arsenic in fish caught in Durban Bay and the Mngeni and Isipingo River estuaries may reflect the fact that inorganic arsenic is found predominantly in the viscera (stomach, intestines, liver, heart and gills) of fish while the arsenic content of muscle tissue is nearly all of the form arsenobetaine (Kirby and Maher, 2002). This said, this does not account for the 'absence' of inorganic arsenic in the tissue of ambassids, as these fish were processed whole and would thus have included these organs. Total arsenic concentrations in mussels (average ± standard deviation = 1.48 ± 0.27 $mg.kg^{-1}$, median = 1.50 $mg.kg^{-1}$) were substantially higher than in fish (average ± standard deviation = 0.69 ± 1.18 $mg.kg^{-1}$, median = 0.37 $mg.kg^{-1}$), a trend that is widely reported in the scientific literature (*e.g.* Munoz *et al*., 2000; Larsen *et al.*, 2005; Sloth et al., 2005; see Lorenzana *et al*. (2009) for review). Thus, if it is assumed that 10% of the total arsenic in fish caught and mussels collected in Durban Bay and the uMngeni and Isipingo River estuaries was present as inorganic arsenic then this would, on average, have resulted in a (in some cases considerable) overestimate of the risk of exposure to inorganic arsenic through a fish and mussel consumption pathway.

Of the 15 polycyclic aromatic hydrocarbon isomers analysed, five or fewer were detected in any particular

fish species across all systems or in mussels at any location in Durban Bay. Polycyclic aromatic hydrocarbons were, on average, more frequently detected in mussels (median of four isomers) compared to fish (median of one isomer), although the highest number of isomers (five) was detected in a fish species (one composite of the mullet *Myxus capensis* caught in Durban Bay). Total polycyclic aromatic hydrocarbon concentrations were, on average, considerably higher in the tissue of mussels compared to fish, although the highest concentration was detected in a fish species (the abovementioned composite of the mullet *Myxus capensis* caught in Durban Bay) (Figure 3.3). The higher average total polycyclic aromatic hydrocarbon concentrations in mussels probably reflects the fact that finfish are able metabolise polycyclic aromatic hydrocarbons more efficiently than shellfish (Varanasi *et al*., 1989; Meador *et al*., 1995). The benefit of mussels as biomonitors of polycyclic aromatic hydrocarbons in aquatic ecosystems is not only evident in this comparison but also in the fact that in Durban Bay polycyclic aromatic hydrocarbons are very rarely detected in the water column, and when so at very low concentrations (CSIR, unpublished data). With regards to fish, total polycyclic aromatic hydrocarbon concentrations were, on average, higher in the tissue of fish caught in the uMngeni River estuary compared to Durban Bay and the Isipingo River estuary. This is interesting since total polycyclic aromatic hydrocarbon concentrations in sediment were highest in Durban Bay and comparable or slightly higher in the Isipingo River and estuary compared to the uMngeni River, its estuary and tributaries of the estuary in the 2011 and 2012 surveys (see Chapters 1 and 2).

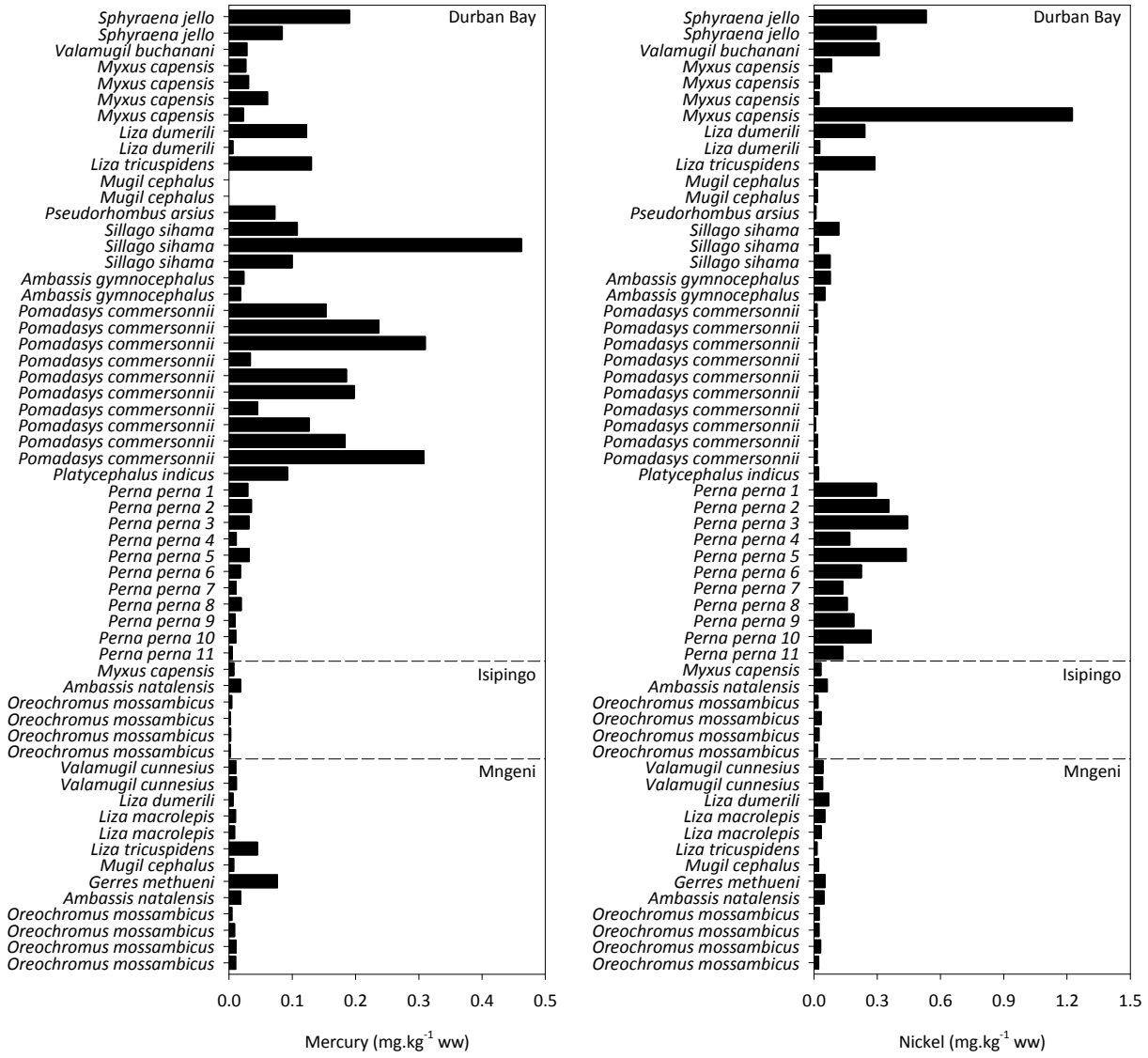

Figure 3.2 continued. Metal concentrations in the tissue of fish caught and mussels collected in Durban Bay and the uMngeni and Isipingo River estuaries in 2013.

Ratios between various isomers have been proposed as tool for diagnosing whether polycyclic aromatic hydrocarbons in fish and shellfish had a predominantly petrogenic or pyrogenic source, in a similar manner discussed for sediment in Chapters 1 and 2. Because most polycyclic aromatic hydrocarbon isomers were present at concentrations below the method detection limit in the tissue of fish caught and mussels collected in Durban Bay and the uMngeni and Isipingo River estuaries, the only ratios that could realistically be used for diagnostic purposes were between the sum of low and high molecular weight isomers and between fluoranthene and pyrene. In all fish species in each system and mussels at all locations in Durban Bay the low to high molecular weight isomer ratio far exceeded a value of one, suggesting the polycyclic aromatic hydrocarbons had a predominantly petrogenic source. The ratio between fluoranthene and pyrene could only be calculated for one fish species (one composite of the mullet *Myxus capensis* caught in Durban Bay) and mussels at nine of the eleven locations in Durban Bay. In all cases the ratio was less than one, again suggesting the polycyclic aromatic hydrocarbons had a predominantly petrogenic source. A predominantly petrogenic source for polycyclic aromatic hydrocarbons accumulated by mussels makes sense when it is considered that low molecular weight isomers, which characterise petrogenically derived hydrocarbons, are more soluble and hence more bioavailable than high molecular weight isomers, which typically partition to sediment. Furthermore, of the possible uptake routes, namely through the food chain,

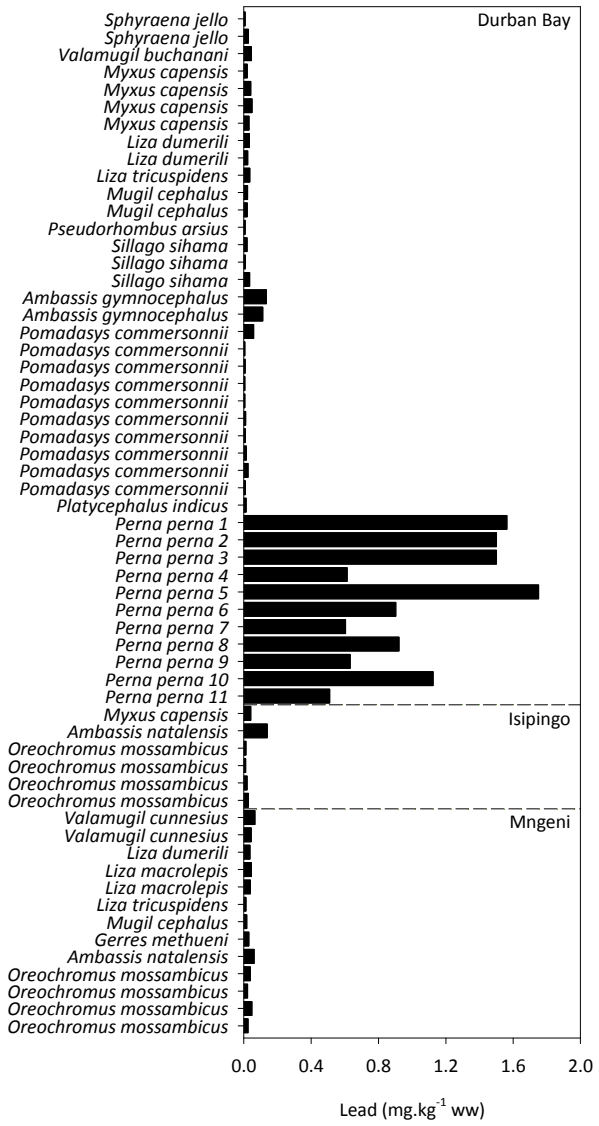

Figure 3.2 continued. Metal concentrations in the tissue of f uMngeni and Isipingo River estuaries in 2013.

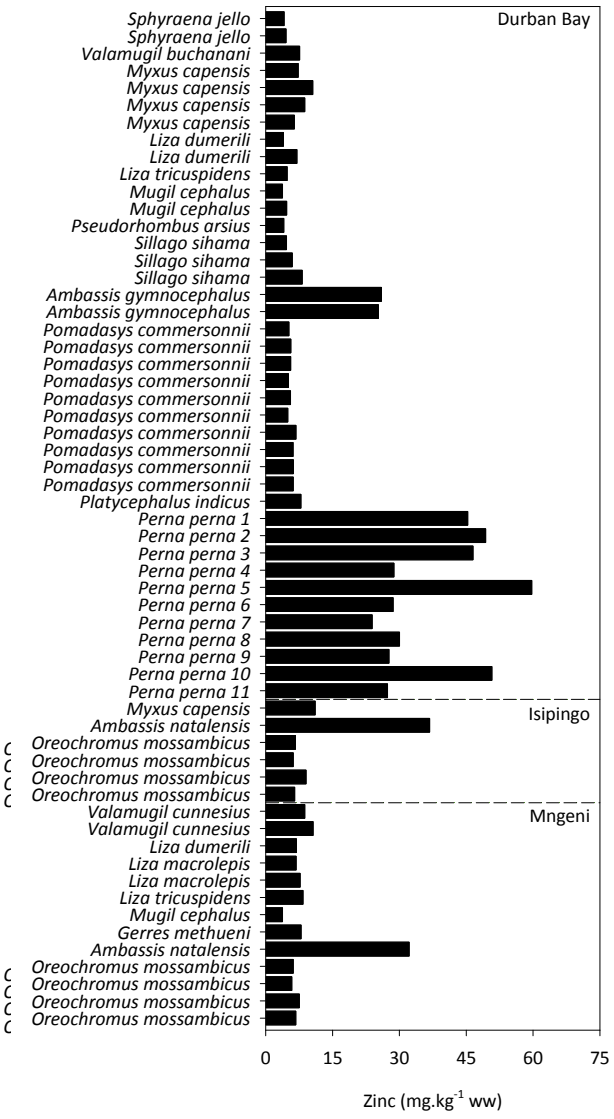

Figure 3.2 continued. Metal concentrations in the tissue of fish caught and mussels collected in Durban Bay and the uMngeni and Isipingo River estuaries in 2013.

from water, and from contaminated sediment, the waterborne route (*i.e.* uptake across the gills) is considered the dominant route (Meador *et al*., 1995). For fish that feed predominantly in the benthic environment a greater contribution of high molecular weight polycyclic aromatic hydrocarbons could theoretically be expected, but was not evident in this study. For example, the spotted grunter *Pomadasys commersonnii*, which feeds predominantly on burrowing thalanassid prawns (by 'blowing' the prawns from their burrows), could be expected to ingest polycyclic aromatic hydrocarbons adsorbed onto sediment disturbed during feeding and taken in when prawns are ingested. However, high molecular weight polycyclic aromatic hydrocarbons were present at concentrations below the method detection limit in all individuals of this fish.

Of the wide suite of organochlorine pesticides analysed, only DDT and its metabolites and dieldrin were detected in fish and mussels at concentrations exceeding the method detection limit. However, dieldrin was only detected in the tissue of a single individual of spotted grunter *Pomadasys commersonnii* caught in Durban Bay, and then at a concentration (0.014 mg.kg^{-1} dry weight) that only marginally exceeded the method detection limit (0.01 mg.kg^{-1} dry weight). In contrast to metals, DDT and its metabolites were typically present at higher concentrations in the tissue of fish compared to mussels (Figure 3.4).

This is a common trend reported in the scientific literature and is ascribed to the fact that pesticides are

lipophilic and tend thus to accumulate in fish, which generally have a higher lipid content than mussels. DDX concentrations in the tissue of fish in Durban Bay were generally considerably higher compared to fish in the uMngeni and Isipingo River estuaries. DDT and/or its metabolites were detected in ten of the eleven fish species caught and in mussels collected at seven of the eleven locations in Durban Bay. In contrast, DDX was detected in one of the three fish species caught in the Isipingo River estuary and in three of the eight fish species caught in the uMngeni River estuary (Figure 3.4). DDT is rapidly metabolised to DDD by dechlorination and more slowly to DDE by dehydrochlorination, or through DDD to DDE by hepatic microsomal enzymes in organisms (Sheridan, 1975). Technical DDT was detected in the majority of fish species and in mussels at seven of the eleven locations in Durban Bay, but in only one fish species caught in the Isipingo River estuary and in none of the fish species caught in the uMngeni River estuary. This suggests a more recent source of DDT in Durban Bay compared to the Isipingo and uMngeni River estuaries. The more frequent detection and higher concentrations of DDX in Durban Bay agrees with the results of sediment analyses discussed in Chapter 2, which showed that the highest or amongst the highest DDX concentrations in sediment were inevitably evident in the Bay, or in rivers and canals that discharge into the Bay. This was, however, not the case for the survey discussed in Chapter 1, when DDX was infrequently detected in Durban Bay and often at lower concentrations compared to the uMngeni and Isipingo Rivers and estuaries.

Polychlorinated biphenyls were detected in the tissue of mussels collected at all locations in Durban Bay and in the majority of fish caught in each system (Figure 3.5). Of the 21 congeners analysed, the highest number detected in any fish species was 11, in the ambassid *Ambassis natalensis* caught in the Isipingo River estuary, followed by nine in the mullet *Liza dumerilii* and *Liza tricuspidens* caught in Durban Bay. Total polychlorinated biphenyl concentrations in some fish species were considerably higher than in mussels, although for the bulk of the fish species concentrations were generally comparable to the range of concentrations detected in mussels (Figure 3.5). Polychlorinated biphenyl concentrations were generally more frequently detected and at higher concentrations in fish caught in Durban Bay compared to fish caught in the uMngeni and Isipingo River estuaries, albeit that the highest concentration was for the ambassid *Ambassis natalensis* caught in the Isipingo River estuary. This was closely followed by concentrations in *Ambassis gymnocephalus* caught in two areas of Durban Bay. The more frequent detection and generally higher concentrations of polychlorinated biphenyls in fish caught in Durban Bay broadly agrees with the results of sediment analyses discussed in Chapters 1 and 2, which showed that the highest or amongst the highest polychlorinated biphenyl concentrations were inevitably evident in sediment in the Bay or in rivers and canals that discharge riverine and surface runoff into the Bay.

Although the trend for polycyclic aromatic hydrocarbon, polychlorinated biphenyl and metal contamination of sediment in the catchments of Durban Bay and the uMngeni and Isipingo River estuaries generally reflected trends for these chemicals in fish and mussel tissue, there was a difference between pesticide contamination of sediment and accumulation by fish and mussels. Thus, chlordanes, which were fairly frequently detected in sediment in the survey discussed in Chapter 2 and less frequently in the survey discussed in Chapter 1, were never detected in the tissue of fish and mussels. Dieldrin was detected in one fish species but never in sediment, although as mentioned above the concentration detected in the single fish specimen was very low. Endosulfans, which were detected in sediment at one station, were never detected in fish or mussels.

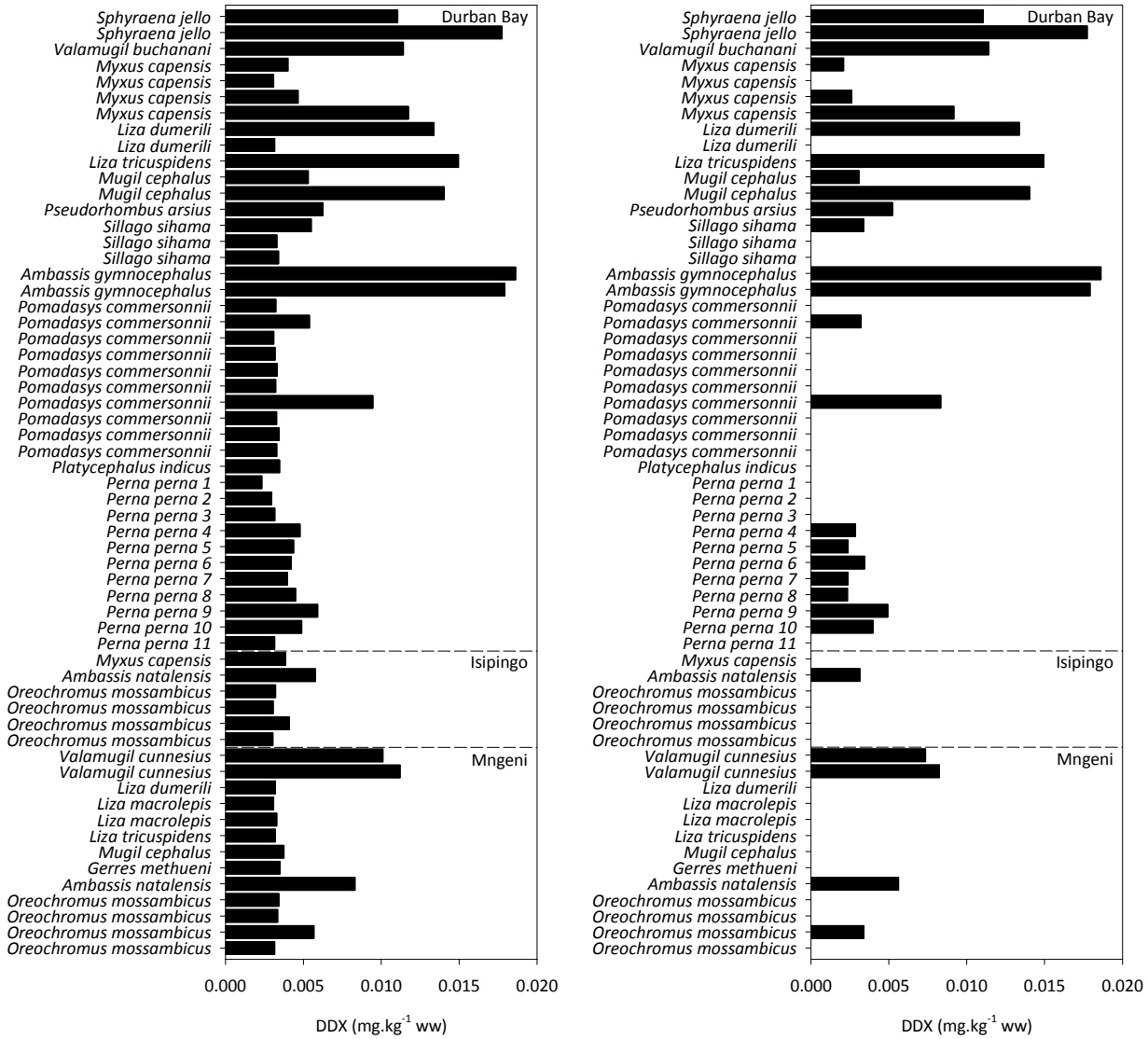

Figure 3.4. DDX concentrations in the tissue of fish caught and mussels collected in Durban Bay and the uMngeni and Isipingo River estuaries in 2013. The graph on the left represents the total concentration calculated with non-detects replaced with a value of one-half the method detection limit and on the right with non-detects replaced with a value of zero.

The higher concentrations of DDX, polychlorinated biphenyls, the majority of metals, and to a lesser degree polycyclic aromatic hydrocarbons in the tissue of the ambassids *Ambassis gymnocephalus* and *Ambassis natalensis* compared to other fish species (Figures 3.2-3.5) suggests the ambassids might be useful sentinels for contaminant monitoring in estuaries, particularly when it is considered they are abundant, far easier to catch compared to other fish, and are likely to spend their entire life in a single estuary.

They may also have relatively small home ranges, which may make them useful for identifying spatial trends in contamination in relatively large estuaries and estuarine embayments, such as Durban Bay. Although certain other fish species sampled are also likely to spend a major portion of, or their entire life in estuaries (*e.g.* mullet), they are likely to have considerably wider home ranges than the ambassids, while other fish species, including the barracuda *Sphyraena jello* and the spotted grunter *Pomadasys commersonnii*, are known to spend only part of their life in estuaries and in the case of *Pomadasys commersonnii* to also move between estuaries (*e.g.* Webb, 2002). The high concentration of many chemicals in the tissue of ambassids was unexpected because contaminant concentrations in fish generally increase with size, age and trophic position. Thus, large, long-lived predatory fish usually accumulate contaminants to higher concentrations in their tissue compared to small, short-lived fish, although

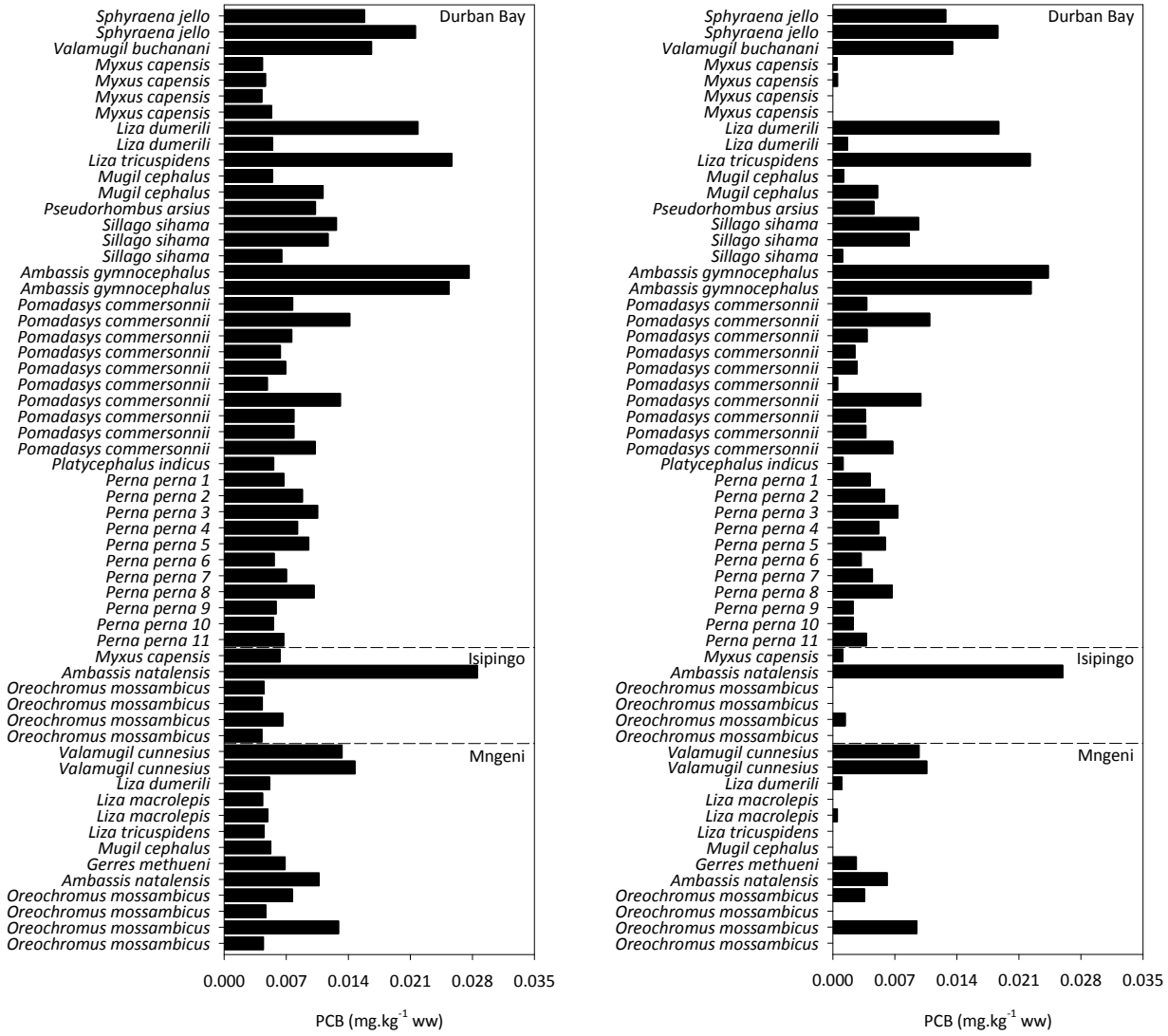

Figure 3.5. Total polychlorinated biphenyl (PCB) concentrations in the tissue of fish caught and mussels collected in Durban Bay and the uMngeni and Isipingo River estuaries in 2013. The graph on the left represents the total concentration calculated with non-detects replaced with a value of one-half the method detection limit and on the right with non-detects replaced with a value of zero.

accumulation of chlorinated contaminants is also strongly influenced by lipid content. In the context of this study the highest trophic level fish caught was the barracuda *Sphyraena jello*. While the two sub-adult individuals of this species caught in Durban Bay had amongst the highest concentrations of DDX and polychlorinated biphenyls in their tissue, the concentrations were nevertheless lower or comparable to concentrations in *Ambassis gymnocephalus* caught at two locations in the Bay. As mentioned previously, ambassids are small (<10 cm total length) shoaling fish. They feed on plankton and other small organisms in the water column and thus occupy a low trophic position. Fish of this type are often referred to as forage or bait fish because they are preyed on by a variety of piscivorous fish and birds. The high concentrations of chemicals in the tissue of ambassids thus also highlight the potentially significant role these fish may play in the transfer of contaminants through the food web, including to avian predators. Other workers have reported as high or higher concentrations of contaminants in the tissue of forage fish compared to larger fish, including mercury (*e.g.* Yeardley, 2000; Suchanek *et al*., 2008; Greenfield and Jahn, 2010) and polychlorinated biphenyls (*e.g.* Greenfield and Allen, 2013). Greenfield and Allen (2013) reported a strong correlation between polychlorinated biphenyl concentrations in the tissue of forage fish and in sediment in San Francisco Bay, and spatial variation in concentrations that was more pronounced than for large fish. Greenfield and Allen (2013) suggested that uptake was associated with polychlorinated biphenyl contamination of sediment within the relatively small home ranges of these fish. Caution should, however,

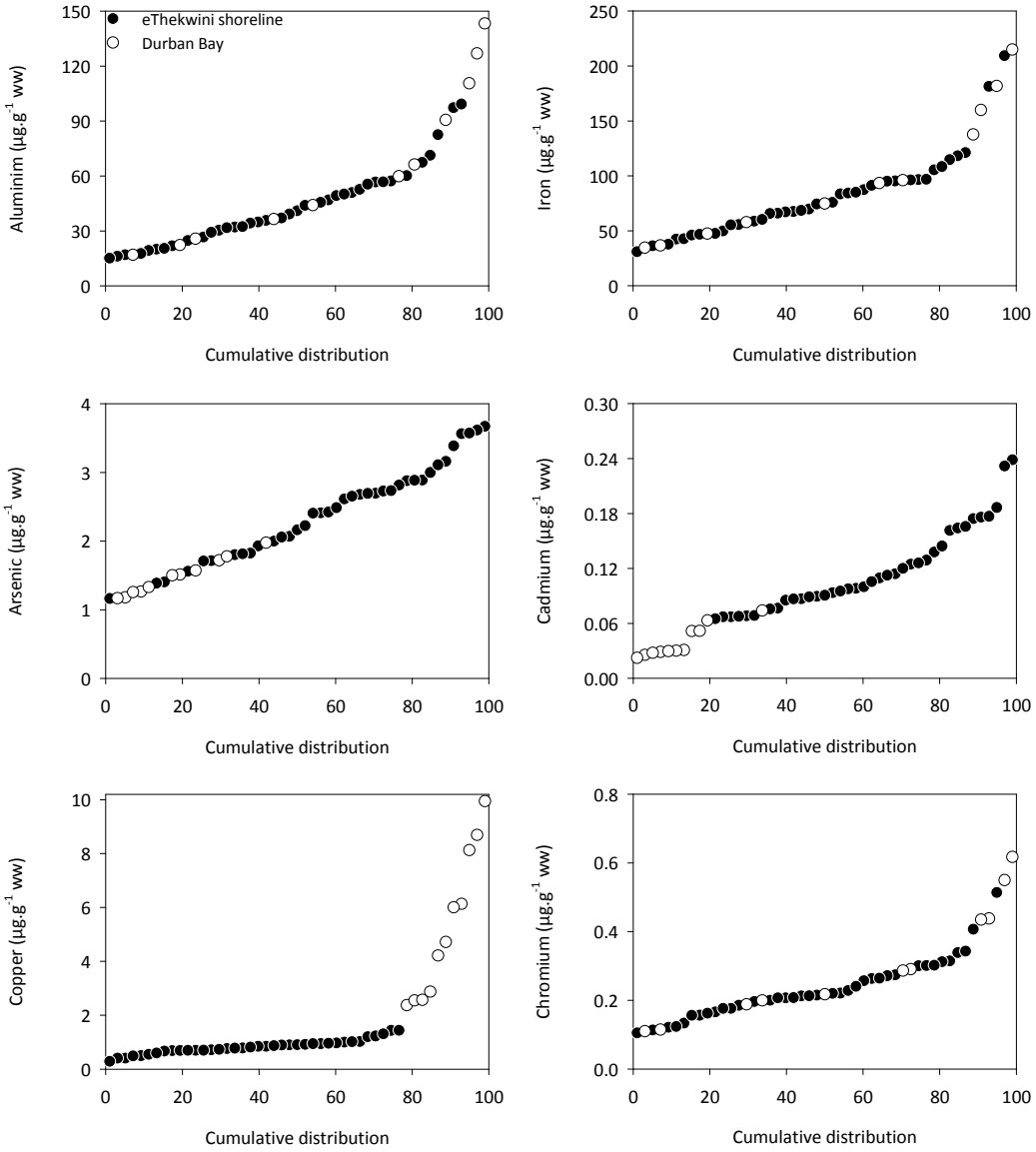

Figure 3.6. Comparison of metal concentrations in the tissue of mussels collected in Durban Bay in 2013 to concentrations in the tissue of mussels collected along the eThekwini shoreline in July and December 2013.

be exercised when directly comparing chemical concentrations in the tissue of ambassids to other fish since only muscle tissue was analysed in other fish while the entire body was analysed for ambassids. Tissues such as the liver, where some chemicals are known to accumulate to significantly higher concentrations than in muscle tissue (*e.g.* Dural *et al*., 2006; Agusa *et al*., 2007; Lavandier *et al*., 2013; Bodin *et al*., 2014), were thus analysed for ambassids but not for other fish. Because of the small sample size for ambassids in each estuarine system further research is required to determine the usefulness of these fish as sentinels for contaminant monitoring. This should include a comparison of chemical concentrations in the tissue of these fish from 'clean' and putatively contaminated systems, to clarify whether these fish naturally accumulate higher concentrations of metals in their tissue compared to other fish.

To place the concentrations of metal and organic chemical concentrations in the tissue of fish caught and mussels collected in Durban Bay and the uMngeni and Isipingo River estuaries into context these are compared to concentrations reported in fish caught and mussels collected in coastal areas in South Africa and in other parts of the world. Figure 3.6 compares metal concentrations in the tissue of mussels collected in Durban Bay to concentrations in mussels collected at 19 locations along the eThekwini shoreline of KwaZulu-Natal in July and December of 2013 for the eThekwini Mussel Watch programme. The eThekwini Mussel Watch programme collection locations encompassed sites within the limits of the city of Durban

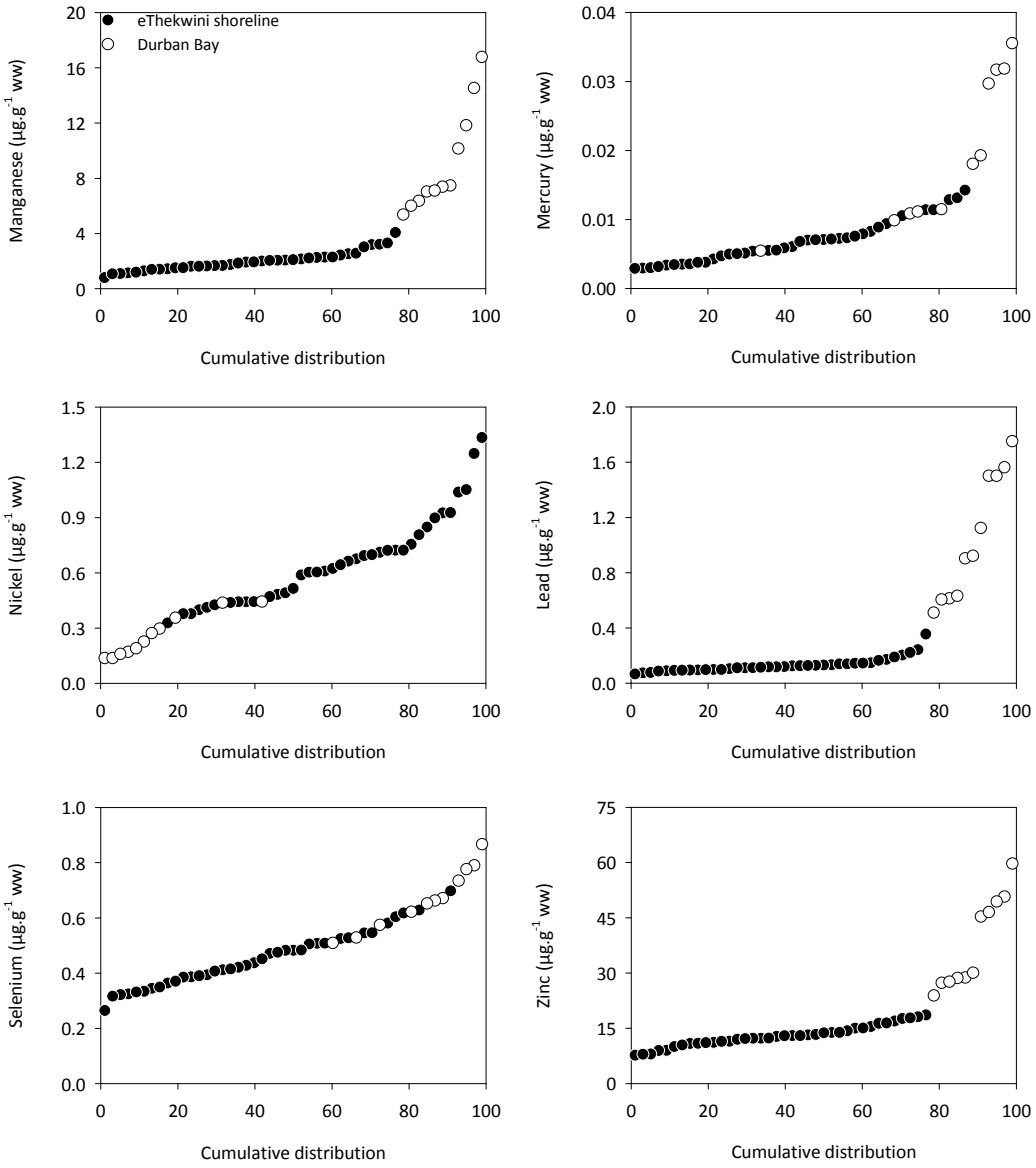

Figure 3.6 continued. Comparison of metal concentrations in the tissue of mussels collected in Durban Bay in 2013 to concentrations in the tissue of mussels collected along the eThekwini shoreline in July and December 2013.

and in relatively rural and lightly urbanised areas to the north and south of the city. Direct comparison of the data is confounded by the fact that mussels were, on average, slightly larger in Durban Bay. There was also variability in mussel size between locations within Durban Bay and along the eThekwini shoreline. Nevertheless, it is apparent that mussels in Durban Bay had higher concentrations of several metals in their tissue compared to mussels collected along the eThekwini shoreline (Figure 3.6). The most pronounced differences were for iron, copper, lead, manganese, mercury and zinc.

The outward implication is that mussels at some to all collection locations in Durban Bay had accumulated these metals to anomalously high concentrations in their tissue. However, it is not entirely certain whether the accumulation was due to a difference in natural availability of metals between Durban Bay and the nearshore marine environment along the eThekwini shoreline, since there is anecdotal evidence that the concentrations of copper, lead and zinc in sediment in Durban Bay (and by implication the catchment for the Bay) are naturally higher compared to the sediment in the nearshore environment off the eThekwini area. This said, sharp inflections and gaps in the cumulative distribution plots for most of the latter metals suggests strongly that the higher concentrations in the tissue of mussels collected in Durban Bay was a consequence of their exposure to metal contaminated water and food. Arsenic, inorganic arsenic, cadmium and nickel concentrations in the tissue of mussels collected along the eThekwini shoreline were, in contrast generally, higher than concentrations in the tissue of mussels collected in Durban Bay (Figure 3.6). This

should not be taken as indicating that mussels along the eThekwini shoreline accumulated these metals to higher concentrations in their tissue due to exposure to contaminated water and food since there is no evidence the latter metals are contaminants of the water column in the nearshore marine environment along the eThekwini shoreline. There were also no particularly marked inflections and gaps in the cumulative concentration distribution plots for these metals. This may thus reflect a natural difference in the availability of these metals due to factors such as local geology.

Polycyclic aromatic hydrocarbon concentrations in the tissue of mussels collected in Durban Bay were generally higher than in mussels collected along the eThekwini shoreline, albeit that the second highest concentration was detected in mussels collected at a shoreline station (Figure 3.7). DDX was only detected in mussels collected in Durban Bay (Figure 3.8). No other organochlorine pesticides were detected in mussels collected in Durban Bay, nor in mussels collected along the eThekwini shoreline. Polychlorinated biphenyls were only detected in mussels collected at two locations along the eThekwini shoreline in June 2013, but at very low concentrations (0.31 and 0.85 $ng.g^{-1}$ wet weight), represented by one and two congeners respectively. Polychlorinated biphenyl concentrations in mussels collected in Durban Bay were thus considerably higher than in mussels collected along the eThekwini shoreline (Figure 3.9).

There is thus little doubt mussels collected in Durban Bay had accumulated polycyclic aromatic hydrocarbons, DDX and polychlorinated biphenyls in their tissue to higher concentrations than mussels collected along the eThekwini shoreline due to their more frequent and prolonged exposure to these chemicals in food and water. The lower concentrations of polycyclic aromatic hydrocarbons, DDX and polychlorinated biphenyls in mussels collected along the eThekwini shoreline is not surprising considering this is a high energy coastline (*i.e.* characterised by strong currents and large waves), and contaminants introduced into this environment from point and non-point sources (e.g. rivers, stormwater outfalls) are thus likely to be rapidly diluted and dispersed.

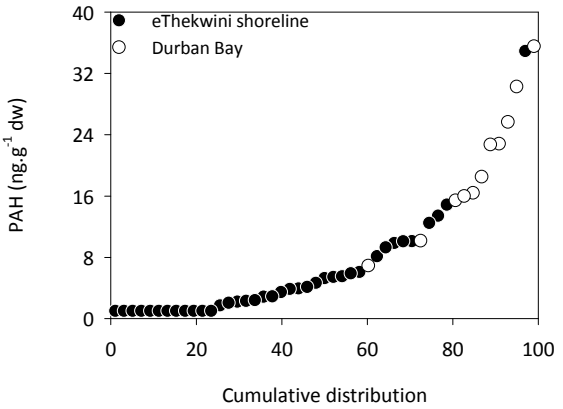

Figure 3.7. Comparison of total polycyclic aromatic hydrocarbon (PAH) concentrations in the tissue of mussels collected in Durban Bay in 2013 to concentrations in the tissue of mussels collected along the eThekwini shoreline in July and December 2013.

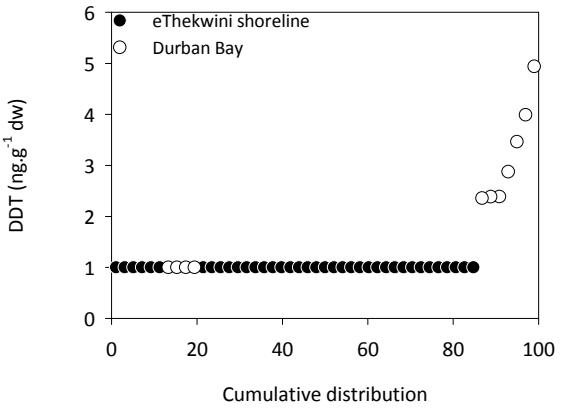

Figure 3.8. Comparison of DDX concentrations in the tissue of mussels collected in Durban Bay in 2013 to concentrations in the tissue of mussels collected along the eThekwini shoreline in July and December 2013.

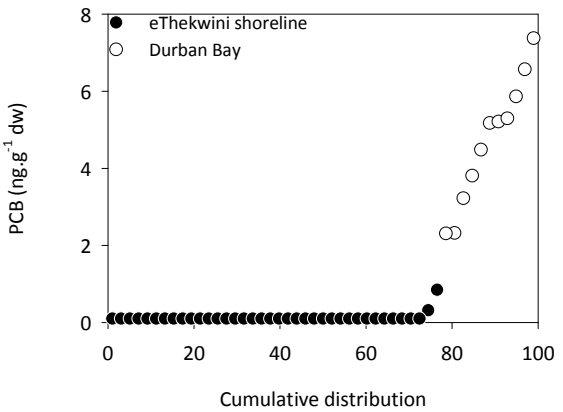

Figure 3.9. Comparison of total polychlorinated biphenyl (PCB) concentrations in the tissue of mussels collected in Durban Bay in 2013 to concentrations in the tissue of mussels collected along the eThekwini shoreline in July and December 2013.

Figures 3.10-3.13 compare concentrations of metals and organic chemicals in the tissue of mussels

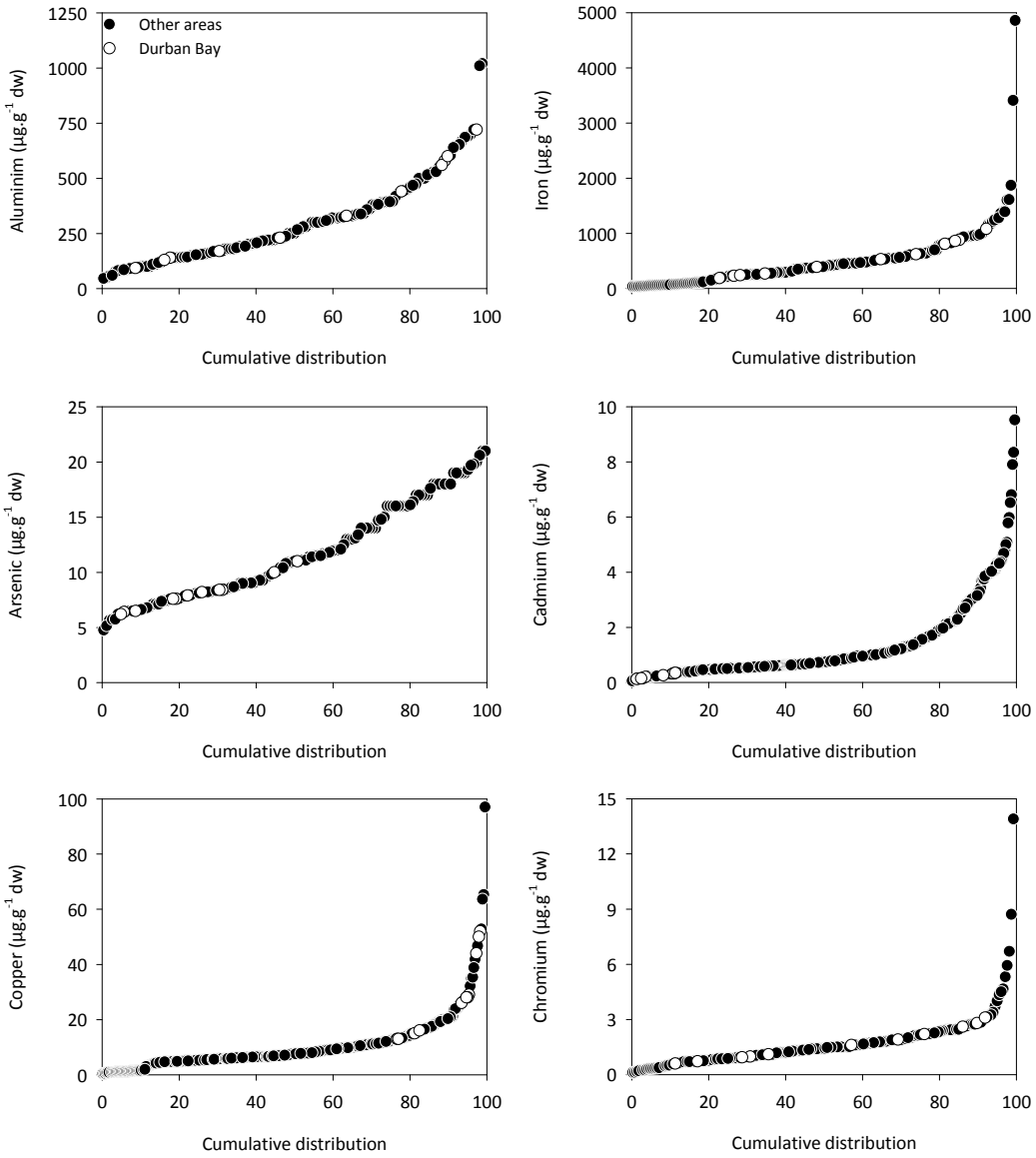

Figure 3.10. Comparison of metal concentrations in the tissue of mussels collected in Durban Bay in 2013 to concentrations in the tissue of mussels in other parts of the world (data from Besada *et al*., 2002; Corsi *et al*., 2002; Yap *et al*., 2003; Belabed *et al*., 2013; USEPA Musselwatch, 2012; *Bellas et al.*, 2014).

collected in Durban Bay to mussels of various genera, including *Perna perna*, collected in other parts of South Africa and the world. Concentrations of arsenic, cadmium and nickel in mussels collected at many to most locations in Durban Bay are within the mid to lower end of range of concentrations for mussels in other parts of the world. In contrast, concentrations of copper, lead, manganese, selenium and zinc in mussels at some to most locations are nearer the upper end of the range of concentrations for mussels in other parts of the world (Figure 3.10). The concentrations of polycyclic aromatic hydrocarbons (Figure 3.11) and polychlorinated biphenyls (Figure 3.12) are within the mid-range of concentrations for mussels in other parts of the world, while DDX concentrations (Figure 3.13) in mussels at many locations are nearer the upper end of the range for mussels in other parts of the world.

There is little data on concentrations of chemicals analysed in fish for this study in fish from South African coastal waters apart from historic studies on metals (*e.g*. Connell *et al*., 1975; Oliff and Turner, 1976) and a study on chlorinated compounds in fish collected in the Isipingo River estuary (Grobler *et al*., 1996). It is difficult making comparisons to these studies and to studies in other parts of the world since the same species were usually not investigated. Figures 3.14-3.17 compare metal and organic chemical concentrations in the tissue of fish caught in Durban Bay and the uMngeni and Isipingo River estuaries to

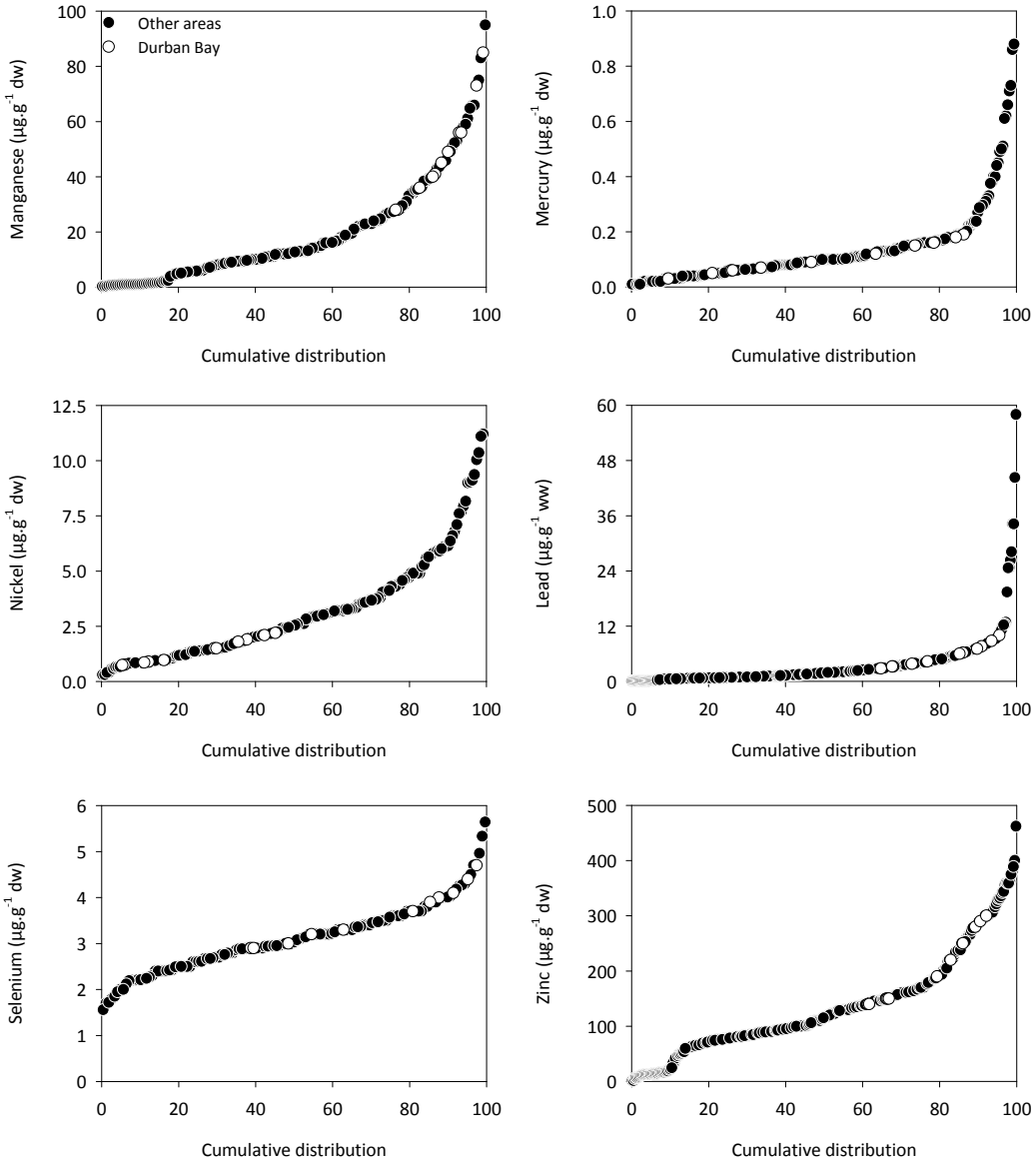

Figure 3.10 continued. Comparison of metal concentrations in the tissue of mussels collected in Durban Bay in 2013 to concentrations in the tissue of mussels in other parts of the world (data from Besada *et al*., 2002; Corsi *et al*., 2002; Yap *et al*., 2003; Belabed *et al*., 2013; USEPA Musselwatch, 2012; *Bellas et al.*, 2014).

concentrations in a range of fish species in other parts of the world. As is evident, fish in Durban Bay and the uMngeni and Isipingo River estuaries had amongst the highest concentrations of some metals in their tissue, including arsenic in *Sillago sihama* caught at two locations in Durban Bay, cadmium in *Ambassis gymnocephalus* caught at two locations in Durban Bay, selenium in *Myxus capensis* caught in the uMngeni River estuary, and zinc in *Ambassis gymnocephalus* caught at two locations in Durban Bay and *Ambassis natalensis* caught in the uMngeni and Isipingo River estuaries.

Polycyclic aromatic hydrocarbon concentrations in fish caught in Durban Bay and the uMngeni and Isipingo River estuaries are in the mid to upper end, and DDX and polychlorinated biphenyl concentrations in the mid to lower end of the range of concentrations for fish in other parts of the world (Figures 3.14-3.17).
Although the comparator data included polycyclic aromatic hydrocarbon and polychlorinated biphenyl concentrations calculated from varying numbers of isomers and congeners respectively, the distribution does not change significantly if concentrations were compared to studies that analysed comparable numbers of polycyclic aromatic hydrocarbon isomers and polychlorinated biphenyl congeners to those analysed in this study.

4.4.2 Risk assessment

It is necessary to reiterate that certain of the fish species included in this risk assessment are seemingly rarely or never consumed by recreational and subsistence fishers (see Table 3.2). These include the ambassids *Ambassis gymnocephalus* and *Ambassis natalensis*, silver sillago *Sillago sihama*, pursemouth *Gerres methueni*, and largetooth flounder *Pseudorhombus arsius* (or at least the size class of the latter fish species analysed for this study). As stated previously, these fish species were nevertheless included in the risk assessment as it places chemical concentrations in their tissue into perspective with the more commonly consumed species and with mussels.

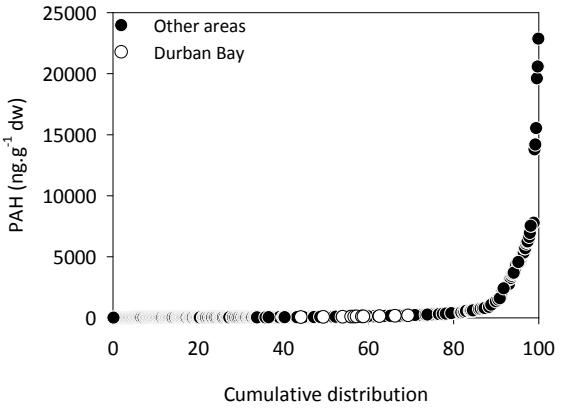

Figure 3.11. Comparison of total polycyclic aromatic hydrocarbon (PAH) concentrations in the tissue of mussels collected in Durban Bay in 2013 to concentrations in the tissue of mussels in other areas of the world (data from Baumard *et al*., 1998a,b; Wei *et al*., 2006; Francioni *et al*., 2007; Isobe *et al*., 2007; León, 2007; Fang *et al*., 2009; Choi *et al*., 2010; USA Musselwatch, 2012; Yoshimine *et al*., 2012).

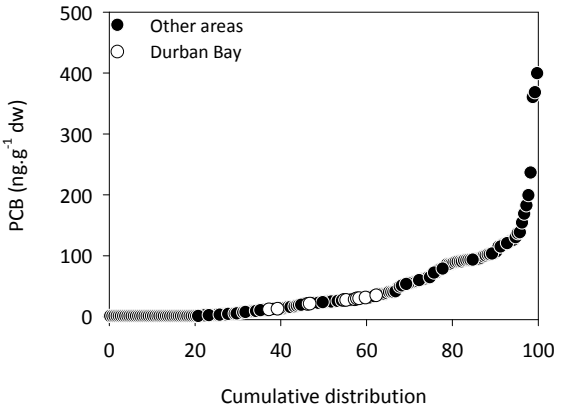

Figure 3.12. Comparison of total polychlorinated biphenyl (PCB) concentrations in the tissue of mussels collected in Durban Bay in 2013 to concentrations in the tissue of mussels in other areas of the world (data from Wei *et al*., 2006; Fang *et al*., 2009; Kozůl *et al*., 2009; Choi *et al*., 2010; USA Musselwatch, 2012).

Hazard Quotients and Hazard Indices for recreational and subsistence fishers are provided in Table 3.3. Hazard Quotients and Hazard Indices for mussels at all locations in Durban Bay, fish in all systems, and collectively for all frequently consumed fish (*i.e.* excluding the species listed above) were less than one for recreational consumers under Scenario 1. Thus, recreational fishers that consume 17.5 g of fish or mussel tissue per day, which is equivalent to a little over two meals of 227 g per month, are unlikely to face chronic health risks due to chemical exposure through a fish and mussel consumption pathway.

For recreational fishers under Scenario 2, Hazard Quotients did not exceed a value of one for any fish species in any system or mussels at any location in Durban Bay apart from mercury in *Sillago sihama* and *Pomadasys commersonnii* in Durban Bay (Table 3.3). The Hazard Quotients for these fish had values of 1.51 and 1.21 respectively, that is, relatively low values. Hazard indices for *Sphyraena jello*, *Liza dumerilii, Liza tricuspidens*, *Sillago sihama*, *Ambassis gymnocephalus*, *Pomadasys commersonnii* and mussels at two locations in Durban Bay, and for *Ambassis natalensis* in the Isipingo River estuary exceeded a value of one if non-detects were replaced with a value equivalent to one half the method detection limit. The highest Hazard Index was 1.98. If non-detects were replaced with a value equivalent to zero then Hazard Indices for five of the above fish species in Durban Bay, for mussels at one location in Durban bay, and for one fish species in the Isipingo River estuary still exceeded a value of one, with the highest index value of 1.84 (Table 3.3). Hazard Indices for all frequently consumed fish collectively exceeded a value of one for Durban Bay only if non-detects were replaced with a value equivalent to one half the method detection limit, but the index value was only 1.12. The chemicals that contributed most to Hazard Indices exceeding a value of one for the majority of fish species were polychlorinated biphenyls, but with mercury important for *Sphyraena jello*, *Liza tricuspidens*, *Sillago sihama* and *Pomadasys commersonnii*. For mussels at two locations in Durban Bay numerous chemicals contributed roughly equivalently to the exceedance.

Thus, recreational fishers that consume 45.4 g per day, or about six 227 g meals per month, of mussels collected at one location in Durban Bay, the latter mentioned fish species caught in Durban Bay and the Isipingo River estuary, or a mixed diet of commonly consumed fish face possible chronic health risks due to exposure to chemicals accumulated by these organisms. It is important to consider that the Hazard Indices were the sum of Hazard Quotients for all chemicals, regardless of the target organ or tissue affected by the chemicals. Furthermore, Hazard Quotients and Hazard Indices for numerous fish species and for mussels were relatively low.

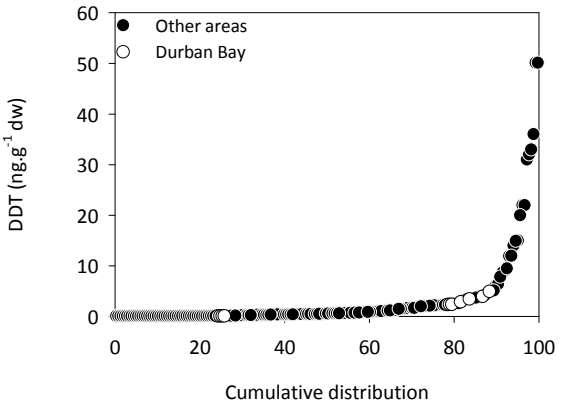

Figure 3.13. Comparison of DDX concentrations in the tissue of mussels collected in Durban Bay in 2013 to concentrations in the tissue of mussels in other areas of the world (data from Tanabe *et al*., 2000; McIntosh *et al*., 2003; Bayen *et al*., 2004; Bellas *et al*., 2014).

The situation was different for subsistence consumers since Hazard Quotients for mercury in seven fish species in Durban Bay and one fish species in the uMngeni River estuary, for polychlorinated biphenyls in seven fish species and mussels at three locations in Durban Bay, for one fish species in the Isipingo River estuary, and for two fish species in the uMngeni River estuary exceeded a value of one if non-detects were replaced with a value equivalent to one half the detection limit (Table 3.3). If polychlorinated biphenyl non-detects were replaced with a value of zero then Hazard Quotients for five fish species in Durban Bay and one fish species in each of the uMngeni and Isipingo River estuaries still exceeded a value of one. Hazard Indices exceeded a value of one for mussels at all locations in Durban Bay and for fish in all systems apart from the tilapia *Oreochromus mossambicus* in the Isipingo River estuary and the mullet *Liza macrolepis* in the uMngeni River estuary if non-detects were replaced with a value equivalent to one-half the method detection limit. The Highest Hazard Index was 6.21 for the silver sillago *Sillago sihama*, followed by 5.94 for the mullet *Liza tricuspidens*, 5.27 for the barracuda *Sphyraena jello*, and 4.99 for the spotted grunter *Pomadasys commersonnii*, all caught in Durban Bay.

If non-detects were replaced with a value of zero then the Hazard Indices were lower, but only fell below a value of one for one fish species in Durban Bay, one fish species in the Isipingo River estuary and two fish species in the uMngeni River estuary. Hazard Indices were still highest for *Sillago sihama*, *Liza tricuspidens*, *Sphyraena jello* and *Pomadasys commersonnii*, caught in Durban Bay, with values of 5.76, 5.54, 4.91 and 4.53 respectively. Hazard Indices for fish in Durban Bay were generally considerably higher than for fish in the uMngeni and Isipingo River estuaries. Hazard Indices for all frequently consumed fish collectively exceeded a value of one for Durban Bay and uMngeni and Isipingo River estuaries, although for the uMngeni and Isipingo River estuaries only if non-detects were replaced with a value equivalent to one half the method detection.

Thus, subsistence fishers that consume 142.4 g per day, which is equivalent to about nineteen 227 g meals per month, of mussels collected at all locations and most fish species caught in Durban Bay and the uMngeni and Isipingo River estuaries, or for all frequently consumed fish collectively, face a higher likelihood of chronic health effects compared to recreational consumers due to exposure to chemicals accumulated by these organisms. As was the case for recreational consumers, the chemicals of most concern in this context are mercury and polychlorinated biphenyls.

Excess Cancer Risks for recreational and subsistence fishers are provided in Table 3.4. The Excess Cancer Risk for recreational fishers under Scenario 1 equalled or exceeded 1×10^{-5} for (inorganic) arsenic in mussels at eight of the eleven collection locations in Durban Bay, for polycyclic aromatic hydrocarbons in

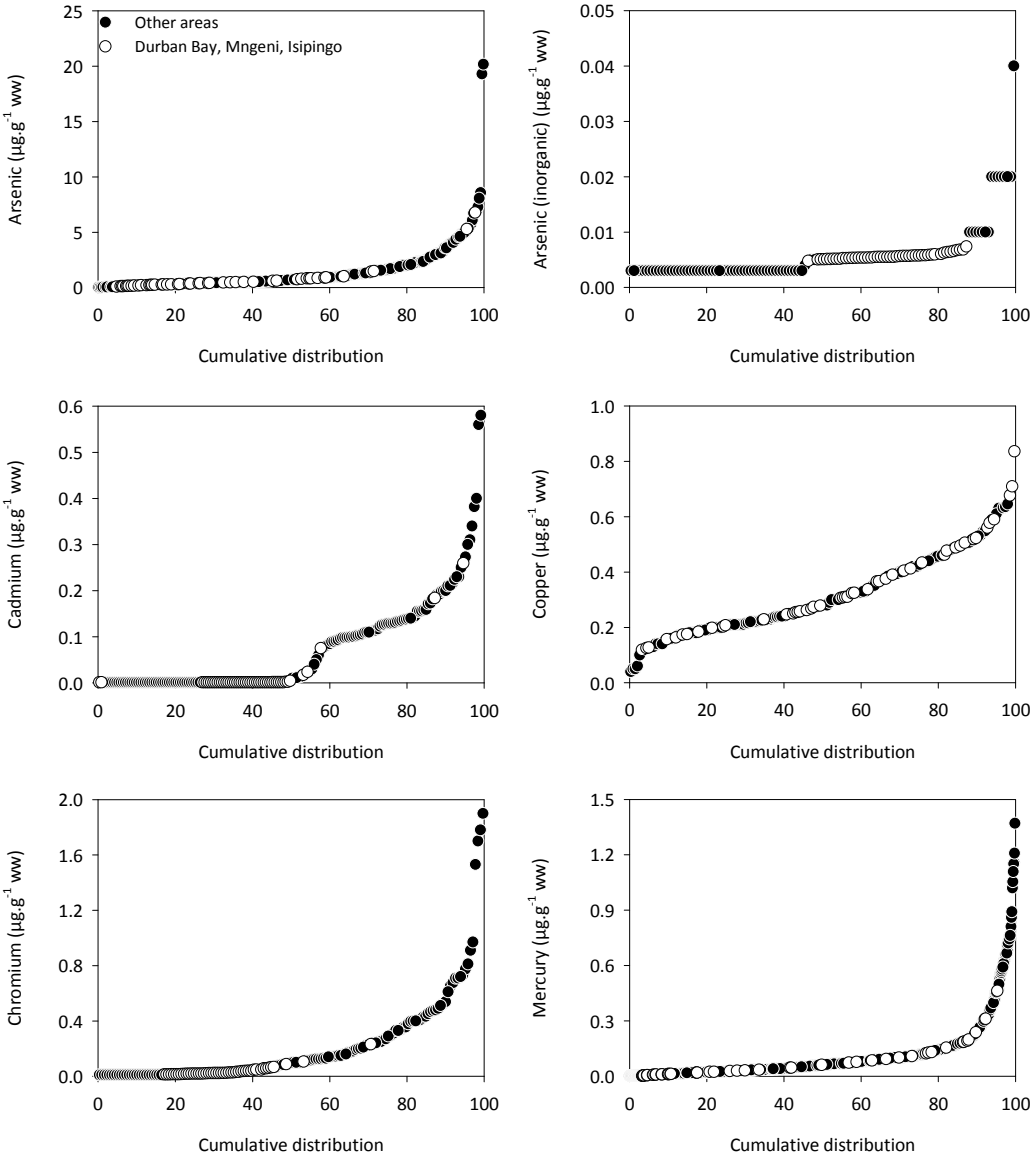

Figure 3.14. Comparison of metal concentrations in the tissue of fish caught in Durban Bay and the uMngeni and Isipingo River estuaries in 2013 to concentrations in the tissue of fish in other areas of the world (data from NOAA, 2000; Allen *et al*., 2004; NYC, 2004; UKFSA, 2005; Azmat and Tala, 2006; Denton *et al*., 2006; EPAV, 2007; Snyder and Rao, 2008; Tepe, 2008; Karouna-Renier, 2011; Stunz and Robillard, 2011; Pheiffer *et al*., 2014).

the mullet *Mugil cephalus* in Durban Bay, and for polychlorinated biphenyls in the mullet *Liza tricuspidens* and the ambassid *Ambassis gymnocephalus* in Durban Bay and the ambassid *Ambassis natalensis* in the Isipingo River estuary. Apart from polycyclic aromatic hydrocarbons in the mullet *Mugil cephalus* in Durban Bay, the Excess Cancer Risk exceeded 1×10^{-5} regardless of whether non-detects were replaced with a value equivalent to one-half the method detection limit or zero. The highest Excess Cancer Risk was for arsenic in mussels at one location in Durban Bay, at 3.1×10^{-5}, that is, the possibility of three extra incidences of cancer per 100 000 population. The Total Cancer Risk exceeded 1×10^{-5} for all fish species in all systems and mussels at all collection locations in Durban Bay if non-detects were replaced with a value equivalent to one-half the method detection limit. If non-detects were replaced with a value of zero then the Total Cancer Risk for all but one fish species in the Isipingo River estuary and for all fish species in the uMngeni River estuary were below 1×10^{-5}, but exceeded 1×10^{-5} for two fish species and mussels at ten collection locations in Durban Bay. Total Cancer Risks for all frequently consumed fish collectively exceeded 1×10^{-5} for each system, although only if non-detects were replaced with a value equivalent to one half the method detection. No Excess Cancer Risks or Total Cancer Risks exceeded 1×10^{-4}.

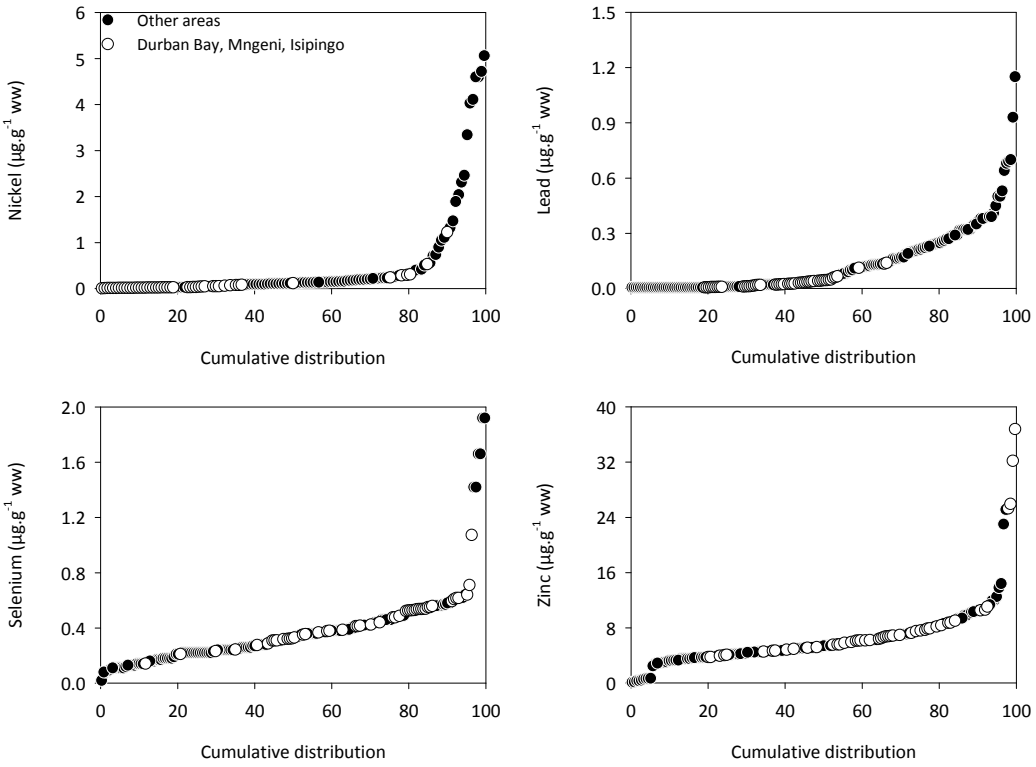

Figure 3.14 continued. Comparison of metal concentrations in the tissue of fish caught in Durban Bay and the uMngeni and Isipingo River estuaries in 2013 to concentrations in the tissue of fish in other areas of the world (data from NOAA, 2000; Allen *et al*., 2004; NYC, 2004; UKFSA, 2005; Azmat and Tala, 2006; Denton *et al*., 2006; EPAV, 2007; Snyder and Rao, 2008; Tepe, 2008; Karouna-Renier, 2011; Stunz and Robillard, 2011; Pheiffer *et al*., 2014).

The Excess Cancer Risk for recreational consumers under Scenario 2 exceeded 1×10^{-5} for (inorganic) arsenic in mussels at all collection locations in Durban Bay, but not for any fish species. If non-detects for polycyclic aromatic hydrocarbons were replaced with a value equivalent to one-half the method detection limit then the Excess Cancer Risk exceeded 1×10^{-5} for mussels at all collection locations in Durban Bay and for all fish species in all systems. In contrast, the Excess Cancer Risk for only one fish species, namely the mullet *Mugil cephalus* caught in Durban Bay, exceeded 1×10^{-5} if non-detects were replaced with a value of zero. None of the Excess Cancer Risks for arsenic and polycyclic aromatic hydrocarbons exceeded 1×10^{-4}. If polychlorinated biphenyl non-detects were replaced with a value equivalent to one-half the method detection limit then mussels at five locations and all but two of fish species caught in Durban Bay, and one fish species in the Isipingo River estuary and three fish species in uMngeni River estuary provided Excess Cancer Risks exceeding 1×10^{-5}. If polychlorinated biphenyl non-detects were replaced with a value of zero then five fish species in Durban Bay and one fish species in each of the uMngeni and Isipingo River estuaries provided Excess Cancer Risks exceeding 1×10^{-5}. The highest Excess Cancer Risk was for arsenic in mussels at one location in Durban Bay, at 8.0×10^{-5}, that is, a possibility of 8 extra incidences of cancer per 100 000 population. Mussels generally provided higher Excess Cancer Risks than fish, due to the higher inorganic arsenic concentrations in their tissue. If fish only are considered then the highest Excess Cancer Risk was 3.9×10^{-5} for polychlorinated biphenyls in *Ambassis gymnocephalus* in the Isipingo River estuary (non-detects replaced with a value equivalent to one half the method detection limit). The highest Total Cancer Risk was 1.1×10^{-4}, for mussels at three locations in Durban Bay. Total Cancer Risks for the majority of fish species in Durban Bay exceeded 1.0×10^{-5} regardless of whether non-detects were replaced with a value equivalent to one half the method detection limit or zero. Total Cancer Risks for all fish species in the uMngeni and Isipingo River estuaries exceeded 1.0×10^{-5} if non-detects were replaced with a value equivalent to one half the method detection, but only for a single species in each system if non-detects were replaced with a value of zero. The Total Cancer Risk for all frequently consumed fish collectively

exceeded 1×10^{-5} for each system if non-detects were replaced with a value equivalent to one half the method detection limit, but only for Durban Bay if non-detects were replaced with a value of zero.

As expected, because their higher fish and shellfish consumption rate the Excess Cancer Risk for subsistence consumers exceeded 1×10^{-5} more frequently than for recreational consumers. Excess Cancer Risks for (inorganic) arsenic in mussels at seven locations in Durban Bay exceeded 1×10^{-4}. Excess Cancer Risks for two fish species in Durban Bay and one fish species in the Isipingo River estuary exceeded 1×10^{-4} if polychlorinated biphenyl non-detects were replaced with a concentration equivalent to one-half the method detection limit. If polychlorinated biphenyl non-detects were replaced with a value of zero then an Excess Cancer Risk exceeding 1×10^{-4} was evident for one fish species in the Isipingo River estuary. The highest Total Cancer Risk was for mussels at one location in Durban Bay, at 3.3×10^{-4}, or a possibility of 33 extra incidences of cancer per 100 000 population. This decreased to 2.7×10^{-4} if non-detects were replaced with a value of zero. If fish only are considered then the highest Total Excess Cancer Risk was for *Ambassis natalensis* in the Isipingo River estuary, at 2.0×10^{-4}, or a possibility of 20 extra incidences of cancer per 100 000 population. This decreased to 1.1×10^{-4} if non-detects were replaced with a value of zero. The Total Cancer Risk for all frequently consumed fish exceeded 1×10^{-4} for Durban Bay and the uMngeni River estuary if non-detects were replaced with a value equivalent to one half the method detection limit, but only exceeded 1×10^{-5} when replaced with a value of zero. For the Isipingo River estuary the Total Cancer Risk only exceeded 1×10^{-5} if non-detects were replaced with a value equivalent to one half the method detection limit, but not when replaced with a value of zero.

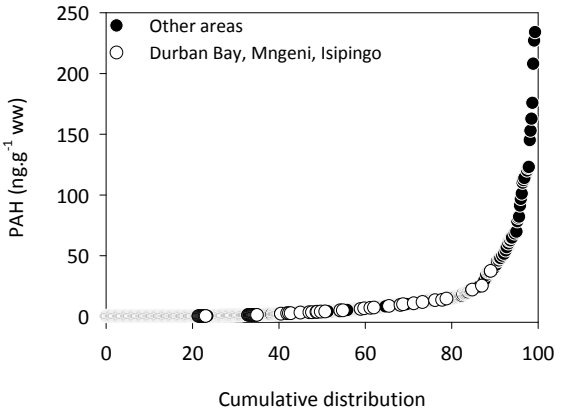

Figure 3.15. Comparison of total polycyclic aromatic hydrocarbon (PAH) concentrations in the tissue of fish caught in Durban Bay and the uMngeni and Isipingo River estuaries in 2013 to concentrations in the tissue of fish in other areas of the world (data from Porte and Albaigés, 1993; Corsi *et al*., 2002; Cheng *et al*., 2007).

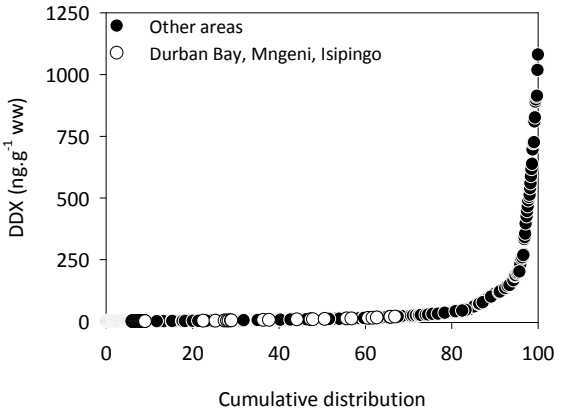

Figure 3.16. Comparison of DDX concentrations in the tissue of fish caught in Durban Bay and the uMngeni and Isipingo River estuaries in 2013 to concentrations in the tissue of fish in other areas of the world (data from NOAA, 2000; Allen *et al*., 2004; Yang *et al*., 2006; Cheng *et al*., 2007; EPAV, 2007; Karouna-Renier, 2011; Schnitzler *et al*., 2011).

Polycyclic aromatic hydrocarbons are rarely identified in the scientific literature as a source of risk to consumers of fish, and the high incidence of Excess Cancer Risks exceeding 1×10^{-5} for subsistence consumers and for recreational consumers under scenario 2 when non-detects were replaced with a value of one half the method detection limit reflects the relatively high method detection limits for polycyclic aromatic hydrocarbon isomers. A similar situation applies to polychlorinated biphenyls and (inorganic) arsenic in fish. In other words, the high method detection limits lead to an overstatement of the risk for some chemicals if the non-detects are replaced with a value equivalent to one half the method detection limit.

The above discussion on the risk posed by chemicals accumulated by fish and mussels did not take into account Aroclor equivalent concentrations calculated from polychlorinated biphenyl congener concentrations, as recommended by some workers (*e.g*. Lauenstein and Cantillo, 1993). If Aroclor

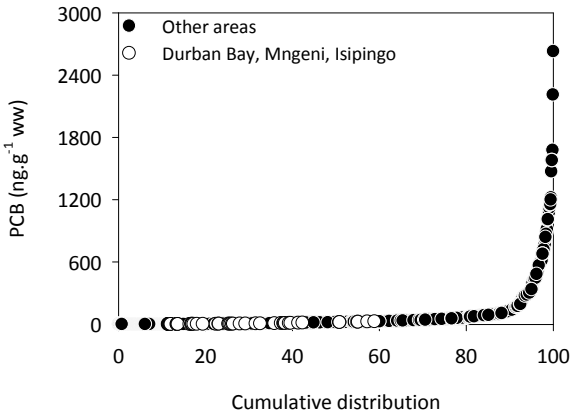

Figure 3.17. Comparison of total polychlorinated biphenyl (PCB) concentrations in the tissue of fish caught in Durban Bay and the uMngeni and Isipingo River estuaries in 2013 to concentrations in the tissue of fish in other areas of the world (data from Porte and Albaigés, 1993; NOAA, 2000; Corsi *et al*., 2002; Allen *et al*., 2004; NYC, 2004; Denton *et al*., 2006; Yang *et al*., 2006; EPAV, 2007; Snyder and Rao, 2008; Snyder and Karouna-Renier, 2009; Karouna-Renier, 2011; Schnitzler *et al*., 2011; Stunz and Robillard, 2011; MDEP/MDMF, 2012).

equivalent concentrations are considered, by using a conversion factor of two for the sum of the eighteen National Oceanic and Atmospheric Agency polychlorinated biphenyl congeners, then there would still be no incidences of Hazard Quotients exceeding a value of one for recreational consumers under Scenario 1, but five incidences under Scenario 2 if non-detects were replaced with a value equivalent to one-half the method detection limit and two incidences if non-detects were replaced with a value of zero, all for fish in Durban Bay and the Isipingo River estuary. For subsistence consumers all but two fish species and mussels at two collection locations in Durban Bay would have had Hazard Quotients exceeding a value of one if non-detects are replaced with a value equivalent to one half the method detection limit. This decreased to four fish species and mussels at six collection locations if non-detects were replaced with a value of zero. Two fish species in the Isipingo River estuary and four species in the uMngeni River estuary had Hazard Quotients exceeding a value of one, but one and two species respectively if non-detects were replaced with a value of zero. Under recreational consumer scenario 1 there were five incidences of the Excess Cancer Risk exceeding 1×10^{-5} for Durban Bay and one each for the Isipingo River and uMngeni River estuary, regardless of whether polychlorinated biphenyl non-detects were replaced with a value equivalent to one-half the method detection limit or a value of zero. The Excess Cancer Risk never exceeded 1×10^{-4}. For recreational consumers under scenario 2 all but one fish species in Durban Bay and two species in the uMngeni River estuary provided an Excess Cancer Risk exceeding 1×10^{-5}, but none exceeded 1×10^{-4}. If non-detects were replaced with a value of zero then all but two fish species and mussels at four locations in Durban Bay provided an Excess Cancer Risk exceeding 1×10^{-5}, but none exceeded 1×10^{-4}. The excess Cancer risk for three fish species in the Isipingo River estuary and for six species in the uMngeni River estuary fell below 1×10^{-5} if non-detects were replaced with a value of zero. For subsistence consumers, mussels at all locations in Durban Bay and fish in all systems provided an Excess Cancer Risk exceeding 1×10^{-5}, with the Excess Cancer Risk for five fish species in Durban Bay and one species in each of the Isipingo and uMngeni River estuaries also exceeding 1×10^{-4}. If non-detects were replaced with a value of zero then all but one fish species in Durban Bay, two species in the Isipingo River estuary, and four species in uMngeni River estuary would still have provided an Excess Cancer Risk exceeding 1×10^{-5}. Here, however, only three fish species in Durban Bay and one species in the Isipingo River estuary would have provided an Excess Cancer Risk exceeding 1×10^{-4}.

The question that arises is whether humans that consume fish caught and mussels collected in Durban Bay and the uMngeni and Isipingo River estuaries face chronic and carcinogenic health risks due to excessive exposure to chemicals that these organisms have accumulated in their tissue, and thus whether consumption advisories are required. This is not an easy question to answer for the reasons provided below, irrespective of the fact that the risk assessment discussed above identified potential risks to the health of human consumers.

- Fish and mussel tissue consumption rates for recreational and subsistence consumers (fishers) in South Africa are unknown, albeit that there is information on fish consumption for the South African population at large (see section 3.4.9). However, it seems unlikely that the latter consumption rates apply to recreational and subsistence fishers, who generally consume more fish and shellfish than the

average person. This creates uncertainty on the degree of potential risk since consumption rate is an important determinant of risk. The consumption rates used are those recommended for the population of the United States of America, and exceed consumption rates for the South African population at large, as provided by Nel and Steyn (2002).

- It is unknown whether recreational and subsistence consumers have historically or will in future consume fish and mussels from each system studied at the stipulated intake rates for the 30 year exposure period assumed for chronic health risks and the 70 year exposure period assumed for carcinogenic health risks. This is important as exposure period an important determinant of risk.

Table 3.3. Hazard Quotients and Hazard Indices for adult recreational consumers under Scenarios 1 and 2 and for adult subsistence consumers for fish and mussels collected in Durban Bay and the uMngeni and Isipingo River estuaries. Hazard Quotients and Hazard Indices equal to or exceeding a value of one are highlighted in grey shading. As = inorganic arsenic, Cd = cadmium, Hg = mercury, TBT = tributyltin, DDX = sum p,p'-DDD, p,p'-DDD and p,p'-DDT, PCB = sum polychlorinated biphenyl congeners, Aroclor = polychlorinated biphenyl Aroclor equivalents, Hazard Index 1 = total risk calculated for non-detects replaced by a value of one-half the method detection limit, Hazard Index 2 = total risk calculated for non-detects replaced by a value =0, nd = non-detect, MDL = method detection limit.

					Hazard Quotients												
Category	**Location**	**Species**	**As (nd = ½ MDL)**	**As (nd = 0)**	**Cd (nd = ½ MDL)**	**Cd (nd = 0)**	**Hg**	**Se**	**TBT**	**DDX (nd = ½ MDL)**	**DDX (nd = 0)**	**PCB (nd = ½ MDL)**	**PCB (nd = 0)**	**Aroclor (nd = ½ MDL)**	**Aroclor (nd = 0)**	**Hazard Index 1**	**Hazard Index 2**
Adult recreational	Durban Bay	*Sphyraena jello*	0.00	0.00	0.00	0.00	0.36	0.02	0.02	0.01	0.01	0.24	0.20	0.44	0.37	0.65	0.60
Scenario 1	Durban Bay	*Valamugil buchanani*	0.01	0.00	0.00	0.00	0.07	0.02	0.01	0.01	0.01	0.22	0.18	0.39	0.30	0.33	0.28
	Durban Bay	*Myxus capensis*	0.00	0.00	0.00	0.00	0.09	0.03	0.00	0.00	0.00	0.06	0.00	0.10	0.01	0.19	0.13
	Durban Bay	*Liza dumerilii*	0.00	0.00	0.00	0.00	0.17	0.02	0.01	0.00	0.00	0.18	0.13	0.33	0.25	0.39	0.34
	Durban Bay	*Liza tricuspidens*	0.01	0.00	0.00	0.00	0.34	0.02	0.02	0.01	0.01	0.34	0.29	0.62	0.52	0.73	0.68
	Durban Bay	*Mugil cephalus*	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.00	0.11	0.04	0.20	0.12	0.14	0.07
	Durban Bay	*Pseudorhombus arsius*	0.00	0.00	0.00	0.00	0.19	0.02	0.01	0.00	0.00	0.13	0.06	0.24	0.18	0.36	0.28
	Durban Bay	*Sillago sihama*	0.00	0.00	0.00	0.00	0.58	0.03	0.01	0.00	0.00	0.13	0.08	0.24	0.15	0.76	0.71
	Durban Bay	*Ambassis gymnocephalus*	0.01	0.00	0.06	0.06	0.05	0.02	0.01	0.01	0.01	0.35	0.31	0.64	0.54	0.50	0.46
	Durban Bay	*Pomadasys commersonnii*	0.00	0.00	0.00	0.00	0.47	0.02	0.00	0.00	0.00	0.11	0.06	0.20	0.11	0.61	0.56
	Durban Bay	*Platycephalus indicus*	0.01	0.00	0.00	0.00	0.24	0.02	0.02	0.00	0.00	0.07	0.02	0.13	0.03	0.36	0.30
	Durban Bay	*Perna perna* DBN1	0.06	0.06	0.01	0.01	0.08	0.04	0.06	0.00	0.00	0.09	0.06	0.16	0.11	0.33	0.30
	Durban Bay	*Perna perna* DBN2	0.07	0.07	0.02	0.02	0.09	0.04	0.08	0.00	0.00	0.12	0.08	0.21	0.14	0.41	0.37
	Durban Bay	*Perna perna* DBN3	0.07	0.07	0.02	0.02	0.08	0.05	0.10	0.00	0.00	0.14	0.10	0.25	0.18	0.46	0.42
	Durban Bay	*Perna perna* DBN4	0.04	0.04	0.01	0.01	0.03	0.03	0.07	0.00	0.00	0.11	0.07	0.19	0.12	0.28	0.24
	Durban Bay	*Perna perna* DBN5	0.07	0.07	0.01	0.01	0.08	0.04	0.05	0.00	0.00	0.12	0.08	0.22	0.16	0.38	0.33
	Durban Bay	*Perna perna* DBN6	0.05	0.05	0.01	0.01	0.05	0.03	0.03	0.00	0.00	0.07	0.04	0.13	0.07	0.25	0.22
	Durban Bay	*Perna perna* DBN7	0.02	0.02	0.01	0.01	0.03	0.03	0.04	0.00	0.00	0.09	0.06	0.16	0.10	0.21	0.18
	Durban Bay	*Perna perna* DBN8	0.02	0.02	0.01	0.01	0.05	0.03	0.06	0.00	0.00	0.13	0.09	0.23	0.15	0.31	0.26
	Durban Bay	*Perna perna* DBN9	0.02	0.02	0.01	0.01	0.03	0.03	0.05	0.00	0.00	0.08	0.03	0.14	0.06	0.21	0.17
	Durban Bay	*Perna perna* DBN10	0.03	0.03	0.01	0.01	0.03	0.04	0.06	0.00	0.00	0.07	0.03	0.13	0.06	0.24	0.19
	Durban Bay	*Perna perna* DBN11	0.01	0.01	0.01	0.01	0.01	0.03	0.06	0.00	0.00	0.09	0.05	0.16	0.09	0.21	0.17
	Durban Bay	*All species*	0.00	0.00	0.00	0.00	0.21	0.02	0.01	0.01	0.00	0.18	0.13	0.33	0.24	0.43	0.38
	Isipingo	*Myxus capensis*	0.01	0.00	0.00	0.00	0.02	0.02	0.00	0.00	0.00	0.08	0.02	0.14	0.03	0.13	0.05
	Isipingo	*Ambassis natalensis*	0.01	0.00	0.01	0.01	0.05	0.03	0.00	0.00	0.00	0.37	0.34	0.71	0.59	0.46	0.42
	Isipingo	*Oreochromus mossambicus*	0.00	0.00	0.00	0.00	0.01	0.03	0.00	0.00	0.00	0.06	0.00	0.11	0.01	0.11	0.04
	Isipingo	*All species*	0.01	0.00	0.00	0.00	0.01	0.02	0.00	0.00	0.00	0.07	0.01	0.13	0.02	0.12	0.05
	Mngeni	*Valamugil cunnesius*	0.01	0.00	0.00	0.00	0.03	0.02	0.00	0.01	0.00	0.18	0.13	0.34	0.26	0.25	0.19

					Hazard Quotients												
Category	**Location**	**Species**	**As (nd = ½ MDL)**	**As (nd = 0)**	**Cd (nd = ½ MDL)**	**Cd (nd = 0)**	**Hg**	**Se**	**TBT**	**DDX (nd = ½ MDL)**	**DDX (nd = 0)**	**PCB (nd = ½ MDL)**	**PCB (nd = 0)**	**Aroclor (nd = ½ MDL)**	**Aroclor (nd = 0)**	**Hazard Index 1**	**Hazard Index 2**
	Mngeni	*Liza dumerilii*	0.00	0.00	0.00	0.00	0.02	0.03	0.00	0.00	0.00	0.07	0.01	0.12	0.03	0.12	0.06
	Mngeni	*Liza macrolepis*	0.00	0.00	0.00	0.00	0.02	0.03	0.00	0.00	0.00	0.06	0.00	0.10	0.01	0.12	0.06
	Mngeni	*Liza tricuspidens*	0.00	0.00	0.00	0.00	0.12	0.01	0.00	0.00	0.00	0.06	0.00	0.10	0.00	0.19	0.12
	Mngeni	*Mugil cephalus*	0.01	0.00	0.00	0.00	0.02	0.03	0.00	0.00	0.00	0.07	0.00	0.12	0.00	0.12	0.05
	Mngeni	*Gerres methueni*	0.01	0.00	0.00	0.00	0.20	0.03	0.00	0.00	0.00	0.09	0.03	0.16	0.07	0.33	0.26
	Mngeni	*Ambassis natalensis*	0.01	0.00	0.02	0.02	0.05	0.03	0.00	0.00	0.00	0.14	0.08	0.26	0.16	0.25	0.18
	Mngeni	*Oreochromus mossambicus*	0.00	0.00	0.00	0.00	0.02	0.03	0.00	0.00	0.00	0.10	0.04	0.17	0.09	0.16	0.09
	Mngeni	*All species*	0.01	0.00	0.00	0.00	0.04	0.02	0.00	0.00	0.00	0.09	0.03	0.16	0.06	0.16	0.10
Adult recreational	Durban Bay	*Sphyraena jello*	0.01	0.00	0.00	0.00	0.93	0.04	0.04	0.02	0.02	0.63	0.53	1.15	0.96	1.68	1.57
Scenario 2	Durban Bay	*Valamugil buchanani*	0.01	0.00	0.00	0.00	0.19	0.04	0.02	0.02	0.02	0.56	0.46	1.01	0.79	0.85	0.73
	Durban Bay	*Myxus capensis*	0.01	0.00	0.00	0.00	0.24	0.04	0.01	0.01	0.00	0.16	0.01	0.27	0.02	0.49	0.33
	Durban Bay	*Liza dumerilii*	0.01	0.00	0.00	0.00	0.44	0.05	0.03	0.01	0.01	0.46	0.35	0.85	0.66	1.01	0.87
	Durban Bay	*Liza tricuspidens*	0.01	0.00	0.00	0.00	0.88	0.04	0.05	0.02	0.02	0.87	0.76	1.60	1.35	1.89	1.76
	Durban Bay	*Mugil cephalus*	0.01	0.00	0.00	0.00	0.01	0.03	0.01	0.01	0.01	0.28	0.11	0.52	0.31	0.36	0.17
	Durban Bay	*Pseudorhombus arsius*	0.01	0.00	0.00	0.00	0.49	0.06	0.02	0.01	0.01	0.35	0.16	0.63	0.46	0.94	0.73
	Durban Bay	*Sillago sihama*	0.01	0.00	0.00	0.00	1.51	0.08	0.02	0.01	0.00	0.35	0.22	0.62	0.40	1.98	1.84
	Durban Bay	*Ambassis gymnocephalus*	0.01	0.00	0.15	0.15	0.14	0.04	0.03	0.02	0.02	0.90	0.79	1.66	1.41	1.31	1.19
	Durban Bay	*Pomadasys commersonnii*	0.01	0.00	0.00	0.00	1.21	0.06	0.01	0.01	0.00	0.29	0.16	0.52	0.29	1.59	1.44
	Durban Bay	*Platycephalus indicus*	0.01	0.00	0.00	0.00	0.63	0.08	0.05	0.00	0.00	0.19	0.04	0.33	0.08	0.95	0.78
	Durban Bay	*Perna perna* DBN1	0.15	0.15	0.03	0.03	0.20	0.10	0.15	0.00	0.00	0.23	0.14	0.42	0.29	0.87	0.78
	Durban Bay	*Perna perna* DBN2	0.17	0.17	0.04	0.04	0.24	0.11	0.21	0.00	0.00	0.30	0.20	0.54	0.36	1.07	0.97
	Durban Bay	*Perna perna* DBN3	0.18	0.18	0.05	0.05	0.21	0.10	0.27	0.00	0.00	0.36	0.25	0.65	0.46	1.19	1.08
	Durban Bay	*Perna perna* DBN4	0.10	0.10	0.02	0.02	0.08	0.09	0.17	0.01	0.00	0.28	0.18	0.50	0.32	0.73	0.62
	Durban Bay	*Perna perna* DBN5	0.18	0.18	0.04	0.04	0.22	0.10	0.12	0.01	0.00	0.32	0.20	0.58	0.40	0.98	0.85
	Durban Bay	*Perna perna* DBN6	0.13	0.13	0.02	0.02	0.12	0.08	0.09	0.01	0.00	0.19	0.11	0.34	0.19	0.65	0.57
	Durban Bay	*Perna perna* DBN7	0.05	0.05	0.02	0.02	0.08	0.08	0.11	0.01	0.00	0.24	0.15	0.42	0.27	0.56	0.47
	Durban Bay	*Perna perna* DBN8	0.06	0.06	0.02	0.02	0.13	0.09	0.16	0.01	0.00	0.34	0.23	0.60	0.40	0.80	0.68
	Durban Bay	*Perna perna* DBN9	0.05	0.05	0.02	0.02	0.07	0.09	0.12	0.01	0.01	0.20	0.08	0.36	0.16	0.56	0.43
	Durban Bay	*Perna perna* DBN10	0.09	0.09	0.02	0.02	0.07	0.08	0.15	0.01	0.01	0.19	0.08	0.34	0.16	0.61	0.50
	Durban Bay	*Perna perna* DBN11	0.04	0.04	0.02	0.02	0.04	0.06	0.15	0.00	0.00	0.23	0.13	0.40	0.23	0.54	0.44
	Durban Bay	*All species*	0.01	0.00	0.00	0.00	0.56	0.04	0.03	0.01	0.01	0.47	0.34	0.85	0.62	1.12	0.98
	Isipingo	*Myxus capensis*	0.01	0.00	0.00	0.00	0.05	0.06	0.00	0.01	0.00	0.21	0.04	0.37	0.08	0.33	0.13

					Hazard Quotients												
Category	Location	Species	As (nd = ½ MDL)	As (nd = 0)	Cd (nd = ½ MDL)	Cd (nd = 0)	Hg	Se	TBT	DDX (nd = ½ MDL)	DDX (nd = 0)	PCB (nd = ½ MDL)	PCB (nd = 0)	Aroclor (nd = ½ MDL)	Aroclor (nd = 0)	Hazard Index 1	Hazard Index 2
	Isipingo	*Ambassis natalensis*	0.01	0.00	0.02	0.02	0.12	0.07	0.00	0.01	0.00	0.97	0.88	1.84	1.54	1.20	1.10
	Isipingo	*Oreochromus mossambicus*	0.01	0.00	0.00	0.00	0.02	0.08	0.00	0.00	0.00	0.17	0.01	0.29	0.03	0.28	0.11
	Isipingo	*All species*	0.01	0.00	0.00	0.00	0.04	0.07	0.00	0.00	0.00	0.19	0.03	0.33	0.05	0.31	0.12
	Mngeni	*Valamugil cunnesius*	0.02	0.00	0.00	0.00	0.08	0.05	0.00	0.01	0.01	0.48	0.35	0.89	0.66	0.64	0.48
	Mngeni	*Liza dumerilii*	0.01	0.00	0.00	0.00	0.04	0.07	0.00	0.00	0.00	0.17	0.04	0.30	0.07	0.31	0.15
	Mngeni	*Liza macrolepis*	0.01	0.00	0.00	0.00	0.06	0.07	0.00	0.00	0.00	0.16	0.01	0.27	0.02	0.31	0.15
	Mngeni	*Liza tricuspidens*	0.01	0.00	0.00	0.00	0.30	0.05	0.00	0.00	0.00	0.15	0.00	0.26	0.00	0.49	0.32
	Mngeni	*Mugil cephalus*	0.01	0.00	0.00	0.00	0.05	0.08	0.00	0.01	0.00	0.18	0.00	0.31	0.00	0.32	0.13
	Mngeni	*Gerres methueni*	0.01	0.00	0.00	0.00	0.52	0.08	0.00	0.00	0.00	0.23	0.09	0.42	0.18	0.85	0.69
	Mngeni	*Ambassis natalensis*	0.02	0.00	0.05	0.05	0.13	0.09	0.00	0.01	0.01	0.36	0.21	0.67	0.42	0.65	0.48
	Mngeni	*Oreochromus mossambicus*	0.01	0.00	0.00	0.00	0.06	0.08	0.00	0.01	0.00	0.25	0.11	0.45	0.22	0.40	0.25
	Mngeni	*All species*	0.01	0.00	0.00	0.00	0.10	0.07	0.00	0.01	0.00	0.23	0.08	0.41	0.16	0.41	0.25
Adult subsistence	Durban Bay	*Sphyraena jello*	0.04	0.00	0.00	0.00	2.92	0.13	0.13	0.06	0.06	1.99	1.67	3.62	3.01	5.27	4.91
	Durban Bay	*Valamugil buchanani*	0.04	0.00	0.00	0.00	0.61	0.13	0.06	0.05	0.05	1.77	1.44	3.18	2.47	2.66	2.29
	Durban Bay	*Myxus capensis*	0.04	0.00	0.00	0.00	0.75	0.20	0.02	0.03	0.01	0.49	0.03	0.85	0.05	1.54	1.02
	Durban Bay	*Liza dumerilii*	0.04	0.00	0.00	0.00	1.37	0.16	0.10	0.04	0.03	1.45	1.08	2.66	2.07	3.16	2.74
	Durban Bay	*Liza tricuspidens*	0.04	0.00	0.00	0.00	2.77	0.16	0.17	0.06	0.06	2.73	2.37	5.02	4.23	5.94	5.54
	Durban Bay	*Mugil cephalus*	0.04	0.00	0.00	0.00	0.02	0.10	0.05	0.04	0.04	0.88	0.33	1.62	0.97	1.14	0.54
	Durban Bay	*Pseudorhombus arsius*	0.04	0.00	0.00	0.00	1.54	0.18	0.06	0.03	0.02	1.10	0.50	1.99	1.43	2.94	2.30
	Durban Bay	*Sillago sihama*	0.04	0.00	0.00	0.00	4.75	0.24	0.08	0.02	0.00	1.09	0.69	1.95	1.25	6.21	5.76
	Durban Bay	*Ambassis gymnocephalus*	0.04	0.00	0.47	0.47	0.45	0.14	0.10	0.08	0.08	2.82	2.48	5.21	4.43	4.10	3.72
	Durban Bay	*Pomadasys commersonnii*	0.04	0.00	0.01	0.01	3.79	0.18	0.03	0.02	0.00	0.92	0.52	1.63	0.92	4.99	4.53
	Durban Bay	*Platycephalus indicus*	0.04	0.00	0.00	0.00	1.97	0.19	0.15	0.01	0.00	0.59	0.13	1.04	0.25	2.96	2.44
	Durban Bay	*Perna perna* DBN1	0.47	0.47	0.11	0.11	0.63	0.31	0.48	0.01	0.00	0.72	0.45	1.33	0.90	2.72	2.44
	Durban Bay	*Perna perna* DBN2	0.55	0.55	0.13	0.13	0.76	0.34	0.64	0.01	0.00	0.94	0.62	1.69	1.14	3.37	3.04
	Durban Bay	*Perna perna* DBN3	0.55	0.55	0.16	0.16	0.67	0.37	0.85	0.01	0.00	1.12	0.78	2.03	1.44	3.74	3.39
	Durban Bay	*Perna perna* DBN4	0.30	0.30	0.06	0.06	0.24	0.24	0.54	0.02	0.01	0.88	0.55	1.57	1.00	2.29	1.96
	Durban Bay	*Perna perna* DBN5	0.55	0.55	0.11	0.11	0.68	0.33	0.37	0.02	0.01	1.02	0.63	1.82	1.27	3.07	2.68
	Durban Bay	*Perna perna* DBN6	0.42	0.42	0.06	0.06	0.38	0.28	0.28	0.02	0.01	0.60	0.34	1.05	0.60	2.04	1.78
	Durban Bay	*Perna perna* DBN7	0.15	0.15	0.05	0.05	0.24	0.22	0.34	0.02	0.01	0.75	0.48	1.31	0.84	1.75	1.47
	Durban Bay	*Perna perna* DBN8	0.18	0.18	0.06	0.06	0.41	0.26	0.50	0.02	0.01	1.08	0.71	1.90	1.26	2.51	2.14
	Durban Bay	*Perna perna* DBN9	0.15	0.15	0.06	0.06	0.21	0.28	0.39	0.03	0.02	0.62	0.25	1.12	0.49	1.74	1.36

					Hazard Quotients												
Category	**Location**	**Species**	**As (nd = ½ MDL)**	**As (nd = 0)**	**Cd (nd = ½ MDL)**	**Cd (nd = 0)**	**Hg**	**Se**	**TBT**	**DDX (nd = ½ MDL)**	**DDX (nd = 0)**	**PCB (nd = ½ MDL)**	**PCB (nd = 0)**	**Aroclor (nd = ½ MDL)**	**Aroclor (nd = 0)**	**Hazard Index 1**	**Hazard Index 2**
	Durban Bay	*Perna perna* DBN10	0.27	0.27	0.07	0.07	0.23	0.29	0.46	0.02	0.02	0.59	0.25	1.07	0.49	1.93	1.58
	Durban Bay	*Perna perna* DBN11	0.12	0.12	0.05	0.05	0.12	0.22	0.46	0.01	0.00	0.71	0.40	1.26	0.72	1.70	1.38
	Durban Bay	*All species*	0.04	0.00	0.00	0.00	1.75	0.15	0.08	0.04	0.04	1.46	1.06	2.65	1.96	3.53	3.08
	Isipingo	*Myxus capensis*	0.05	0.00	0.00	0.00	0.16	0.13	0.00	0.02	0.00	0.67	0.12	1.18	0.25	1.03	0.42
	Isipingo	*Ambassis natalensis*	0.05	0.00	0.05	0.05	0.39	0.22	0.00	0.02	0.01	3.04	2.76	5.78	4.83	3.77	3.44
	Isipingo	*Oreochromus mossambicus*	0.04	0.00	0.00	0.00	0.06	0.25	0.00	0.01	0.00	0.52	0.04	0.90	0.10	0.89	0.34
	Isipingo	*All species*	0.04	0.00	0.00	0.00	0.11	0.19	0.00	0.02	0.00	0.60	0.08	1.04	0.17	1.05	0.38
	Mngeni	*Valamugil cunnesius*	0.05	0.00	0.00	0.00	0.24	0.16	0.00	0.05	0.03	1.49	1.08	2.80	2.08	1.99	1.52
	Mngeni	*Liza dumerilii*	0.04	0.00	0.00	0.00	0.14	0.23	0.00	0.01	0.00	0.54	0.11	0.95	0.22	0.97	0.48
	Mngeni	*Liza macrolepis*	0.04	0.00	0.00	0.00	0.20	0.23	0.00	0.01	0.00	0.49	0.03	0.85	0.06	0.96	0.46
	Mngeni	*Liza tricuspidens*	0.04	0.00	0.00	0.00	0.96	0.06	0.00	0.01	0.00	0.48	0.00	0.82	0.00	1.55	1.02
	Mngeni	*Mugil cephalus*	0.04	0.00	0.00	0.00	0.16	0.23	0.00	0.02	0.00	0.56	0.00	0.96	0.00	1.02	0.39
	Mngeni	*Gerres methueni*	0.04	0.00	0.00	0.00	1.63	0.24	0.00	0.01	0.00	0.73	0.28	1.31	0.57	2.66	2.15
	Mngeni	*Ambassis natalensis*	0.05	0.00	0.16	0.16	0.40	0.26	0.00	0.04	0.02	1.14	0.65	2.10	1.31	2.04	1.50
	Mngeni	*Oreochromus mossambicus*	0.04	0.00	0.00	0.00	0.19	0.23	0.00	0.02	0.00	0.79	0.35	1.41	0.71	1.27	0.77
	Mngeni	*All species*	0.04	0.00	0.00	0.00	0.31	0.19	0.00	0.02	0.01	0.73	0.26	1.30	0.51	1.29	0.77

Table 3.4. Excess Cancer Risks and Total Cancer Risks for adult recreational consumers under Scenarios 1 and 2 and for adult subsistence consumers for fish and mussels collected in Durban Bay and the uMngeni and Isipingo River estuaries. Excess Cancer Risks exceeding 1×10^{-5} are highlighted in grey shading, and those exceeding 1×10^{-4} in red shading. As = inorganic arsenic, DDX = sum p,p'-DDD, p,p'-DDD and p,p'-DDT, PCB = sum polychlorinated biphenyl congeners, Aroclor = polychlorinated biphenyl Aroclor equivalents, Total Cancer Risk 1 = total risk calculated for non-detects replaced by a value of one-half the method detection limit, Total Cancer Risk 2 = total risk calculated for non-detects replaced by a value =0, nd = non-detect, MDL = method detection limit.

				Excess Cancer Risk										
Category	**Location**	**Species**	**As (nd = ½ MDL)**	**As (nd = 0)**	**PAH (nd = ½ MDL)**	**PAH (nd = 0)**	**DDX (nd = ½ MDL)**	**DDX (nd = 0)**	**PCB (nd = ½ MDL)**	**PCB (nd = 0)**	**Aroclor (nd = ½ MDL)**	**Aroclor (nd = 0)**	**Total Cancer Risk 1**	**Total Cancer Risk 2**
Adult recreational	Durban Bay	*Sphyraena jello*	2.1E-06	0.0E+00	5.6E-06	0.0E+00	1.3E-06	1.3E-06	8.2E-06	9.8E-06	1.8E-05	1.5E-05	1.9E-05	9.5E-06
Scenario 1	Durban Bay	*Valamugil buchanani*	2.3E-06	0.0E+00	6.2E-06	0.0E+00	1.0E-06	1.0E-06	7.1E-06	8.7E-06	1.6E-05	1.2E-05	1.8E-05	8.1E-06
	Durban Bay	*Myxus capensis*	2.1E-06	0.0E+00	5.8E-06	2.7E-07	5.2E-07	3.1E-07	1.4E-07	2.4E-06	4.2E-06	2.7E-07	1.1E-05	7.2E-07
	Durban Bay	*Liza dumerilii*	2.1E-06	0.0E+00	5.7E-06	1.6E-07	7.4E-07	5.9E-07	5.3E-06	7.1E-06	1.3E-05	1.0E-05	1.6E-05	6.1E-06
	Durban Bay	*Liza tricuspidens*	2.4E-06	0.0E+00	6.3E-06	0.0E+00	1.3E-06	1.3E-06	1.2E-05	1.3E-05	2.5E-05	2.1E-05	2.3E-05	1.3E-05
	Durban Bay	*Mugil cephalus*	2.2E-06	0.0E+00	1.2E-05	7.0E-06	8.6E-07	7.6E-07	1.6E-06	4.3E-06	8.0E-06	4.8E-06	1.9E-05	9.4E-06
	Durban Bay	*Pseudorhombus arsius*	2.0E-06	0.0E+00	5.4E-06	2.0E-07	5.6E-07	4.7E-07	2.4E-06	5.4E-06	9.8E-06	7.0E-06	1.3E-05	3.1E-06
	Durban Bay	*Sillago sihama*	2.2E-06	0.0E+00	5.8E-06	1.9E-07	3.6E-07	1.0E-07	3.4E-06	5.4E-06	9.6E-06	6.1E-06	1.4E-05	3.7E-06
	Durban Bay	*Ambassis gymnocephalus*	2.3E-06	0.0E+00	6.1E-06	0.0E+00	1.6E-06	1.6E-06	1.2E-05	1.4E-05	2.6E-05	2.2E-05	2.4E-05	1.4E-05
	Durban Bay	*Pomadasys commersonnii*	2.1E-06	0.0E+00	5.6E-06	0.0E+00	3.6E-07	1.0E-07	2.5E-06	4.5E-06	8.0E-06	4.5E-06	1.3E-05	2.6E-06
	Durban Bay	*Platycephalus indicus*	2.3E-06	0.0E+00	5.6E-06	0.0E+00	3.1E-07	0.0E+00	6.2E-07	2.9E-06	5.1E-06	1.2E-06	1.1E-05	6.2E-07
	Durban Bay	*Perna perna* DBN1	2.6E-05	2.6E-05	4.1E-06	0.0E+00	2.1E-07	0.0E+00	2.2E-06	3.5E-06	6.5E-06	4.4E-06	3.4E-05	2.8E-05
	Durban Bay	*Perna perna* DBN2	3.0E-05	3.0E-05	5.5E-06	4.6E-07	2.6E-07	0.0E+00	3.1E-06	4.6E-06	8.3E-06	5.6E-06	4.1E-05	3.4E-05
	Durban Bay	*Perna perna* DBN3	3.1E-05	3.1E-05	5.9E-06	4.4E-07	2.8E-07	0.0E+00	3.9E-06	5.5E-06	1.0E-05	7.1E-06	4.2E-05	3.5E-05
	Durban Bay	*Perna perna* DBN4	1.7E-05	1.7E-05	5.0E-06	0.0E+00	4.3E-07	2.6E-07	2.7E-06	4.3E-06	7.7E-06	4.9E-06	2.6E-05	1.9E-05
	Durban Bay	*Perna perna* DBN5	3.0E-05	3.0E-05	5.2E-06	0.0E+00	3.9E-07	2.1E-07	3.1E-06	5.0E-06	8.9E-06	6.2E-06	4.1E-05	3.4E-05
	Durban Bay	*Perna perna* DBN6	2.3E-05	2.3E-05	3.9E-06	0.0E+00	3.7E-07	3.1E-07	1.7E-06	2.9E-06	5.2E-06	3.0E-06	3.0E-05	2.5E-05
	Durban Bay	*Perna perna* DBN7	8.1E-06	8.1E-06	4.5E-06	4.1E-07	3.5E-07	2.1E-07	2.3E-06	3.7E-06	6.4E-06	4.1E-06	1.7E-05	1.1E-05
	Durban Bay	*Perna perna* DBN8	1.0E-05	1.0E-05	5.8E-06	2.9E-07	4.0E-07	2.1E-07	3.5E-06	5.3E-06	9.3E-06	6.2E-06	2.2E-05	1.4E-05
	Durban Bay	*Perna perna* DBN9	8.5E-06	8.5E-06	5.1E-06	0.0E+00	5.3E-07	4.4E-07	1.2E-06	3.1E-06	5.5E-06	2.4E-06	1.7E-05	1.0E-05
	Durban Bay	*Perna perna* DBN10	1.5E-05	1.5E-05	6.3E-06	2.3E-06	4.3E-07	3.5E-07	1.2E-06	2.9E-06	5.3E-06	2.4E-06	2.5E-05	1.9E-05
	Durban Bay	*Perna perna* DBN11	6.4E-06	6.4E-06	5.3E-06	6.7E-07	2.8E-07	0.0E+00	2.0E-06	3.5E-06	6.2E-06	3.5E-06	1.6E-05	9.1E-06
	Durban Bay	*All species*	2.2E-06	0.0E+00	6.7E-06	1.1E-06	8.7E-07	7.7E-07	5.2E-06	7.2E-06	1.3E-05	9.6E-06	1.7E-05	7.1E-06
	Isipingo	*Myxus capensis*	2.5E-06	0.0E+00	6.7E-06	0.0E+00	3.4E-07	0.0E+00	6.0E-07	3.3E-06	5.8E-06	1.2E-06	1.3E-05	6.0E-07
	Isipingo	*Ambassis natalensis*	2.6E-06	0.0E+00	6.8E-06	0.0E+00	5.1E-07	2.8E-07	1.4E-05	1.5E-05	2.8E-05	2.4E-05	2.5E-05	1.4E-05
	Isipingo	*Oreochromus mossambicus*	2.2E-06	0.0E+00	5.8E-06	0.0E+00	3.0E-07	0.0E+00	1.9E-07	2.6E-06	4.4E-06	4.8E-07	1.1E-05	1.9E-07
	Isipingo	*All species*	2.4E-06	0.0E+00	6.3E-06	0.0E+00	3.2E-07	0.0E+00	4.0E-07	2.9E-06	5.1E-06	8.4E-07	1.2E-05	4.0E-07
	Mngeni	*Valamugil cunnesius*	2.8E-06	0.0E+00	7.4E-06	0.0E+00	9.5E-07	6.9E-07	5.3E-06	7.3E-06	1.4E-05	1.0E-05	1.8E-05	6.0E-06

				Excess Cancer Risk										
Category	Location	Species	As (nd = ½ MDL)	As (nd = 0)	PAH (nd = ½ MDL)	PAH (nd = 0)	DDX (nd = ½ MDL)	DDX (nd = 0)	PCB (nd = ½ MDL)	PCB (nd = 0)	Aroclor (nd = ½ MDL)	Aroclor (nd = 0)	Total Cancer Risk 1	Total Cancer Risk 2
	Mngeni	*Liza dumerilii*	2.1E-06	0.0E+00	5.6E-06	0.0E+00	2.9E-07	0.0E+00	5.5E-07	2.7E-06	4.7E-06	1.1E-06	1.1E-05	5.5E-07
	Mngeni	*Liza macrolepis*	2.1E-06	0.0E+00	5.5E-06	0.0E+00	2.8E-07	0.0E+00	1.4E-07	2.4E-06	4.2E-06	2.8E-07	1.0E-05	1.4E-07
	Mngeni	*Liza tricuspidens*	2.1E-06	0.0E+00	5.6E-06	0.0E+00	2.9E-07	0.0E+00	0.0E+00	2.3E-06	4.0E-06	0.0E+00	1.0E-05	0.0E+00
	Mngeni	*Mugil cephalus*	2.5E-06	0.0E+00	6.5E-06	0.0E+00	3.3E-07	0.0E+00	0.0E+00	2.7E-06	4.7E-06	0.0E+00	1.2E-05	0.0E+00
	Mngeni	*Gerres methueni*	2.3E-06	0.0E+00	6.0E-06	0.0E+00	3.1E-07	0.0E+00	1.4E-06	3.6E-06	6.4E-06	2.8E-06	1.2E-05	1.4E-06
	Mngeni	*Ambassis natalensis*	2.6E-06	0.0E+00	7.0E-06	0.0E+00	7.4E-07	5.0E-07	3.2E-06	5.6E-06	1.0E-05	6.4E-06	1.6E-05	3.7E-06
	Mngeni	*Oreochromus mossambicus*	2.2E-06	0.0E+00	5.9E-06	8.9E-08	3.5E-07	7.6E-08	1.7E-06	3.9E-06	7.0E-06	3.5E-06	1.2E-05	1.9E-06
	Mngeni	*All species*	2.3E-06	0.0E+00	6.1E-06	1.5E-08	4.1E-07	1.3E-07	1.3E-06	3.6E-06	6.4E-06	2.5E-06	1.2E-05	1.4E-06
Adult recreational	Durban Bay	*Sphyraena jello*	5.5E-06	0.0E+00	1.5E-05	0.0E+00	3.3E-06	3.3E-06	2.5E-05	2.1E-05	4.6E-05	3.8E-05	4.9E-05	2.5E-05
Scenario 2	Durban Bay	*Valamugil buchanani*	6.0E-06	0.0E+00	1.6E-05	0.0E+00	2.6E-06	2.6E-06	2.3E-05	1.8E-05	4.1E-05	3.1E-05	4.7E-05	2.1E-05
	Durban Bay	*Myxus capensis*	5.4E-06	0.0E+00	1.5E-05	7.1E-07	1.4E-06	8.0E-07	6.3E-06	3.5E-07	1.1E-05	7.0E-07	2.8E-05	1.9E-06
	Durban Bay	*Liza dumerilii*	5.5E-06	0.0E+00	1.5E-05	4.1E-07	1.9E-06	1.5E-06	1.9E-05	1.4E-05	3.4E-05	2.6E-05	4.1E-05	1.6E-05
	Durban Bay	*Liza tricuspidens*	6.1E-06	0.0E+00	1.6E-05	0.0E+00	3.4E-06	3.4E-06	3.5E-05	3.0E-05	6.4E-05	5.4E-05	6.1E-05	3.4E-05
	Durban Bay	*Mugil cephalus*	5.8E-06	0.0E+00	3.0E-05	1.8E-05	2.2E-06	2.0E-06	1.1E-05	4.3E-06	2.1E-05	1.2E-05	4.9E-05	2.4E-05
	Durban Bay	*Pseudorhombus arsius*	5.1E-06	0.0E+00	1.4E-05	5.3E-07	1.4E-06	1.2E-06	1.4E-05	6.3E-06	2.5E-05	1.8E-05	3.4E-05	8.1E-06
	Durban Bay	*Sillago sihama*	5.6E-06	0.0E+00	1.5E-05	4.8E-07	9.4E-07	2.6E-07	1.4E-05	8.8E-06	2.5E-05	1.6E-05	3.6E-05	9.5E-06
	Durban Bay	*Ambassis gymnocephalus*	5.9E-06	0.0E+00	1.6E-05	0.0E+00	4.2E-06	4.2E-06	3.6E-05	3.2E-05	6.6E-05	5.7E-05	6.2E-05	3.6E-05
	Durban Bay	*Pomadasys commersonnii*	5.5E-06	0.0E+00	1.5E-05	0.0E+00	9.4E-07	2.7E-07	1.2E-05	6.6E-06	2.1E-05	1.2E-05	3.3E-05	6.9E-06
	Durban Bay	*Platycephalus indicus*	5.9E-06	0.0E+00	1.5E-05	0.0E+00	8.0E-07	0.0E+00	7.6E-06	1.6E-06	1.3E-05	3.2E-06	2.9E-05	1.6E-06
	Durban Bay	*Perna perna* DBN1	6.7E-05	6.7E-05	1.1E-05	0.0E+00	5.4E-07	0.0E+00	9.1E-06	5.7E-06	1.7E-05	1.1E-05	8.7E-05	7.2E-05
	Durban Bay	*Perna perna* DBN2	7.8E-05	7.8E-05	1.4E-05	1.2E-06	6.8E-07	0.0E+00	1.2E-05	7.9E-06	2.2E-05	1.5E-05	1.1E-04	8.7E-05
	Durban Bay	*Perna perna* DBN3	8.0E-05	8.0E-05	1.5E-05	1.2E-06	7.3E-07	0.0E+00	1.4E-05	1.0E-05	2.6E-05	1.8E-05	1.1E-04	9.1E-05
	Durban Bay	*Perna perna* DBN4	4.3E-05	4.3E-05	1.3E-05	0.0E+00	1.1E-06	6.6E-07	1.1E-05	7.1E-06	2.0E-05	1.3E-05	6.8E-05	5.1E-05
	Durban Bay	*Perna perna* DBN5	7.9E-05	7.9E-05	1.3E-05	0.0E+00	1.0E-06	5.5E-07	1.3E-05	8.1E-06	2.3E-05	1.6E-05	1.1E-04	8.8E-05
	Durban Bay	*Perna perna* DBN6	6.0E-05	6.0E-05	1.0E-05	0.0E+00	9.7E-07	8.0E-07	7.6E-06	4.4E-06	1.3E-05	7.7E-06	7.8E-05	6.5E-05
	Durban Bay	*Perna perna* DBN7	2.1E-05	2.1E-05	1.2E-05	1.1E-06	9.2E-07	5.5E-07	9.5E-06	6.1E-06	1.7E-05	1.1E-05	4.3E-05	2.9E-05
	Durban Bay	*Perna perna* DBN8	2.6E-05	2.6E-05	1.5E-05	7.5E-07	1.0E-06	5.4E-07	1.4E-05	9.1E-06	2.4E-05	1.6E-05	5.6E-05	3.7E-05
	Durban Bay	*Perna perna* DBN9	2.2E-05	2.2E-05	1.3E-05	0.0E+00	1.4E-06	1.1E-06	7.9E-06	3.1E-06	1.4E-05	6.3E-06	4.5E-05	2.6E-05
	Durban Bay	*Perna perna* DBN10	3.9E-05	3.9E-05	1.6E-05	6.1E-06	1.1E-06	9.2E-07	7.6E-06	3.1E-06	1.4E-05	6.3E-06	6.4E-05	4.9E-05
	Durban Bay	*Perna perna* DBN11	1.7E-05	1.7E-05	1.4E-05	1.7E-06	7.3E-07	0.0E+00	9.1E-06	5.2E-06	1.6E-05	9.2E-06	4.0E-05	2.4E-05
	Durban Bay	*All species*	5.7E-06	0.0E+00	1.7E-05	2.8E-06	2.3E-06	2.0E-06	1.9E-05	1.4E-05	3.4E-05	2.5E-05	4.4E-05	1.8E-05
	Isipingo	*Myxus capensis*	6.5E-06	0.0E+00	1.7E-05	0.0E+00	8.9E-07	0.0E+00	8.5E-06	1.6E-06	1.5E-05	3.1E-06	3.3E-05	1.6E-06
	Isipingo	*Ambassis natalensis*	6.7E-06	0.0E+00	1.8E-05	0.0E+00	1.3E-06	7.3E-07	3.9E-05	3.5E-05	7.4E-05	6.2E-05	6.4E-05	3.6E-05

				Excess Cancer Risk											
Category	Location	Species	As (nd = ½ MDL)	As (nd = 0)	PAH (nd = ½ MDL)	PAH (nd = 0)	DDX (nd = ½ MDL)	DDX (nd = 0)	PCB (nd = ½ MDL)	PCB (nd = 0)	Aroclor (nd = ½ MDL)	Aroclor (nd = 0)	Total Cancer Risk 1	Total Cancer Risk 2
	Isipingo	*Oreochromus mossambicus*	5.7E-06	0.0E+00	1.5E-05	0.0E+00	7.7E-07	0.0E+00	6.7E-06	4.8E-07	1.2E-05	1.2E-06	2.8E-05	4.8E-07
	Isipingo	*All species*	6.1E-06	0.0E+00	1.6E-05	0.0E+00	8.3E-07	0.0E+00	7.6E-06	1.0E-06	1.3E-05	2.2E-06	3.1E-05	1.0E-06
	Mngeni	*Valamugil cunnesius*	7.2E-06	0.0E+00	1.9E-05	0.0E+00	2.5E-06	1.8E-06	1.9E-05	1.4E-05	3.6E-05	2.6E-05	4.8E-05	1.6E-05
	Mngeni	*Liza dumerilii*	5.4E-06	0.0E+00	1.4E-05	0.0E+00	7.4E-07	0.0E+00	6.9E-06	1.4E-06	1.2E-05	2.8E-06	2.8E-05	1.4E-06
	Mngeni	*Liza macrolepis*	5.4E-06	0.0E+00	1.4E-05	0.0E+00	7.4E-07	0.0E+00	6.3E-06	3.6E-07	1.1E-05	7.2E-07	2.7E-05	3.6E-07
	Mngeni	*Liza tricuspidens*	5.4E-06	0.0E+00	1.4E-05	0.0E+00	7.4E-07	0.0E+00	6.1E-06	0.0E+00	1.0E-05	0.0E+00	2.7E-05	0.0E+00
	Mngeni	*Mugil cephalus*	6.4E-06	0.0E+00	1.7E-05	0.0E+00	8.7E-07	0.0E+00	7.1E-06	0.0E+00	1.2E-05	0.0E+00	3.1E-05	0.0E+00
	Mngeni	*Gerres methueni*	5.9E-06	0.0E+00	1.6E-05	0.0E+00	8.0E-07	0.0E+00	9.3E-06	3.6E-06	1.7E-05	7.2E-06	3.2E-05	3.6E-06
	Mngeni	*Ambassis natalensis*	6.8E-06	0.0E+00	1.8E-05	0.0E+00	1.9E-06	1.3E-06	1.5E-05	8.3E-06	2.7E-05	1.7E-05	4.1E-05	9.6E-06
	Mngeni	*Oreochromus mossambicus*	5.7E-06	0.0E+00	1.5E-05	2.3E-07	9.0E-07	2.0E-07	1.0E-05	4.4E-06	1.8E-05	9.0E-06	3.2E-05	4.9E-06
	Mngeni	*All species*	5.9E-06	0.0E+00	1.6E-05	3.9E-08	1.1E-06	3.3E-07	9.3E-06	3.3E-06	1.7E-05	6.5E-06	3.2E-05	3.7E-06
Adult subsistence	Durban Bay	*Sphyraena jello*	1.7E-05	0.0E+00	4.6E-05	0.0E+00	1.0E-05	1.0E-05	8.0E-05	6.7E-05	1.4E-04	1.2E-04	1.5E-04	7.7E-05
	Durban Bay	*Valamugil buchanani*	1.9E-05	0.0E+00	5.0E-05	0.0E+00	8.3E-06	8.3E-06	7.1E-05	5.8E-05	1.3E-04	9.9E-05	1.5E-04	6.6E-05
	Durban Bay	*Myxus capensis*	1.7E-05	0.0E+00	4.7E-05	2.2E-06	4.3E-06	2.5E-06	2.0E-05	1.1E-06	3.4E-05	2.2E-06	8.7E-05	5.8E-06
	Durban Bay	*Liza dumerilii*	1.7E-05	0.0E+00	4.7E-05	1.3E-06	6.0E-06	4.8E-06	5.8E-05	4.3E-05	1.1E-04	8.3E-05	1.3E-04	5.0E-05
	Durban Bay	*Liza tricuspidens*	1.9E-05	0.0E+00	5.1E-05	0.0E+00	1.1E-05	1.1E-05	1.1E-04	9.5E-05	2.0E-04	1.7E-04	1.9E-04	1.1E-04
	Durban Bay	*Mugil cephalus*	1.8E-05	0.0E+00	9.4E-05	5.7E-05	7.0E-06	6.2E-06	3.5E-05	1.3E-05	6.5E-05	3.9E-05	1.5E-04	7.7E-05
	Durban Bay	*Pseudorhombus arsius*	1.6E-05	0.0E+00	4.4E-05	1.7E-06	4.5E-06	3.8E-06	4.4E-05	2.0E-05	7.9E-05	5.7E-05	1.1E-04	2.5E-05
	Durban Bay	*Sillago sihama*	1.8E-05	0.0E+00	4.7E-05	1.5E-06	2.9E-06	8.2E-07	4.4E-05	2.8E-05	7.8E-05	5.0E-05	1.1E-04	3.0E-05
	Durban Bay	*Ambassis gymnocephalus*	1.9E-05	0.0E+00	4.9E-05	0.0E+00	1.3E-05	1.3E-05	1.1E-04	9.9E-05	2.1E-04	1.8E-04	1.9E-04	1.1E-04
	Durban Bay	*Pomadasys commersonnii*	1.7E-05	0.0E+00	4.6E-05	0.0E+00	3.0E-06	8.4E-07	3.7E-05	2.1E-05	6.5E-05	3.7E-05	1.0E-04	2.2E-05
	Durban Bay	*Platycephalus indicus*	1.8E-05	0.0E+00	4.6E-05	0.0E+00	2.5E-06	0.0E+00	2.4E-05	5.0E-06	4.2E-05	1.0E-05	1.9E-04	5.0E-06
	Durban Bay	*Perna perna* DBN1	2.1E-04	2.1E-04	3.3E-05	0.0E+00	1.7E-06	0.0E+00	2.9E-05	1.8E-05	5.3E-05	3.6E-05	2.9E-04	2.3E-04
	Durban Bay	*Perna perna* DBN2	2.5E-04	2.5E-04	4.5E-05	3.8E-06	2.1E-06	0.0E+00	3.8E-05	2.5E-05	6.7E-05	4.6E-05	3.3E-04	2.7E-04
	Durban Bay	*Perna perna* DBN3	2.5E-04	2.5E-04	4.8E-05	3.6E-06	2.3E-06	0.0E+00	4.5E-05	3.1E-05	8.1E-05	5.8E-05	2.9E-04	2.8E-04
	Durban Bay	*Perna perna* DBN4	1.3E-04	1.3E-04	4.1E-05	0.0E+00	3.5E-06	2.1E-06	3.5E-05	2.2E-05	6.3E-05	4.0E-05	2.7E-04	1.6E-04
	Durban Bay	*Perna perna* DBN5	2.5E-04	2.5E-04	4.2E-05	0.0E+00	3.2E-06	1.7E-06	4.1E-05	2.5E-05	7.3E-05	5.1E-05	3.0E-04	2.7E-04
	Durban Bay	*Perna perna* DBN6	1.9E-04	1.9E-04	3.2E-05	0.0E+00	3.0E-06	2.5E-06	2.4E-05	1.4E-05	4.2E-05	2.4E-05	1.9E-04	2.0E-04
	Durban Bay	*Perna perna* DBN7	6.6E-05	6.6E-05	3.6E-05	3.4E-06	2.9E-06	1.7E-06	3.0E-05	1.9E-05	5.2E-05	3.4E-05	1.4E-04	9.0E-05
	Durban Bay	*Perna perna* DBN8	8.2E-05	8.2E-05	4.7E-05	2.3E-06	3.3E-06	1.7E-06	4.3E-05	2.9E-05	7.6E-05	5.0E-05	1.7E-04	1.1E-04
	Durban Bay	*Perna perna* DBN9	6.9E-05	6.9E-05	4.2E-05	0.0E+00	4.3E-06	3.6E-06	2.5E-05	9.8E-06	4.5E-05	2.0E-05	1.7E-04	8.3E-05
	Durban Bay	*Perna perna* DBN10	1.2E-04	1.2E-04	5.2E-05	1.9E-05	3.5E-06	2.9E-06	2.4E-05	9.9E-06	4.3E-05	2.0E-05	1.7E-04	1.5E-04
	Durban Bay	*Perna perna* DBN11	5.2E-05	5.2E-05	4.3E-05	5.5E-06	2.3E-06	0.0E+00	2.9E-05	1.6E-05	5.1E-05	2.9E-05	1.1E-04	7.4E-05

				Excess Cancer Risk											
Category	Location	Species	As (nd = ½ MDL)	As (nd = 0)	PAH (nd = ½ MDL)	PAH (nd = 0)	DDX (nd = ½ MDL)	DDX (nd = 0)	PCB (nd = ½ MDL)	PCB (nd = 0)	Aroclor (nd = ½ MDL)	Aroclor (nd = 0)	Total Cancer Risk 1	Total Cancer Risk 2
	Durban Bay	*All species*	1.8E-05	0.0E+00	5.4E-05	8.7E-06	7.1E-06	6.3E-06	5.8E-05	4.3E-05	1.1E-04	7.8E-05	1.4E-04	5.7E-05
	Isipingo	*Myxus capensis*	2.1E-05	0.0E+00	5.4E-05	0.0E+00	2.8E-06	0.0E+00	2.7E-05	4.9E-06	4.7E-05	9.8E-06	1.0E-04	4.9E-06
	Isipingo	*Ambassis natalensis*	1.9E-05	0.0E+00	5.6E-05	0.0E+00	4.2E-06	2.3E-06	1.2E-04	1.1E-04	2.3E-04	1.9E-04	2.0E-04	1.1E-04
	Isipingo	*Oreochromus mossambicus*	1.7E-05	0.0E+00	4.7E-05	0.0E+00	2.4E-06	0.0E+00	2.1E-05	1.5E-06	3.6E-05	3.9E-06	8.7E-05	1.5E-06
	Isipingo	*All species*	1.9E-05	0.0E+00	5.1E-05	0.0E+00	2.6E-06	0.0E+00	2.4E-05	3.2E-06	4.2E-05	6.9E-06	9.6E-05	3.2E-06
	Mngeni	*Valamugil cunnesius*	2.3E-05	0.0E+00	6.0E-05	0.0E+00	7.7E-06	5.6E-06	6.0E-05	4.3E-05	1.1E-04	8.3E-05	1.5E-04	4.9E-05
	Mngeni	*Liza dumerilii*	1.7E-05	0.0E+00	4.5E-05	0.0E+00	2.3E-06	0.0E+00	2.2E-05	4.5E-06	3.8E-05	8.9E-06	8.6E-05	4.5E-06
	Mngeni	*Liza macrolepis*	1.7E-05	0.0E+00	4.5E-05	0.0E+00	2.3E-06	0.0E+00	2.0E-05	1.1E-06	3.4E-05	2.2E-06	8.4E-05	1.1E-06
	Mngeni	*Liza tricuspidens*	1.9E-05	0.0E+00	4.5E-05	0.0E+00	2.3E-06	0.0E+00	1.9E-05	0.0E+00	3.3E-05	0.0E+00	8.5E-05	0.0E+00
	Mngeni	*Mugil cephalus*	1.9E-05	0.0E+00	5.3E-05	0.0E+00	2.7E-06	0.0E+00	2.2E-05	0.0E+00	3.8E-05	0.0E+00	9.7E-05	0.0E+00
	Mngeni	*Gerres methueni*	2.0E-05	0.0E+00	4.9E-05	0.0E+00	2.5E-06	0.0E+00	2.9E-05	1.1E-05	5.2E-05	2.3E-05	1.0E-04	1.1E-05
	Mngeni	*Ambassis natalensis*	2.0E-05	0.0E+00	5.7E-05	0.0E+00	6.0E-06	4.1E-06	4.5E-05	2.6E-05	8.4E-05	5.2E-05	1.3E-04	3.0E-05
	Mngeni	*Oreochromus mossambicus*	1.8E-05	0.0E+00	4.8E-05	7.3E-07	2.8E-06	6.2E-07	3.2E-05	1.4E-05	5.7E-05	2.8E-05	1.0E-04	1.5E-05
	Mngeni	*All species*	1.9E-05	0.0E+00	4.9E-05	1.2E-07	3.4E-06	1.0E-06	2.9E-05	1.0E-05	5.2E-05	2.0E-05	1.0E-04	1.2E-05

Table 3.5. Species specific 227 g meal limits per month for fish and mussels collected in Durban Bay and the uMngeni and Isipingo River estuaries. Instances where less than 30 meals per month should be consumed are highlighted in red shading. As = arsenic, Cd = cadmium, DDX = sum p,p'-DDD, p,p'-DDD and p,p'-DDT, Hg = mercury, Se = selenium, PCB = sum polychlorinated biphenyl congeners, Aroclor = polychlorinated biphenyl Aroclor equivalents. As, Cd, DDX and PCB non-detects replaced with a value of zero for calculations. Meal Limit = number of meals that can be consumed based on all chemicals for chronic or carcinogenic health risks, but excluding Aroclor equivalents. Combined Meal Limit = number of meals that can be consumed based on chronic and carcinogenic health risks, but excluding Aroclor equivalents.

		Chronic								Carcinogenic						
Location	Species	As	Cd	Hg	Se	DDX	PCB	Aroclor	Meal Limit	As	DDX	PAH	PCB	Aroclor	Meal Limit	Combined Meal Limit
Durban Bay	*Sphyraena jello*	≥30	≥30	7	≥30	≥30	11	6	7	≥30	18	≥30	3	2	3	3
Durban Bay	*Valamugil buchanani*	≥30	≥30	≥30	≥30	≥30	13	8	13	≥30	23	≥30	3	2	3	3
Durban Bay	*Myxus capensis*	≥30	≥30	25	≥30	≥30	≥30	≥30	25	≥30	≥30	≥30	≥30	≥30	≥30	25
Durban Bay	*Liza dumerilii*	≥30	≥30	14	≥30	≥30	18	9	14	≥30	≥30	≥30	4	2	4	4
Durban Bay	*Liza tricuspidens*	≥30	≥30	7	≥30	≥30	8	5	7	≥30	18	≥30	2	1	2	2
Durban Bay	*Mugil cephalus*	≥30	≥30	≥30	≥30	≥30	≥30	20	≥30	≥30	≥30	3	14	5	3	3
Durban Bay	*Pseudorhombus arsius*	≥30	≥30	12	≥30	≥30	≥30	13	12	≥30	≥30	≥30	10	3	10	10
Durban Bay	*Silago sihama*	≥30	≥30	4	≥30	≥30	28	15	4	≥30	≥30	≥30	7	4	7	4
Durban Bay	*Ambassis gymnocephalus*	≥30	≥30	≥30	≥30	≥30	8	4	8	≥30	14	≥30	2	1	2	2
Durban Bay	*Pomadasys commersonnii*	≥30	≥30	5	≥30	≥30	≥30	21	5	≥30	≥30	≥30	9	5	9	5
Durban Bay	*Platycephalus indicus*	≥30	≥30	10	≥30	≥30	≥30	≥30	10	≥30	≥30	≥30	≥30	19	≥30	10
Durban Bay	*Perna perna* DBN1	≥30	≥30	≥30	≥30	≥30	≥30	21	≥30	1	≥30	≥30	11	5	1	1
Durban Bay	*Perna perna* DBN2	≥30	≥30	25	≥30	≥30	≥30	17	25	1	≥30	≥30	8	4	1	1
Durban Bay	*Perna perna* DBN3	≥30	≥30	28	≥30	≥30	24	13	24	1	≥30	≥30	6	3	1	1
Durban Bay	*Perna perna* DBN4	≥30	≥30	≥30	≥30	≥30	≥30	19	≥30	1	≥30	≥30	9	5	1	1
Durban Bay	*Perna perna* DBN5	≥30	≥30	28	≥30	≥30	≥30	15	28	1	≥30	≥30	8	4	1	1
Durban Bay	*Perna perna* DBN6	≥30	≥30	≥30	≥30	≥30	≥30	≥30	≥30	1	≥30	≥30	14	8	1	1
Durban Bay	*Perna perna* DBN7	≥30	≥30	≥30	≥30	≥30	≥30	23	≥30	3	≥30	≥30	10	6	3	3
Durban Bay	*Perna perna* DBN8	≥30	≥30	≥30	≥30	≥30	27	15	27	2	≥30	≥30	7	4	2	2
Durban Bay	*Perna perna* DBN9	≥30	≥30	≥30	≥30	≥30	≥30	≥30	≥30	3	≥30	≥30	19	10	3	3
Durban Bay	*Perna perna* DBN10	≥30	≥30	≥30	≥30	≥30	≥30	≥30	≥30	2	≥30	10	19	10	2	2
Durban Bay	*Perna perna* DBN11	≥30	≥30	≥30	≥30	≥30	≥30	27	≥30	4	≥30	≥30	12	7	4	4
Isipingo	*Myxus capensis*	≥30	≥30	≥30	≥30	≥30	≥30	≥30	≥30	≥30	≥30	≥30	≥30	19	≥30	≥30
Isipingo	*Ambassis natalensis*	≥30	≥30	≥30	≥30	≥30	7	4	7	≥30	≥30	≥30	2	1	2	2
Isipingo	*Oreochromus mossambicus*	≥30	≥30	≥30	≥30	≥30	≥30	≥30	≥30	≥30	≥30	≥30	≥30	≥30	≥30	≥30
Mngeni	*Valamugil cunnesius*	≥30	≥30	≥30	≥30	575	18	9	18	≥30	≥30	≥30	4	2	4	4
Mngeni	*Liza dumerilii*	≥30	≥30	≥30	≥30	≥30	≥30	≥30	≥30	≥30	≥30	≥30	≥30	21	≥30	≥30
Mngeni	*Liza macrolepis*	≥30	≥30	≥30	≥30	≥30	≥30	≥30	≥30	≥30	≥30	≥30	≥30	≥30	≥30	≥30
Mngeni	*Liza tricuspidens*	≥30	≥30	20	≥30	≥30	≥30	≥30	20	≥30	≥30	≥30	≥30	≥30	≥30	20

Location	Species	Chronic								Carcinogenic						Combined Meal Limit
		As	Cd	Hg	Se	DDX	PCB	Aroclor	Meal Limit	As	DDX	PAH	PCB	Aroclor	Meal Limit	
Mngeni	*Mugil cephalus*	≥30	≥30	≥30	≥30	≥30	≥30	≥30	≥30	≥30	≥30	≥30	≥30	≥30	≥30	≥30
Mngeni	*Gerres methueni*	≥30	≥30	12	≥30	≥30	≥30	≥30	12	≥30	≥30	≥30	17	8	17	12
Mngeni	*Ambassis natalensis*	≥30	≥30	≥30	≥30	≥30	29	15	29	≥30	≥30	≥30	7	4	7	7
Mngeni	*Oreochromus mossambicus*	≥30	≥30	≥30	≥30	≥30	≥30	27	≥30	≥30	≥30	≥30	14	7	14	14

- It is unknown whether concentrations of chemicals in mussels and fish were historically or will in future remain at the levels identified in this study over the 30 and 70 year exposure periods assumed for chronic and carcinogenic health risks respectively. If the concentrations were historically different and/or change in future, this will alter the risk.
- In this study an acceptable Excess Cancer Risk of 1×10^{-5} was used as this is the most common risk level used internationally. However, some jurisdictions use an acceptable Excess Cancer Risk of 1×10^{-4}, partly due to the significant health benefits associated with fish and shellfish consumption (see below), but also for political (economic) reasons. Using an acceptable Excess Cancer Risk of 1×10^{-4} results in a very different estimate of the potential carcinogenic risk facing recreational and subsistence consumers.
- Potential chronic and/or carcinogenic health risks for recreational and/or subsistence consumers were associated with the consumption of mussels at all collection locations in Durban Bay. However, there was little evidence in the field that mussels were being harvested to any significant degree. Thus, there were no bare patches between mussels, or patches of mussels of a noticeably smaller size compared to neighbouring mussels, on navigation markers. The most likely reason is that it is difficult to access stands of mussels without a vessel, as they are generally restricted to floating structures in Durban Bay. This suggests there is limited consumption of mussels collected in the Bay.
- Relatively 'large' individuals of various commonly consumed fish were analysed. In many fish, particularly piscivores, concentrations of contaminants increase with size (age), meaning that the consumption of larger fish increases the risk of exposure to contaminants in their tissue. However, subsistence fishers in South Africa often retain all fish caught (*e.g.* Ellender *et al*., 2009), which may reduce the risk of exposure to contaminants. Conversely, large individuals of some fish species were not analysed and hence the risk for these species may be understated. This is most appropriate to the barracuda *Sphyraena jello* and the spotted grunter *Pomadasys commersonnii*.
- It is always difficult deciding whether chemical concentrations below the method detection limit should be replaced with a value equivalent to one-half the method detection limit or a value of zero, apart from instances where all concentrations for a chemical are below the method detection limit. As discussed above the degree of risk posed by some chemicals in some fish species and mussels differed considerably if concentrations below the method detection limit should be replaced with a value equivalent to one half the method detection limit or a value of zero.
- For many fish species the most significant potential health risks were attributable to polychlorinated biphenyls. However, only 21 of the possible 209 congeners were analysed, because of technical and cost implications. The total concentration calculated from these congeners undoubtedly represents an underestimate of the total polychlorinated biphenyl concentration and hence an underestimate of the potential risk. Although many workers use a factor to calculate the 'total' polychlorinated biphenyl concentration for risk assessment purposes when relatively few congeners are analysed, there is no universal conversion factor.
- Although the consumption rate (meal size) was considered to be proportional to body size, children, infants and the developing foetus may face greater health risks and an alternate approach could have been to modify the consumption rate for these sensitive segments of the population, and for females that are pregnant, intending to become pregnant, and nursing.
- The risk assessment for some fish species was based on the analysis of tissue for a single specimen. Depending on whether the specimen had a lower or higher than average concentration of any particular chemical in its tissue the health risk may have been under- or over-estimated. Examples of variability in chemical concentrations that may exist between the tissue of individuals of the same species caught in the same system are provided by mercury concentrations in the silver sillago *Sillago sihama* and the spotted grunter *Pomadasys commersonnii* caught in Durban Bay (see Figure 3.2).
- The risk assessment pertains only to the fish species caught. Several species of fish that are commonly retained for consumption in Durban Bay and uMngeni River estuary by recreational and subsistence consumers were not analysed. For example, one of the most commonly retained fish by shoreline

fishers in Durban Bay is the white karanteen *Crenidens crenidens* (Table 3.1), yet no individuals of this species were analysed. The most commonly retained fish by shoreline fishers in Durban Bay and the uMngeni River estuary is *Mugil cephalus*, yet only three and one individuals were analysed for these systems respectively.

However, even if these limitations and uncertainties are taken into account and a conservative approach is followed, by replacing non-detects with a value of zero, by only considering fish species that are likely to be regularly consumed (*e.g.* mullet, spotted grunter), and by considering the highest meal consumption rate as six 227 g meals per month, then it is evident that humans consuming fish caught in Durban Bay and the uMngeni and Isipingo River estuaries face potential chronic and carcinogenic health risks. The most notable risks are for fish caught in Durban Bay. However, for individual species the highest Hazard Quotient was 1.21 for the spotted grunter *Pomadasys commersonnii* in Durban Bay, which is a relatively low quotient. The highest Excess Cancer Risk was 3.0×10^{-5} for the mullet *Liza tricuspidens* in Durban Bay, or three possible extra incidences of cancer per 100 000 population. If a varied diet of commonly consumed fish is considered then the highest Hazard Index was 0.98 and the highest Total Cancer Risk was 1.8×10^{-5}. Although the Hazard Indices and Total Cancer Risks are relatively low, in many states in the United States of America and in other countries these would still result in the issuance of a consumption advisory.

As a further variant on the approach followed above the Excess Cancer Risk was calculated for a varied diet of fish likely to be commonly consumed by recreational and subsistence fishers, using the same input parameters as above apart from the fact that the exposure duration for carcinogenic risks was taken as 30 years rather than 70 years. Following this approach the highest total Cancer Risk decreased from 1.8×10^{-5} to 7.9×10^{-6} for Durban Bay, from 1.0×10^{-6} to 4.4×10^{-7} for the Isipingo River estuary, and from 3.7×10^{-6} to 1.6×10^{-6} for the uMngeni River estuary. In other words, under this scenario there would be no evident health risk.

It is important to place the carcinogenic risks into perspective, by comparing them to the cancer incidence rate for the South African population. According to the latest data (for 2007) from the National Cancer Registry, South African males have an overall age standardised cancer incidence rate of 110.69 per 100 000, while South African females have an age standardised cancer incidence rate of 99.47 per 100 000. Thus, at the highest Excess Cancer Risk identified for commonly consumed fish in this study, namely 2.5×10^{-4}, an additional 25 individuals (male and female) per 100 000 population may develop cancer in their lifetime. This increases to 33 individuals if the Total Cancer Risk is considered.

Despite the uncertainties associated with this risk assessment, as a precaution it is recommended that recreational and subsistence fishers not consume more 227 g meals of fish and mussels than those indicated in the column denoted Combined Meal Limit in Table 3.5. This represents the number of meals of this size that can be consumed without chronic and carcinogenic health risks by a person with a body weight of 67 kilograms. For fish the main drivers of meal consumption limits were typically polychlorinated biphenyls, but mercury for some fish species. It is important to note the meal consumption limits presented in Table 3.5 were calculated by replacing non-detects with a concentration equivalent to zero, and would be lower if non-detects were replaced by a concentration equivalent to one half the method detection limit. The meal consumption limits would also be lower for the majority of fish species if Aroclor equivalents were used in the calculations instead of polychlorinated biphenyl concentrations based on congener concentrations. The fewest meals (two) of fish that should be consumed per month are for the mullet *Liza tricuspidens* and the ambassid *Ambassis gymnocephalus* in Durban Bay, and the ambassid *Ambassis natalensis* in the Isipingo River estuary. It is, however, worth noting that the ambassids appear to be seemingly rarely or never consumed (see Table 3.2) and that the meal consumption limit for *Liza tricuspidens* was based on chemical concentrations analysed in a single specimen. However, five or fewer meals of the majority of fish species caught in Durban Bay, including the species most commonly retained

by shoreline and boat fishers, namely the spotted grunter *Pomadasys commersonnii* (see Table 3.2), should be consumed per month. *Pomadasys commersonnii* is also one of the most commonly retained fish species by shoreline fishers in the uMngeni River estuary, but was not caught in this estuary for this study (note that vessel based fishing is not permitted in the uMngeni River estuary). Considerably more meals of 'edible' fish caught in the uMngeni and Isipingo River estuaries can be consumed compared to Durban Bay with the obvious exception of *Valamugil cunnesius*, although the number of species analysed was smaller in comparison to Durban Bay. For mussels the main drivers of meal consumption limits were inorganic arsenic and polychlorinated biphenyls (Table 3.5). It is worth noting there are no documented cases of arsenic related toxicity in humans or mammals through the consumption of fish and shellfish (Kaise *et al*., 1985; Yamauchi *et al.*, 1986; Edmonds and Francesconi, 1993). It is worth noting further that the inorganic arsenic concentration in rice and grains is typically somewhat higher compared to fish and shellfish, even though the total arsenic concentration is usually lower in these foods.

It is important to note that children under the age of 12 and females that are pregnant, intending to become pregnant or are nursing should consume fewer meals of fish and shellfish than indicated in Table 3.5. Authorities in some countries in fact recommend that females of childbearing age, including those that are pregnant, intend to become pregnant or are nursing, restrict their consumption of certain fish to a single meal per month and avoid eating fish that are known to accumulate mercury and other contaminants to high concentrations in their tissue altogether, especially during pregnancy and while breastfeeding (*e.g.* USFDA, 2003). This is to protect the developing foetus and nursing infant from excessive exposure to contaminants, either through transfer from the mother across the placenta in the womb or through milk during breastfeeding. The developing foetus, infants and children are particularly susceptible to mercury as their nervous systems develop, since mercury is a known neurotoxicant and excessive exposure to this chemical may lead to mental impairment, impaired coordination and developmental abnormalities (USEPA, 1997). The effects of chronic low-level mercury exposure on adults are less clear, but may include increased risk of cardiovascular disease (Mozaffarian, 2009).

Although the consumption of fish is recognised as the most important route of exposure to contaminants and fish and shellfish and consumption advisories are routinely issued in many countries to protect consumers, research has linked seafood in diets to numerous health benefits for developing foetuses, infants and adults. These include improved vision, increased pregnancy length and improved cognitive development for infants and young children, and lower risk of heart disease (Daviglus *et al*., 2002; Daniels *et al*., 2004; Oken *et al*., 2005; IOM, 2006; Mozaffarian and Rimm, 2006; Hibbeln *et al*., 2007). Fish are an excellent low-fat source of protein and one of the best sources of long-chain omega-3 fatty acids (USEPA, 2009). Certain of these fatty acids cannot be synthesised by humans and are required in the diet (IOM, 2005). Since concentrations of certain of these fatty acids are low in other foods, fish or fish oil is by far the most important dietary source (Marszalek and Lodish, 2005). Fish is the most significant source of naturally-occurring Vitamin D. Health professionals and government advisory committees (*e.g.* Scientific Advisory Committee on Nutrition of the United Kingdom (SACN, 2004) and the United States Dietary Guidelines Advisory Committee endorse the consumption of fish because of the health benefits except in cases where health advisories have been issued. They advise that consumers shift from high risk to low risk fish (*e.g.* Cohen, 2006). The American Heart Association recommends the consumption of at least two servings of fish per week (125 g uncooked fish per serving; Levenson and Axelrad, 2006). The USEPA (2004) also recommends consuming two fish meals per week, but of 170 g per serving. It is this advice relative to fish consumption advisories that recommend limiting the consumption of fish from certain water bodies that tends to confuse consumers. The National Oceanic and Atmospheric Association even states on its website that "Evidence shows that the health benefits from consuming a variety of seafood in the amounts recommended vastly outweigh the health risks associated with potential contaminants, including mercury and PCBs." Nevertheless, because of the potential health risks posed by contaminant concentrations in fish and mussels in Durban Bay and the uMngeni and Isipingo River estuaries to human consumers it is

recommended the meal limits provided in Table 3.5 be adhered to until a detailed risk assessment can be performed. Children under the age of 12 and females that are pregnant, intending to become pregnant or are nursing should consume fewer meals of fish and shellfish than indicated in Table 3.5.

4.5 CONCLUSIONS

- Fish caught and mussels collected in Durban Bay and in the uMngeni and Isipingo River estuaries in 2013 had accumulated polycyclic aromatic hydrocarbons, DDX and polychlorinated biphenyls in their tissue, while one fish species in Durban Bay had also accumulated a low concentration of dieldrin in its tissue.
- The suite of organic chemicals detected in the tissue of fish and mussels generally reflected the suite of chemicals detected in sediment within the catchment of each system studied. A notable exception was chlordane, which was detected in sediment at one station in 2011 and relatively frequently in 2012, but was never detected in the tissue of fish and mussels. As stated above, dieldrin was detected in the tissue of a single fish species but was never detected in sediment. The fish and mussels sampled were thus suitable sentinels for organic contaminant monitoring in the catchments of Durban Bay and uMngeni and Isipingo River estuaries.
- Copper, chromium, manganese, mercury, lead and zinc were accumulated to above background concentrations by mussels at most or all collection locations in Durban Bay. Each of these metals apart from manganese are widespread and in some cases significant contaminants of sediment in Durban Bay. However, cadmium and nickel are also widespread and/or significant contaminants of sediment in Durban Bay, yet there was no evidence that mussels in the Bay had accumulated these metals to higher than background concentrations. In fact, mussels in Durban Bay typically had lower cadmium and nickel concentrations in their tissue compared to mussels collected along the eThekwini shoreline.
- Metal concentrations in fish were, with some exceptions, broadly comparable between species and between fish in the different systems studied. The notable exceptions were *Sillago sihama*, which accumulated arsenic to far higher concentrations than other fish species, the ambassids *Ambassis gymnocephalus* and *Ambassis natalensis*, which had various metals present in their tissue at considerably higher concentrations compared to other fish, and for mercury, which was generally present at higher concentration in the tissue of fish in Durban Bay compared to the uMngeni and Isipingo River estuaries.
- The small, shoaling ambassids *Ambassis gymnocephalus* and *Ambassis natalensis* had accumulated higher concentrations of numerous chemicals in their tissue compared to other fish species and may prove to be useful sentinel species for identifying whether metals and organic chemicals are likely to be accumulating in sediment in estuaries and in the tissue of larger estuarine fish that are consumed by recreational and subsistence fishers. If so, this will considerably reduce monitoring costs as these fish are typically more abundant and far easier to catch compared to larger fish species, which are typically analysed for such studies.
- The concentrations of some chemicals in the tissue of fish and mussels caught or collected in Durban Bay and the uMngeni and Isipingo River estuaries were high by international standards, although direct comparison of data to international studies should be treated with caution because of different analytical methods used, different suites of chemicals analysed (*e.g.* number of polychlorinated biphenyl congeners), and different species and/or sizes of fish analysed.
- The finding that fish and mussels had accumulated contaminants in their tissue is important as it confirms that various metals, polycyclic aromatic hydrocarbons, polychlorinated biphenyls and DDX were in a bioavailable form in each of the systems studied and may thus be posing a toxic risk to other fauna, including sediment-dwelling organisms, organisms that are regularly in close contact with sediment, and piscivorous birds and otters amongst others.
- Recreational and subsistence fishers that consume fish and mussels caught or collected in Durban Bay and the uMngeni and Isipingo River estuaries face potential carcinogenic and non-carcinogenic health risks due to exposure to contaminants accumulated by these organisms. The most significant risks are

for recreational and subsistence fishers that consume fish and mussels caught or collected in Durban Bay, which agrees with the more widespread and significant contamination of sediment in the Bay and in its catchment.

- Although there are limitations and uncertainties associated with the risk assessment component of this study, it is nevertheless recommended that recreational and subsistence fishers restrict the number of meals of fish and mussels they consume each month because of the potential risks associated with exposure to chemicals these organisms have accumulated in their tissue. Infants and children under 12 years age, and females that are pregnant, intending to become pregnant or are nursing, should restrict consumption of fish and mussels caught or collected in each of the systems studied to below the meal limits recommended in this study.
- There are numerous health benefits associated with the consumption of fish and shellfish. Thus, while recreational and subsistence consumers should be warned against eating certain fish caught and mussels collected in Durban Bay and the uMngeni and Isipingo River estuaries, they should not be advised to limit fish consumption altogether but to consume fish caught in other estuaries in the eThekwini area, or fish purchased in retail stores.

CHAPTER 5: OVERALL CONCLUSIONS AND RECOMMENDATIONS

5.1 OVERALL CONCLUSIONS

This overarching objective of this study was to improve the understanding on whether polycyclic aromatic hydrocarbons, polychlorinated biphenyls, and organochlorine and organophosphorous pesticides are widespread and significant contaminants of sediment and biological tissue in aquatic ecosystems in the eThekwini area of KwaZulu-Natal, and if so to determine whether they are cause for concern from an ecological and human health risk perspective. The eThekwini area was used as a case study, under the assumption that contamination trends evident in this large coastal city may be replicated in other coastal cities. The findings and recommendations arising from this study may thus be applicable to other coastal cities in South Africa.

The findings showed that polycyclic aromatic hydrocarbons, polychlorinated biphenyls, and DDT and metabolites were widespread and at times significant contaminants of sediment in rivers, estuaries and canals in the eThekwini area. Chlordanes were less frequent, but often significant contaminants of sediment in the survey performed in 2012. At numerous stations, specifically in catchments that are urbanised and industrialised, the magnitude of contamination was sufficient to suspect these chemicals were posing an acute toxic risk to sediment-dwelling organisms. This conclusion was through the comparison of contaminant concentrations to sediment quality guidelines. Although toxicity testing using the H4IIE cell bioassay confirmed toxicity in some sediment samples, there was often only a weak correlation between contaminant concentrations and toxicity. Confirmation of the potential toxic risk posed by the organic chemicals, but particularly polychlorinated biphenyl, was provided by the analysis of contaminant concentrations in the tissue of fish caught and mussels collected in Durban Bay and in the uMngeni and Isipingo River estuaries. This showed that contaminant concentrations in many fish species and in mussels were high enough to pose a potential chronic and carcinogenic health risk to human consumers (and by implication other organisms). This finding has important implications in that it calls for the more frequent monitoring of contaminant monitoring in fish and shellfish and the communication of the findings to recreational and subsistence fishers. Commissioning such monitoring and communicating the findings will largely be the responsibility of local municipalities and/or provincial government departments, and budgets need to be allocated for this purpose.

The findings of this study motivate for similar studies in other coastal cities. Of particular concern in the eThekwini area was the widespread and at times significant contamination of sediment by polychlorinated biphenyls and the accumulation of these chemicals in the tissue of fish and mussels. Polychlorinated biphenyls are highly toxic and pose significant ecological and human health risks. Based on this finding, in the eThekwini area at least there is need for the routine monitoring of these contaminants in aquatic monitoring programmes. Whether similar problems exist in coastal cities in South Africa is unknown.

Although not discussed in this report a collaborative study by the CSIR and Virginia Institute of Marine Sciences on sediment samples collected for the survey discussed in Chapter 1 identified significant and widespread brominated flame retardant contamination of sediment in the eThekwini area (La Guardia *et al*., 2013; see Appendix 1). In fact, brominated flame retardant concentrations in some systems rival those in the Pearl River Delta area of China, where a significant proportion of the world's demand for flame retardants is met, and exceed concentrations in parts of the United States of America (La Guardia *et al*., 2013). Brominated flame retardants are persistent, bioaccumulative and lipophilic, with the result that they may pose similar ecological and human risks to polychlorinated biphenyls. However, little is known on whether brominated flame retardants are widespread and significant contaminants of sediment and biological tissue in South African coastal ecosystems, a situation that warrants further attention.

This study has provided evidence for significant sources of organic and metal contaminants to aquatic ecosystems in the Durban Bay catchment. Inflows from the Amanzimnyama River, Island View Canal, Bayhead Canal, and numerous stormwater outfalls are important vectors for the introduction of contaminants to Durban Bay. There is also evidence that certain port activities are significant sources of contaminants to the Bay. The sources of contaminants need to be identified, controlled and reduced if there is to be any improvement in water and sediment quality in Durban Bay. This will reduce the uptake of contaminants by fish, shellfish and other biota, and thereby reduce potential health risks posed by contaminants in fish and shellfish to human consumers. An Estuarine Management Plan for Durban Bay has been formulated and is in the process of being updated. The plan recognises the need for a catchment scale approach to the sustainable management of the Bay. The findings of this study can be incorporated into the Estuarine Management Plan and used to identify and prioritise areas of the catchment where contaminant source identification, reduction and control procedures should be implemented.

5.2 RECOMMENDATIONS

- Based on the findings of this study, it is recommended that similar studies be performed in other cities along the South African coastline. This will inform whether the trends in metal and organic chemical contamination of sediment and the accumulation of organic chemicals by fish and shellfish in the eThekwini area is also relevant to these cities. These studies should be used to inform whether metals and organic chemicals should be routinely analysed in sediment, fish and shellfish as part of aquatic monitoring programmes. The ultimate purpose of these studies should be to inform whether and what management intervention is required to control and reduce the sources of contaminants to coastal aquatic ecosystems.
- Polycyclic aromatic hydrocarbons were ubiquitous in sediment in the eThekwini area, and in catchments where the predominant land-use is urban or industrial were likely to have been predominantly derived from anthropogenic sources. Based on the scientific literature it seems inevitable this ubiquity will apply to other cities along the South African coastline, and indeed also inland cities. It is recommended, therefore, that polycyclic aromatic hydrocarbons should routinely be analysed in sediment as part of aquatic monitoring programmes in urbanised and industrialised areas. Municipal authorities should make allowance in budgets for such monitoring. In this context, it is strongly recommended that both parent and alkylated polycyclic aromatic hydrocarbons should be analysed, to facilitate source tracking. However, analysing for alkylated polycyclic aromatic hydrocarbons has significant cost implications and the decision on whether to analyse for these hydrocarbons should be made on a case by case basis.
- There are significant sources of polychlorinated biphenyls in highly urbanised and industrialised catchments in the eThekwini area, as reflected in concentrations of these chemicals analysed in sediment for this study. A more comprehensive assessment of the spatial extent and magnitude of contamination of sediment by these chemicals should be performed, for the purpose of source identification, reduction and control. In this context, all 209 possible congeners should be analysed. However, recognising that analyses for all possible 209 congeners is expensive, particularly for routine monitoring, this study should concurrently evaluate the efficacy of using enzyme-linked immunosorbent assay (ELISA) tests as a rapid screening tool for polychlorinated biphenyls in South Africa. This is because ELISA testing is far cheaper than instrumental analysis.
- Although the use of sediment quality guidelines as a tool for assessing sediment quality has numerous limitations (see discussion this report), sediment quality guidelines provide a useful tool for screening contaminant concentrations in sediment so as to prioritise sites that require further attention (*e.g.* through biological assessment). There are sediment quality guidelines for organic chemicals in South African freshwater and coastal ecosystems, and the only metal guidelines are those used for determining whether sediment identified for dredging in South African ports is of a suitable quality for openwater disposal. Because of this lack of sediment quality guidelines there is no consistency in the use of international sediment quality guidelines by South African researchers. There is, therefore, a need

to define sediment quality guidelines for freshwater and coastal ecosystems in South Africa. The guidelines should preferably be derived using co-occurring data on sediment contaminant concentrations, sediment toxicity, and benthic invertebrate community structure and composition. However, as no sediment toxicity testing procedures have been defined for South African freshwater and coastal ecosystems (see below), and generating such data will be both time consuming and expensive, as an interim measure it will be necessary to adopt international sediment quality guidelines for both metals and organic chemicals. However, it is likely that international sediment quality guidelines will not be appropriate to South African freshwater ecosystems, due to differences in the geology of sediment parent material. Sediment quality guidelines should thus only be defined after baseline concentrations for toxicologically significant metals in sediment have been defined for freshwater ecosystems in different areas of South Africa. There is, therefore, an urgent need to define baseline concentrations to toxicologically significant metals in South African freshwater ecosystems. It is further recommended that the Water Research Commission, in partnership with relevant local and national government departments (*e.g.* the Department of Environmental Affairs) establish a working group that is mandated with identifying water and sediment quality guidelines for organic chemicals, and subsequently for metals once baseline concentrations for different areas of South Africa have been defined. This working group should also be mandated with identifying research priorities in this context.

- Although the chemical analysis of sediment can be used to identify whether sediment is contaminated, a significant limitation is that this does not provide an understanding on whether the contaminants are in a bioavailable form. This is important since contaminants can only exert a toxic effect if they are in a bioavailable form, that is, in a form that can cross biological membranes. In this study, although concentrations of several organic contaminants exceeded sediment quality guidelines and were thus identified as cause for concern, it is unknown whether these were actually exerting a toxic effect. It is also uncertain whether other potential contaminants that were not measured may have been causing toxicity. There is, therefore, a need for the development and validation of whole sediment toxicity testing procedures for freshwater and coastal ecosystems in South Africa, as a tool for determining whether contaminants in sediment are exerting a toxic effect on sediment-dwelling organisms.
- The concentrations of several chemicals in the tissue of fish caught and mussels collected in Durban Bay and the uMngeni and Isipingo River estuaries were high enough to pose a potential risk to the health of human consumers. The most notable were polychlorinated biphenyls and mercury. Since it was never the intent of this study to perform a comprehensive human health risk assessment, it is recommended that a comprehensive risk assessment be performed. This study should focus on the analysis of at least ten individuals of target species, which should include species that are commonly consumed by recreational and subsistence fishers in addition to ambassids (see below). Analysing ten individuals represents a compromise between a sufficient sample size to allow an estimate of variability in contaminant accumulation between individuals and the costs of sample analysis. However, because subsistence consumers are likely to retain fish of a range of sizes it is recommended that for the two to three most commonly consumed fish species the relationship between tissue contaminant concentrations and fish size be assessed. The suite of analytes targeted should include those recommended by the United States Environmental Protection Agency. However, such analyses will be extremely expensive and it may be worthwhile to restrict analyses at the outset to polychlorinated biphenyls, mercury and toxaphene. In this context, all possible 209 polychlorinated biphenyl congeners in addition to Aroclors should be analysed.
- A key unknown in the context of determining the potential human health risk posed by contaminants in fish and shellfish tissue are fish and shellfish consumption rates for South African recreational and subsistence fishers. Default consumption rates for the population of the United States of America were thus used. Although these probably encompass consumption rates for the South African population, this is unknown. It is thus recommended that a survey of fish and shellfish consumption rates for recreational and subsistence consumers in the eThekwini area of KwaZulu-Natal be performed. This

study should also determine the how long recreational and subsistence have fished in Durban Bay, whether these fishers are aware of the risk posed by contaminants in fish and shellfish to their health, and whether their consumption patterns are likely to change knowing that contaminants in fish and shellfish in the Bay pose a potential risk to their health. This study is important since fish caught in local estuaries are evidently an important source of protein for economically marginalised sections of the population, yet there is a distrust that any advice against the eating of fish because they pose a health risk is to restrict the catching of fish by these fishers.

- Based on the findings of this study there is a possibility that recreational and subsistence consumers in other large coastal cities may also face potential health risks through the consumption of fish and shellfish caught and collected in estuaries and indeed also the freshwater reaches of catchments. It is, therefore, recommended that the potential risk of exposure to contaminants through a fish and shellfish consumption pathway be extended to other large coastal cities. In fact, a comprehensive assessment of the risks posed by contaminants in fish and mussels in coastal cities should be performed annually, or at least every two years. The resultant information should be communicated to recreational and subsistence fishers, to enable them to make an informed decision on whether to continue catching and consuming fish in contaminated coastal ecosystems.
- This study has highlighted the potential use of small, forage fish (specifically ambassids) as sentinels for contaminant monitoring in South African estuaries, based on the fact that they accumulated numerous contaminants in their tissue to high concentrations. Also, these fish are abundant and far easier to catch compared to other fish, which will reduce the costs associated with fish collection. It is recommended that a study that compares concentrations of chemicals in the tissue of ambassids and larger fish between putatively contaminated and uncontaminated estuarine ecosystems in the eThekwini area of KwaZulu-Natal be performed, as a case study on the potential use of these fish as sentinels for contaminant monitoring. The study should aim to resolve whether ambassids naturally accumulate higher metal concentrations in their tissue compared to other fish, particularly fish that are frequently consumed. The relationship between chemical concentrations in the tissue of ambassids and larger commonly consumed fish should be explored to determine whether concentrations in ambassids can be used to predict likely concentrations in larger, commonly consumed fish. The study should also investigate the importance of small, forage fish as a vector for the transfer of contaminants through estuarine food webs, including to higher trophic level organisms such as birds.

LIST OF REFERENCES

ADAMS MA, BOLGER PM, GUNDERSON EL (1994) Dietary intake and hazards of arsenic. In: Chappell WR, Abernathy CO, Cothern CR (Eds), *Arsenic: Exposure and Health*. Science and Technology Letters, Northwood, UK.

AGUSA T, KUNITO T, SUDARYANTO A, MONIRITH I, KAN-ATIREKLAP S, IWATA H, ISMAIL A, SANGUANSIN J, MUCHTAR M, TANA TS and TANABE S (2007) Exposure assessment for trace elements from consumption of marine fish in Southeast Asia. *Environmental Pollution* 145: 766-777.

ALEXANDER J, FRYLAND L, HEMRE GI, JACOBSEN BK, LUND E, MELTZER HM and SKRE JU (2007) *A comprehensive assessment of fish and other seafood in the Norwegian diet*. Norwegian Scientific Committee for Food Safety, Oslo, Norway.

ALLEN MJ, DIEHL DW and ZENG EY (2004) *Bioaccumulation of contaminants in recreational and forage fishes in Newport Bay, California in 2000-2002*. Southern California Coastal Water Research Project.

ANTIZAR-LADISLAO B (2009) Polycyclic aromatic hydrocarbons, polychlorinated biphenyls, phthalates and organotins in northern Atlantic Spain's coastal marine sediments. *Journal of Environmental Monitoring* 11: 85-91.

ARMBRUSTER G, GEROW KG, GUTENMANN WH, LITTMAN CB and LISK DJ (1987) The effects of several methods of fish preparation on residues of polychlorinated biphenyls and sensory characteristics in striped bass. *Journal of Food Safety* 8: 235-244.

ASHLEY JTF and BAKER JE (1999) Hydrophobic organic contaminants in surficial sediment of Baltimore Harbor: inventories and sources. *Environmental Toxicology and Chemistry* 18: 838-849.

NYC (2004) *New York City Asian Fish Market Study*. Online at: http://www.nyc.gov/html/doh/html/ environmental/mercury-mkt-study.shtml

ATSDR (AGENCY FOR TOXIC SUBSTANCES AND DISEASE REGISTRY) (2000) Toxicological Profile for *Polychlorinated Biphenyls.* Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry. Online at: http://www.atsdr.cdc.gov/ toxprofiles/tp17.html

AWOFOLU RO and FATOKI OS (2003) Persistent organochlorine pesticide residues in freshwater systems and sediments from the Eastern Cape, South Africa. *Water SA* 29: 323-330.

AZMAT R and TALAT R (2006) Metals contamination in edible carnivorous fishes of Arabian Sea. *Journal of Applied Sciences* 6: 1974-1977.

BAARS AJ, BAKKER MI, BAUMANN RA, BOON PE, FREIJER JI, HOOGENBOOM LAP, HOOGERBRUGGE R, VAN KLAVEREN JD, LIEM AKD, TRAAG WA and DE VRIES J (2004) Dioxins, dioxin-like PCBs and non-dioxin-like PCBs in food- stuffs: occurrence and dietary intake in The Netherlands. *Toxicology Letters* 151: 51-61.

BARAKAT AO, KIM M, QIAN Y and WADE TL (2002) Organochlorine pesticides and PCB residues in sediments of Alexandria Harbour, Egypt. *Marine Pollution Bulletin* 44: 1421-1434.

BARNHOORN, IEJ, BORNMAN MS, VAN RENSBURG CJ and BOUWMAN H (2009) DDT residues in water, sediment, domestic and indigenous biota from a currently DDT-sprayed area. *Chemosphere* 77: 1236-1241.

BARRICK R, BECKER S, BROWN L, BELLER H and PASTOROK R (1988) *Sediment quality values refinement: 1988 update and evaluation of Puget Sound AET. Vol 1*. Prepared for the Puget Sound Estuary Program, Office of Puget Sound. PTI Contract C717-01, PTI Environmental Services, WA.

BASTON DS and DENISON MS (2011) Considerations for potency equivalent calculations in the Ah receptor-based CALUX bioassay: Normalization of superinduction results for improved sample potency estimation. *Talanta* 83: 1415-1421.

BATTERMAN SA, CHERNYAK SM, GOUNDEN Y, MATOOANE M and NAIDOO RN (2008) Organochlorine pesticides in ambient air in Durban, South Africa. *Science of the Total Environment* 397: 119-130.

BAUDRIMONT M, SCHÄFER J, MARIE V, MAURY-BRACHET R, BOSSY C, BOUDOU A and BLANC G (2005) Geochemical survey and metal bioaccumulation of three bivalve species (*Crassostrea gigas*, *Cerastoderma edule* and *Ruditapes philippinarum*) in the Nord Médoc salt marshes (Gironde estuary,

France). *Science of the Total Environment* 337: 265-280.

BAUMARD P, BUDZINSKI H, GARRIGUES P, SORBE JC, BURGEOT T and BELLOCQ J (1998) Concentrations of PAHs (Polycyclic Aromatic Hydrocarbons) in various marine organisms in relation to those in sediments and to trophic level. *Marine Pollution Bulletin* 36: 951-960.

BAUMARD P, BUDZINSKI H and GARRIGUES P (1998) Determination of polycyclic aromatic hydrocarbons (PAHs) in sediments and mussels of the Western Mediterranean sea. *Environmental Toxicology and Chemistry* 17: 765-776.

BAUMARD P, BUDZINSKI H, GUARRIGUES P, DIZER H and HANSEN PD (1999) Polycyclic aromatic hydrocarbons in recent sediments and mussels (*Mytilus edulis*) from the Western Baltic Sea: occurrence, bioavailability and seasonal variations. *Marine and Environmental Research* 47: 17-47.

BAYEN S, THOMAS GO, LEE HK and OBBARD JP (2004) Orgaonchlorine pesticides and heavy metals in green mussel, *Perna viridis*, in Singapore. *Water, Air, and Soil Pollution* 155: 103-116.

BEHNISCH PA, HOSOE K and SAKAI S (2001) Bioanalytical screening methods for dioxins and dioxin-like compounds-a review of bioassay/biomarker technology. *Environment International* 27: 413-439.

BELABED BE, LAFFRAY X, DHIB A, FERTOUNA-BELAKHAL M, TURKI S and ALEYA L (2013) Factors contributing to heavy metal accumulation in sediments and in the intertidal mussel *Perna perna* in the Gulf of Annaba (Algeria). *Marine Pollution Bulletin* 74: 477-489.

BELLAS J, ALBENTOSA M, VIDAL-LIÑÁN L, BESADA V, FRANCO MA, FUMEGA J, GONZÁLEZ-QUIJANO A, VIÑAS L and BEIRAS R (2014) Combined use of chemical, biochemical and physiological variables in mussels for the assessment of marine pollution along the N-NW Spanish coast. *Marine Environmental Research* 96: 105-117.

BEN AMEUR W, TRABELSI S, El BEDOUI B and DRISS MR (2011) Polychlorinated Biphenyls in sediments from Ghar El Melh lagoon, Tunisia. *Bulletin of Environmental Contamination and Toxicology* 86: 539-544.

BESADA V, FUMEGA J and VAAMONDE A (2002) Temporal trends of Cd, Cu, Hg, Pb and Zn in mussel (*Mytilus galloprovincialis*) from the Spanish North-Atlantic coast 1991-1999. *Science of the Total Environment* 288: 239-253.

BLOCKSOM KA WALTERS DM, JICHA TM, LAZORCHAK JM, ANGRADI TR and BOLGRIEN DW (2010) Persistent organic pollutants in fish tissue in the mid-continental great rivers of the United States. *Science of the Total Environment* 408: 1180-1189.

BLOOM NS (1992) On the chemical form of mercury in edible fish and marine invertebrate tissue. *Canadian Journal of Fisheries and Aquatic Science* 49:1010-1017.

BODIN N, TAPIE N, LE MÉNACH K, CHASSOT E, ELIE P, ROCHARD E and BUDZINSKI H (2014) PCB contamination in fish community from the Gironde Estuary (France): Blast from the past. *Chemosphere* 98: 66-72.

BOEHM PD and FARRINGTON JW (1984) Aspects of the polycyclic aromatic hydrocarbon geochemistry of recent sediments in the Georges Bank region. *Environmental Science and Technology* 18: 840-845.

BOLLMOHR S, Day JA and SCHUL Z R (2007) Temporal variability in particle-bound pesticide exposure in a temporarily open estuary, South Africa. *Chemosphere* 68: 479-488.

BOLLMOHR S and SCHUL Z R (2008) Seasonal changes of macroinvertebrate community in a Western Cape River receiving nonpoint source insecticide pollution. *Environmental Toxicology and Chemistry* 28: 809-817.

BOLLMOHR S, VAN DEN BRINK PJ, WADE PW, DAY JA and SCHUL Z R (2009) Spatial and temporal variability in particle bound pesticide exposure and their effects on benthic community structure in a temporarily open estuary. *Estuarine Coastal and Shelf Science* 82: 50-60.

BORAK J and HOSGOOD HD (2007) Seafood arsenic: Implications for human risk assessment. *Regulatory Toxicology and Pharmacology* 47: 204-212.

BORNMAN MS, VAN VUREN JHJ, BARNHOORN IEJ, ANECK-HAHN N, DE JAGER CJ, GENTHE B, PIETERSE GM and VAN DYK JC (2010) *Environmental exposure and health risk assessment in an area where ongoing DDT spraying occurs.* Water Research Commission (WRC), Pretoria. Report No. K5/1674.

BOUWMAN H, COETZEE A and SCHUTTE CHJ (1990) Environmental and health implications of DDT-contaminated fish from the Pongolo flood plain. *Journal of African Zoology* 104: 275-286.

BOUWMAN H, SEREDA B and MEINHARDT HM (2006) Simultaneous presence of DDT and pyrethroid residues in human breast milk from a malaria endemic area in South Africa. *Environmental Pollution* 144: 902-917.

BOUWMAN H, POLDER A, VENTER B and SKAARE JH (2008) Organochlorine contaminants in cormorant, darter, egret, and ibis eggs from South Africa. *Chemosphere* 71: 227-241.

BORNMAN R, DE JAGER C, WORKU Z, FARIAS P and REIF S (2010) DDT and urogenital malformations in newborn boys in a malarial area. *International Brazilian Journal Urology* 106: 405-410.

BOUWMAN H, KYLIN H, SEREDA B and BORNMAN R (2012) High levels of DDT in breast milk: intake, risk, lactation duration, and involvement of gender. *Environmental Pollution* 170: 63-70.

BRADSHAW D, DORRINGTON RE and LAUBSCHER R (2012) Rapid mortality surveillance report 2011. Cape Town: South African Medical Research Council. ISBN: 978-1-920618-00-1.

BROWN JN and PEAKE BM (2006) Sources of heavy metals and polycyclic aromatic hydrocarbons in urban stormwater runoff. *Science of the Total Environment* 359: 145-155.

BRACK W (2003) Effect-directed analysis: a promising tool for the identification of organic toxicants in complex mixtures? *Analytical and Bioanalytical Chemistry* 377: 397-407.

BUDZINSKI H, JONES I, BELLOCQ J, PIERRAD C and CARRIGUES P (1997) Evaluation of sediment contamination by polycyclic aromatic hydrocarbons in the Gironde Estuary. *Marine Chemistry* 58: 85-97.

BURREAU S, ZEBUHR Y, BROMAN D and ISHAQ R (2004) Biomagnification of polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) studied in pike (*Esox lucius*), perch (*Perca fluviatilis*) and roach (*Rutilus rutilus*) from the Baltic Sea. *Chemosphere* 55: 1043-1052.

CHENG KC, LEUNG HM, KONG KY and WONG MH (2007) Residual levels of DDTs and PAHs in freshwater and marine fish from Hong Kong markets and their health risk assessment. *Chemosphere* 66: 460-468.

COHEN J (2006) Matters of the heart and mind: Risk-risk tradeoffs in eating fish containing methylmercury. *Risk in Perspective* 14: 1-6.

CHOI HG, MOON HB, CHOI M and YU J (2011) Monitoring of organic contaminants in sediments from the Korean coast: Spatial distribution and temporal trends (2001-2007). *Marine Pollution Bulletin* 62: 1352-1361.

CONNELL AD, TURNER WD, GARDNER BD, MCCLURG TP, LIVINGSTONE DJ, CARTER JE and GERTENBACH WJN (1975) *National Marine Pollution Monitoring Programme, East Coast Section. Progress Report No 2, March 1974 to March 1975.*

CORSI I, MARIOTTINI M, MENCHI V, SENSINI C, BALOCCHI C and FOCARDI S (2002) Monitoring a marine coastal area: Use of *Mytilus galloprovincialis* and *Mullus barbatus* as bioindicators. *Marine Ecology* 23: 138-153.

CRANE JL, MACDONALD DD, INGERSOLL CG, SMORONG DE, LINDSKOOG RA and SEVERN CG (2002) Evaluation of numerical sediment quality targets for the St. Louis River Area of Concern. *Archives of Environmental Contamination and Toxicology* 43: 1-10.

CRANE JL, GROSSENHEIDER K and WILSON CB (2010) *Contamination of stormwater pond sediments by Polycyclic Aromatic Hydrocarbons (PAHs) in Minnesota: The role of coal tar-based sealcoat products as a source of PAHs*. Minnesota Pollution Control Agency, Saint Paul, MN. Report number tdr-g1-07.

CULLEN AC, VORHEES DJ and ALTSHUL AM (1996) Influence of harbour contamination on the level and composition of polychlorinated biphenyls in produce in Greater New Bedford, Massachusetts. *Environmental Science and Technology* 30: 1581-1588.

CUNDY AB, CROUDACE IW, THOMSON J and LEWIS JT (1997) Reliability of salt marshes as ‘‘geochemical recorders’’ of pollutant input: a case study from contrasting estuaries in southern England. *Environmental Science and Technology* 31: 1093-1101.

DALVIE MA, CAIRNCROSS E, SOLOMON A and LONDON L (2003) Contamination of rural surface and ground water by endosulfan in farming areas in the Western Cape, South Africa. Environmental Health: A Global

Access Science Source 2: 1. Online at: http://www.ehjournal.net/content/2/1/1.

DANIELS JL, LONGNECKER MP, ROWLAND AS and GOLDING J (2004) Fish intake during pregnancy and early cognitive development of offspring. *Epidemiology* 15: 394-402.

DAUM T, LOWE S, TOIA R, BARTOW G, FAIREY R, ANDERSON J and JONES J (2000) *Sediment contamination in San Leandro Bay, CA*. San Francisco Estuary Institute, Richmond, CA.

DAVIGLUS M, SHEESHKA J and MURKIN E (2002) Health benefits from eating fish. *Comments on Toxicology* 8: 345-374.

DAVIS JA, HETZEL F, ORAM JJ and MCKEE LJ (2007) Polychlorinated biphenyls (PCBs) in San Francisco Bay. *Environmental Research* 105: 67-86.

DENISON MS, ZHAO B, BASTON DS, CLARK GC, MURATA H and HAN D (2004) Recombinant cell bioassay systems for the detection and relative quantitation of halogenated dioxins and related chemicals. *Talanta* 63: 1123-1133.

DENTON GRW, CONCEPCION LP, WOOD HR and MORRISON RJ (2006) Polychlorinated biphenyls (PCBs) in marine organisms from four harbours in Guam. *Marine Pollution Bulletin* 52: 214-238.

DIAMANTI-KANDARAKIS E, BOURGUIGNON J-P, GIUDICE LC, HAUSER R, PRINS GS, SOTO AM, ZOELLER RT and GORE AC (2009) Endocrine-disrupting chemicals: an Endocrine Society scientific statement. *Endocrine Reviews* 30: 293-342.

DI TORO DM, ZARBA CS, HANSEN DJ, BERRY WJ, SWARTZ RC, COWAN CE, PAVLOU SP, ALLEN HE, THOMAS NA and PAQUIN PR (1991) Annual Review. Technical basis for establishing sediment quality criteria for non-ionic organic chemicals using equilibrium partitioning. *Environmental Toxicology and Chemistry* 10: 1541-1583.

DI TORO DM and DE ROSA LD (1998) Equilibrium partitioning and organic carbon normalisation. In: *National Sediment Bioaccumulation*, 1996. US Environmental Protection Agency, Washington, DC. EPA 823-R-98-002.

DOH (DEPARTMENT OF HEALTH, MEDICAL RESEARCH COUNCIL, ORCMACRO) (2007*) South Africa Demographic and Health Survey 2003.* Pretoria: Department of Health.

DOMINGO JL and BOCIO A (2007) Levels of PCDD/PCDFs and PCBs in edible marine species and human intake: a literature review. *Environment International* 33: 397-405.

DONOHUE JM and ABERNATHY CO (1999) Exposure to inorganic arsenic from fish and shellfish. In: Chappell WR, Abernathy CO and Calderon RL (Eds), *Arsenic Exposure and Health Effects*. Elsevier Science, Amsterdam.

DOONG RA, SUN YC, LIAO PL, PENG CK and WU SC (2002) Distribution and fate of organochlorine pesticide residues in sediments from the selected rivers in Taiwan. *Chemosphere* 48: 237-246.

DOUBEN PET (Ed) (2003) *PAHs: An Ecotoxicological Perspective*. John Wiley and Sons, Chichester, UK.

DOUGHERTY CP, HOLTZ SH, REINERT JC, PANYACOSIT L, AXELRAD DA and WOODRUFF TJ (2000) Dietary exposure to food contaminants across the United States. *Environmental Research* 84: 170-185.

DURAL M, LUGAL GÖKSU M, ÖZAK A and DERICI B (2006) Bioaccumulation of some heavy metals in different tissues of *Dicentrarchus Labrax* L, 1758, *Sparus Aurata* L, 1758 And *Mugil Cephalus* L, 1758 from the Çamlik Lagoon of the Eastern Cost Of Mediterranean (Turkey). *Environmental Monitoring and Assessment* 118: 65-74.

EDGE M, ALLEN NS, TURNER D, ROBINSON J and SEAL K (2001) The enhanced performance of biocidal additives in paints and coatings. *Progress in Organic Coatings* 43: 10-17.

EDMONDS JS and FRANCESCONI KA (1993) Arsenic in seafoods: human health aspects and regulations. *Marine Pollution Bulletin* 25: 665-674.

EITZER BD, MATTINA MI, IANNUCCI-BERGER W (2001) Compositional and chiral profiles of weathered chlordane residues in soil. *Environmental Toxicology and Chemistry* 20: 2198-2204.

ELLENDER BR, WEYL OLF and WINKER H (2009) Who uses the fishery resources in South Africa's largest impoundment? Characterising subsistence and recreational fishing sectors on Lake Gariep. *Water SA* 35: 677-682.

EMAP (ENVIRONMENTAL MONITORING AND ASSESSMENT PROGRAM) DELAWARE AND MARYLAND COASTAL BAYS (1993) Data online at: http://www.epa.gov/emap/html/ pubs/docs/geographic.html.

EMAP (ENVIRONMENTAL MONITORING AND ASSESSMENT PROGRAM) CAROLINIAN PROVINCE (1995-1997) Data online at: http://www.epa.gov/emap/html/ pubs/docs/geographic.html.

EMAP (ENVIRONMENTAL MONITORING AND ASSESSMENT PROGRAM) MID-ATLANTIC INTEGRATED ASSESSMENT Estuaries (1996-1998) Data online at: http://www.epa.gov/emap/html/ pubs/docs/geographic.html.

EMAP (ENVIRONMENTAL MONITORING AND ASSESSMENT PROGRAM) TEXAS (1993-1994) Data online at: http://www.epa.gov/emap/html/ pubs/docs/geographic.html.

EMAP (ENVIRONMENTAL MONITORING AND ASSESSMENT PROGRAM) LOUISIANAN PROVINCE (1994) Data online at: http://www.epa.gov/emap/html/ pubs/docs/geographic.html.

EPAV (ENVIRONMENTAL PROTECTION AGENCY VICTORIA) (2007) *Yarra and Maribyrnong estuaries: Investigation of contamination in fish*. Publication 1094.

FANG JKH, AU DWT, WU RSS, ZHENG GJ, CHAN AKY, LAM PKS and SHIN PKS (2009) Concentrations of polycyclic aromatic hydrocarbons and polychlorinated biphenyls in green-lipped mussel *Perna viridis* from Victoria Harbour: Hong Kong and possible human health risk. *Marine Pollution Bulletin* 58: 601-634.

FIKSLIN TJ and SANTORO ED (2003) PCB samples: Implications for monitoring programs. *Environmental Monitoring and Assessment* 87: 197-212.

FÖRSTNER U (1989) Contaminated sediments. In: Bhattacharji S, Friedman GM, Neugebauer HJ and Seilacher A (Eds), *Lecture notes in earth sciences*. Springer Verlag, Berlin.

FÖRSTNER U and WITTMANN GTW (1979) *Metal Pollution in the Aquatic Environment*. Springer-Verlag, New York.

FORSYTH D, CASEY V, DABEKA RW and MCKENZIE A (2004) Methylmercury levels in predatory fish species marketed in Canada. *Food Additives and Contaminants* 21: 849-856.

FRANCIONI E, WAGENER ALR, SCOFIELD AL, DEPLEDGE MH, CAVALIER B, SETTE CB, CARVALHOSA L, LOZINSKY C and MARIATH R (2007) Polycyclic aromatic hydrocarbon in inter-tidal mussel *Perna perna*: Space-time observations, source investigation and genotoxicity. *Science of the Total Environment* 372: 515-531.

FSA (FOOD STANDARDS AGENCY) (2005) *Arsenic in Fish and Shellfish.* Food Standards Agency: London, UK.

GARNER TR, WEINSTEIN JE and SANGER DN (2009) Polycyclic aromatic hydrocarbon contamination in South Carolina salt marsh-tidal creek systems: Relationships among sediments, biota, and watershed land use. *Archives of Environmental Contamination and Toxicology* 57: 103-115.

GIESY JP, HILSCHEROVA K, JONES P, KANNAN K and MACHALA M (2002) Cell bioassays for detection of aryl hydrocarbon (AhR) and estrogen receptor (ER) mediated activity in environmental samples. *Marine Pollution Bulletin* 45: 3-16.

GREEN J and TRETT MW (1989) *The Fate and Effects of Oil in Freshwater*. Elsevier Applied Science Publishers, London.

GREENFIELD BK and JAHN A (2010) Mercury in San Francisco Bay forage fish. *Environmental Pollution* 15: 2716-2724.

GREENFIELD BK and ALLEN RM (2013) Polychlorinated biphenyl spatial patterns in San Francisco Bay forage fish. *Chemosphere* 90: 1693-1703.

GROBLER DF, BADENHORST JE and KEMPSTER PL (1996) PCBs, Chlorinated hydrocarbon pesticides and chlorophenols in the Isipingo Estuary, Natal, Republic of South Africa. *Marine Pollution Bulletin* 32: 572-575.

GUNTHER AJ, SALOP P, BELL D, FENG A, WIEGEL J and WOOD R (2001) *Initial characterization of PCB, mercury, and PAH concentration in the drainages of Western Alameda County, CA*. Alameda Countywide Clean Water Program, Hayward, CA, USA.

HAMMERSCHMIDT CR and FITZGERALD WF (2006) Methylmercury in freshwater fish linked to atmospheric

mercury deposition. *Environmental Science and Technology* 40: 7764-70.

HANSON P, EVANS D, COLBY D and ZDANOWICS V (1993) Assessment of elemental contamination in estuarine and coastal environments based on geochemical and statistical modeling of sediments. *Marine Environmental Research* 36: 237-266.

HASSETT AJ, VILJOEN PT and LIEBENBERG JJE (1987). An assessment of chlorinated pesticides in the major surface water resources of the Orange Free State during the period September 1984 to September 1985. *Water SA* 13: 133-136.

HIBBELN JR, DAVIS JM, STEER C, EMMETT P, ROGERS I, WILLIAMS C and GOLDING J (2007) Maternal seafood consumption in pregnancy and neurodevelopmental outcomes in childhood (ALSPAC study): An observational cohort. *The Lancet* 369: 578-585.

HITES RA, LAFLAMME RE and WINDSOR JG (1980) Polycyclic aromatic hydrocarbons in the marine/aquatic sediments: Their ubiquity. In: Petrakis L and Weiss FT (Eds), *Petroleum in the Marine Environment*. American Chemical Society, Washington, DC.

HOFFMAN EJ, MILLS GL, LATIMER FS and QUINN JG (1984) Urban runoff as a source of polycyclic aromatic hydrocarbons to coastal waters. *Environmental Science and Technology* 18: 580-587.

HOLLAND AF, SANGER DM, GAWLE CP, LERBERG SB, SANTIAGO MS, RIEKERK GHM, ZIMMERMAN LE and SCOTT GI (2004) Linkages between tidal creek ecosystems and the landscape and demographic attributes of their watersheds. *Journal of Experimental Marine Biology and Ecology* 298: 151-178.

HONG SH, YIM UH, SHIM WJ and OH JR (2005) Congener-specific survey for polychlorinated biphenyls in sediments of industrialized bays in Korea: Regional characteristics and pollution sources. *Environmental Science and Technology* 39: 7380-7388.

HONG S, KHIM JS, NAILE JE, PARK J, KWON B-O, WANG T, LU Y, SHIM WJ, JONES PD and GIESY JP (2012) AhR-mediated potency of sediments and soils in estuarine and coastal areas of the Yellow Sea region: a comparison between Korea and China. *Environmental Pollution* 171: 216-225.

HOROWITZ AJ (1991) *A Primer on Sediment-Trace Element Chemistry*. Lewis Publishers Inc, Michigan.

HOROWITZ AJ and ELRICK KA (1987) The relation of stream sediment surface area, grain size and composition to trace element chemistry. *Applied Geochemistry* 2: 437-451.

HOWELL NL, SUAREZ MP, RIFAI HS and KOENIG L (2008) Concentrations of polychlorinated biphenyls (PCBs) in water, sediment, and aquatic biota in the Houston Ship Channel, Texas. *Chemosphere* 70: 593-606.

HU L, ZHANG G, ZHENG B, QIN Y, LIN T and GUO Z (2009) Occurrence and distribution of organochlorine pesticides (OCPs) in surface sediments of the Bohai Sea, China. *Chemosphere* 77: 663-672.

HUMPHRIES M (2013) DDT residue contamination in sediments from Lake Sibaya in northern KwaZulu-Natal, South Africa: Implications for conservation in a World Heritage Site. *Chemosphere* 93: 1494-1499.

HWANG H-M and FOSTER GD (2006) Characterization of PAHs in urban stormwater runoff flowing into the tidal Anacostia River, Washington, DC, USA. *Environmental Pollution* 140: 416-426.

IARC (International Agency for Research on Cancer) (1991) *Occupational exposures in insecticide application, and some pesticides.* IARC Monographs on the Evaluation of Carcinogenic Risks to Humans. IARC, Lyon, France.

INGERSOLL CG, HAVERLAND PS, BRUNSON EL, CANFIELD TJ, DWYER FJ, HENKE CE, KEMBLE NE, MOUNT DR and FOX RG (1996) Calculation and evaluation of sediment effect concentrations for the amphipod *Hyalella azteca* and the midge *Chironomus riparius*. *Journal of Great Lakes Research* 22: 602-623.

IOM (INSTITUTE OF MEDICINE) (2005) *Dietary reference intakes for energy, carbohydrate, fiber, fat, fatty acids, cholesterol, protein, and amino acids*. National Academy Press, Washington, DC.

IOM (INSTITUTE OF MEDICINE) (2006) *Seafood Choices: Balancing Benefits and Risks*. National Academy Press, Washington, DC.

ISOBE T, TAKADA H, KANAI M, TSUTSUMI S, ISOBE KO, BOONYATUMANOND R and ZAKARIA MP (2007) Distribution of Polycyclic Aromatic Hydrocarbons (PAHs) and phenolic endocrine disrupting chemicals in south and southeast Asian mussels. *Environmental Monitoring and Assessment* 135: 423-440.

JAIKANLAYA C, SETTACHAN D, DENISON MS, RUCHIRAWAT M and VAN DEN BERG M (2009) PCBs

contamination in seafood species at the Eastern Coast of Thailand. *Chemosphere* 76: 239-249.

JOBLING S, BERESFORD N, NOLAN M, RODGERS-GRAY T, BRIGHTY GC, SUMPTER JG and TYLER CR (2002) Altered sexual maturation and gamete production in wild roach (*Rutilus rutilus*) living in rivers that receive treated sewage effluents. *Biology of Reproduction* 66: 272-281.

KAISE T, WATANABE S and ITOH K (1985) The acute toxicity of arsenobetaine. *Chemosphere* 14: 1327-1332.

KANG Y, SHENG G, FU J, MAI B, ZHANG G, LIN Z and MIN Y (2000) Polychlorinated biphenyls in surface sediments from the Pearl River Delta and Macau. *Marine Pollution Bulletin* 40: 794-797.

KANNAN K, SMITH RG Jr, LEE RF, WINDOM HL, HEITMULLER PT, MACAULEY JM and SUMMERS JK (1988) Distribution of total mercury and methyl mercury in water, sediment, and fish from South Florida estuaries. *Archives of Environmental Contamination and Toxicology* 34: 109-118.

KANNAN K, TANABE S, GIESY JP and TATSUKAWA R (1997) Organochlorine pesticides and polychlorinated biphenyls in foodstuffs from Asian and Oceanic countries. *Reviews of Environmental Contamination and Toxicology* 152: 1-55.

KANZARI F, SYAKTI AD, ASIA L, MALLERET L, MILLE G, JAMOUSSI B, ABDERRABBA M and DOUMENQ P (2012) Aliphatic hydrocarbons, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, organochlorine, and organophosphorous pesticides in surface sediments from the Arc river and the Berre lagoon, France. *Environmental Science and Pollution Research* 19: 559-576.

KARICKHOFF S, BROEN D and SCOTT T (1979) Sorption of hydrophobic pollutants on natural sediments. *Water Research* 18: 241-248.

KAROUNA-RENIER NK (2011) Largemouth bass (*Micropterus salmoides*) and striped mullet (*Mugil cephalus*) as vectors of contaminants to human consumers in northwest Florida. *Marine Environmental Research* 72: 96-104

KEITH L and TELLIARD W (1979) Priority pollutants, I - A perspective view. *Environmental Science and Technology* 13: 416-423.

KERSTEN M and SMEDES F (2002) Normalization procedures for sediment contaminants in spatial and temporal trend monitoring. *Journal of Environmental Monitoring* 4: 109-115.

KHIM JS, KANNAN K, VILLENEUVE DL, KOH CH and GIESY JP (1999) Characterization and distribution of trace organic contaminants in sediment from Masan Bay, Korea. 1. Instrumental analysis. *Environmental Science & Technology* 33: 4199-4205.

KIMBROUGH KL and DICKHUT RM (2006) Assessment of polycyclic aromatic hydrocarbon input to urban wetlands in relation to adjacent land use. *Marine Pollution Bulletin* 52: 1355-1363.

KIMBROUGH KL, JOHNSON WE, LAUENSTEIN GG, CHRISTENSEN JD and APETI DA (2008) *An Assessment of Two Decades of Contaminant Monitoring in the Nation's Coastal Zone.* Silver Spring, MD. NOAA Technical Memorandum NOS NCCOS 74.

KIRBY J and MAHER W (2002) Tissue accumulation and distribution of arsenic compounds in three marine fish species: relationship to trophic position. *Applied Organometallic Chemistry* 16: 108-115.

KOZŬL D, ROMANIĆ Sh, KLJAKOVIĆ-GAŠPIĆ Z and VEŽA J (2009) Levels of organochlorine compounds in the Mediterranean blue mussel from the Adriatic Sea. *Bulletin of Environmental Contamination and Toxicology* 83: 880-884.

KRUMGALZ BS, FAINSHTEIN G and COHEN A (1992) Grain size effect on anthropogenic trace metal and organic matter distribution in marine sediments. *Science of the Total Environment* 116: 15-30.

LAMOREE M, SWART K, SENHORST H and VAN HATTUM B (2004) *Validation of the acidic sample clean-up procedure for the DR-CALUX assay*. IVM Report (L-04/02). Institute for Environmental Studies, Vrije Universiteit, Amsterdam.

LARSEN EH, SLOTH JJ, HANSEN M, JORHEM L and ENGMAN J (2005) Determination of inorganic arsenic in white fish using microwave assisted alkaline-alcoholic sample dissolution and HPLC-ICPMS. *Analytical and Bioanalytical Chemistry* 381: 339-346.

LARSSON M, ORBE D and ENGWALL M (2012) Exposure time-dependent effects on the relative potencies and additivity of PAHs in the Ah receptor-based H4IIE-luc bioassay. *Environmental Toxicology and*

Chemistry 31: 1149-1157.

LAUENSTEIN GG and CANTILLO AY (1993) *Sampling and Analytical Methods of the National Status and Trends Program National Benthic Surveillance and Mussel Watch Projects 1984-1992: Overview and Summary of Methods, Volume I.* NOAA Technical Memorandum NOS ORCA 71, Silver Spring, MD.

LAVANDIER R, QUINETE N, HAUSER-DAVIS RA, DIAS PS, TANIGUCHI S, MONTONE R and MOREIRA I (2013) Polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) in three fish species from an estuary in the southeastern coast of Brazil. *Chemosphere* 90: 2435-2443.

LEFKOVITZ LF, NEFF JM, LIZOTTE R and HALL M (2001) *Comparison of two analytical methods for measurement of chlorinated pesticides and PCB congeners in biological tissue – Trends in Boston Harbor lobster tissue.* Boston: Massachusetts Water Resources Authority. Report ENQUAD 2001-02.

LEMAIRE P, MATHIEU A, CARRIERE S, DRAI P, GIUDICELLI J and LAFAURIE M (1990) The uptake metabolism and biological half-life of benzo[a]pyrene in different tissues of sea bass, *Dicentrarchus labrax*. *Ecotoxicology and Environmental Safety* 20: 223-233.

LEVENSON CW and AXELRAD DM (2006) Too much of a good thing? Update on fish consumption and mercury exposure. *Nutrition Reviews* 64: 139-145.

LI W, WEI C, ZHANG C, VAN HULLE M, CORNELIS R and ZHANG X (2003) A survey of arsenic species in Chinese seafood. *Food and Chemical Toxicology* 41: 1103-1110.

LIMA AL, FARRINGTON JW and REDDY CM (2005) Combustion-derived polycyclic aromatic hydrocarbons in the environment - a review. *Environmental Forensics* 6: 109-131.

LIMAME R, WOUTERS A, PAUWELS B, FRANSEN E, PEETERS M, LARDON F, DE WEVER O and PAUWELS P (2012) Comparative analysis of dynamic cell viability, migration and invasion assessments by novel real-time technology and classic endpoint assays. *PloSone* 7 e46536.

LONG ER, MACDONALD DD, SMITH SL and CALDER FD (1995) Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. *Environmental Management* 19: 81-97.

LONG ER, INGERSOLL CG, MACDONALD DD (2006) Calculation and uses of mean Sediment Quality Guidelines Quotients: A critical review. *Environmental Science and Technology* 40: 1726-1736.

LORENZANA RM, YEOW AY, COLMAN JT, CHAPPELL LL and CHOUDHURY H (2009) Arsenic in seafood. *Human and Ecological Risk Assessment* 15: 185-200.

LORING DH (1991) Normalization of heavy-metal data from estuarine and coastal sediments. *ICES Journal of Marine Science* 48: 101-115.

LORING DH and RANTALA RTT (1992) Manual for the geochemical analyses of marine sediments and suspended particulate matter. *Earth-Science Review* 32: 235-283.

LUCH A (2005) *The carcinogenic effects of polycyclic aromatic hydrocarbons.* London: Imperial College Press.

MACDONALD DD (1997) *Sediment injury in the Southern California bight: review of the toxic effects of DDTs and PCBs in sediments.* Prepared for National Oceanic and Atmospheric Administration, US Department of Commerce, Long Beach, CA, USA.

MACDONALD RW and BEWERS JM (1996) Contaminants in the arctic marine environment: priorities for protection. *ICES Journal of Marine Science* 53: 537-563.

MACDONALD DD, INGERSOLL CG and BERGER TA (2000) Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. *Archives of Environmental Contamination and Toxicology* 39: 20-31.

MAHLER BJ, VAN METRE PC, BASHARA TJ, WILSON JT and JOHNS DA (2005) Parking lot sealcoat: An unrecognized source of urban polycyclic aromatic hydrocarbons. *Environmental Science and Technology* 39: 5560-5566.

MARSZALEK JR and LODISH HF (2005) Docosahexaenoic acid, fatty acid-interacting proteins, and neuronal function: Breastmilk and fish are good for you. *Annual Review of Cell and Development Biology* 21: 633-657.

MARTIN JM and WHITFIELD M (1983) The significance of the river inputs to the ocean. In: Wong CS, Boyle E, Bruland EW, Burton JD and Goldberg ED (Eds), *Trace metals in seawater*. Plenum Press, New York.

MARUYA KA, RISEBROUGH RW and HORNE AJ (1996) Partitioning of polynuclear aromatic hydrocarbons between sediments from San Francisco Bay and their porewaters. *Environmental Science and Technology* 30: 2942-2947.

MARTÍNEZ-LLADÓ X, GUBERT O, MARTÍ V, DÍEZ S, ROMO X, BAYONA JM and DE PABLO J (2007) Distribution of polycyclic aromatic hydrocarbons (PAHs) and tributyltin (TBT) in Barcelona harbour sediments and their impact on benthic communities. Environmental Pollution 149: 104-113.

MARUYAMA K, SAHRUL M, TANABE S and TATSUKAWA R (1983) Polychlorinated biphenyl pollution from shipbuilding in Nagasaki Bay, Japan. *Ecotoxicology and Environmental Safety* 7: 514-520.

MASSONE CG, WAGENER Ade L, DE ABREU HM, VEIGA Á (2013) Revisiting hydrocarbons source appraisal in sediments exposed to multiple inputs. *Marine Pollution Bulletin* 73: 345-54.

MDEP/MDMF (Massachusetts Department of Environmental Protection and Massachusetts Division of Marine Fisheries) (2012) *Contaminated Monitoring Report for Seafood Harvested in 2011 from the New Bedford Harbor Superfund Site*.

MCCREADY S, SLEE DJ, BIRCH GF and TAYLOR SE (2000) The distribution of polycyclic aromatic hydrocarbons in surficial sediments of Sydney Harbour, Australia*. Marine Pollution Bulletin* 40: 999-1006.

MCGRODDY SE, FARRINGTON JW and GSCHWEND PM (1996) Comparison of the in situ and desorption sediment-water partitioning of polycyclic aromatic hydrocarbons and polychlorinated biphenyls. *Environmental Science and Technology* 30: 172-177.

MEADOR JP, STEIN JE, REICHERT WL and Varanasi U (1995) Bioaccumulation of polycyclic aromatic hydrocarbons by marine organisms. *Reviews of Environmental Contamination and Toxicology* 143: 79-165.

MEADOR JP (2003) Bioaccumulation of PAHs in marine invertebrates. In: Douben PET (Ed), *PAHs: An Ecotoxicological Perspective*. John Wiley and Sons Ltd., England.

MEANS JC, WOOD SG, HASSETT JJ and BANWARD WL (1980) Sorption of polynuclear aromatic hydrocarbons by sediments and soils. *Environmental Science and Technology* 14: 1524-1528.

METIAN M, CHARBONNIER L, OBERHAËNSLI F, BUSTAMANTE P, JEFFREE R, AMIARD J-C and WARNAU M (2009) Assessment of metal, metalloid, and radionuclide bioaccessibility from mussels to human consumers, using centrifugation and simulated digestion methods coupled with radiotracer techniques. *Ecotoxicology and Environmental Safety* 72: 1499-1502.

MITRA S and DICKHUT RM (1999) Three-phase modeling of polycyclic aromatic hydrocarbon association with pore-water-dissolved organic carbon. *Environmental Toxicology and Chemistry* 18: 1144-1148.

MOSTERT MMR, AYOKO GA and KOKOT S (2010) Application of chemometrics to analysis of soil pollutants. *Trends in Analytical Chemistry* 29: 430-435.

MOYA J, GARRAHAN KG, POSTON TM and DURRELL S (1998) Effects of cooking on levels of PCBs in fillets of winter flounder. *Bulletin of Environmental Contamination and Toxicology* 60: 845-851.

MOZAFFARIAN D and RIMM E (2006) Fish intake, contaminants, and human health-evaluating the risks and the benefits. *Journal of the American Medical Association* 296: 1885-99.

MUNOZ O, DEVESA V, SUNER M, VELEZ D, MONTORO R, URIETA I, MACHO M and JALON M (2000) Total and inorganic arsenic in fresh and processed fish products. *Journal of Agricultural and Food Chemistry* 48: 4369-4376.

NCA (NATIONAL COASTAL ASSESSMENT NORTHEAST REGION) Online at: http://www.epa.gov/emap/nca/html/regions/northeast.html.

NEFF JM (1979) *Polycyclic Aromatic Hydrocarbons in the Aquatic Environment: Sources, Fates, and Biological Effects*. Applied Science, London, Great Britain.

NEFF JM, STOUT SA and GUNSTER DG (2005) Ecological risk assessment of polycyclic aromatic hydrocarbons in sediments: identifying sources and ecological hazard. *Integrated Environmental*

Assessment and Management 1: 22-33.

NEL JH and STEYN NP (2002) *Report on South African food consumption studies undertaken amongst different population groups (1983-2000): Average intakes of foods most commonly consumed*. Pretoria, South Africa.

NIEUWOUDT C, QUINN LP, PIETERS R, JORDAAN I, VISSER M, KYLIN H, BORGEN AR, GIESY JP and BOUWMAN H (2009) Dioxin-like chemicals in soil and sediment from residential and industrial areas in central South Africa. *Chemosphere* 76: 774-783.

NIEUWOUDT C, PIETERS R, QUINN LP, KYLIN H, BORGEN AR and BOUWMAN H (2011) Polycyclic aromatic hydrocarbons (PAHs) in soil and sediment from industrial, residential, and agricultural areas in central South Africa: An initial assessment. *Soil and Sediment Chemistry* 20: 188-204.

NISBET IC and LAGOY PK (1992) Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). *Regulatory Toxicology and Pharmacology* 16: 290-300.

NOAA (NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION) (2000) *Contaminant levels in muscle of four species of recreational fish from the New York Bight Apex*. NOAA Technical Memorandum NMFS-NE-157.

OGATA Y, TAKADA H, MIZUKAWA K, HIRAI H, IWASA S, ENDO S, MATO Y, SAHA M, OKUDA K, NAKASHIMA A, MURAKAMI M, ZURCHER N, BOOYATUMANONDO R, ZAKARIA MP, DUNG LQ, GORDON M, MIGUEZ C, SUZUKI S, MOORE C, KARAPANAGIOTI HK, WEERTS S, MCCLURG T, BURRES E, SMITH W, VAN VELKENBURG M, LANG JS, LANG RC, LAURSEN D, DANNER B, STEWARDSON N and THOMPSON RC (2009) International Pellet Watch: Global monitoring of persistent organic pollutants (POPs) in coastal Waters. 1. Initial phase data on PCBs, DDTs, and HCHs. *Marine Pollution Bulletin* 58: 1437-1446.

OKEN E, WRIGHT RO, KLEINMAN KP, BELLINGER D, AMARASIRIWARDENA CJ, HU H, RICH-EDWARDS JW and GILLMAN MW (2005) Maternal fish consumption, hair mercury, and infant cognition in a U.S. cohort. Environ. *Health Perspectives* 113: 1376-1380.

OLIFF WD and TURNER WD (1976) *National marine pollution surveys, East Coast Section*. 2nd Annual Report, NIWR, Durban.

ORASECOM (2013) *POPs, PAHs and elemental levels in sediment, fish and wild bird eggs in the Orange-Senqu River basin*. Report 002/2013, prepared by Bouwman H, Pieters R, Genthe B and Chamier J for ORASECOM, Pretoria.

PAIT AS, WHITALL DR, JEFFREY CF, CALDOW C, MASON AL, LAUENSTEIN GG and CHRISTENSEN JD (2007) Chemical contamination in southwest Puerto Rico: an assessment of organic contaminants in nearshore sediments. *Marine Pollution Bulletin* 56: 580-587.

PAN S, KADOKAMI K, LI X, DUONG HT and HORIGUCHI T (2014) Target and screening analysis of 940 micro-pollutants in sediments in Tokyo Bay, Japan. *Chemosphere* 99: 109-116.

PHEIFFER W, PIETERS R, VAN DYK JC and SMIT NJ (2014) Metal contamination of sediments and fish from the Vaal River, South Africa. *African Journal of Aquatic Science* 39: 117-121.

PHILLIPS DJH (1988) *Monitoring of toxic contaminants in the San Francisco Bay-Delta: A critical review, emphasizing spatial and temporal trend monitoring.* Aquatic Habitat Institute, Richmond, CA.

PIETERS R (2007) *An assessment of dioxins, dibenzofurans and PCBs in the sediments of selected freshwater bodies and estuaries in South Africa*. PhD Thesis, North-West University, South Africa

POLDER A, VENTER B, SKAARE JU and BOUWMAN H (2008) Polybrominated diphenyl ethers and HBCD in bird eggs of South Africa. *Chemosphere* 73: 148-154.

PORTE C and ALBAIGÉS J (1993) Bioaccumulation patterns of hydrocarbons and polychlorinated biphenyls in bivalves, crustaceans, and fishes. *Archives of Environmental Contamination and Toxicology* 26: 273-281.

PRADERVAND P, BECKLEY LE, MANN BQ and RADEBE PV (2003) *Assessment of the linefishery in two urban estuarine systems in Kwazulu-natal, South Africa. African Journal of Marine Science* 25: 111-130.

QUEREDA J, MARTÍNEZ-ALARCÓN L, MENDOÇA L, MAJADO M, HERRERO-MEDRANO J, PALLARÉS F, RÍOS A, RAMÍREZ P, MUÑOZ A and RAMIS G (2010) Validation of xCELLigence real-time cell analyzer to assess

compatibility in xenotransplantation with pig-to-baboon model. *Transplantation Proceedings* 42: 3239-3243.

QUINN L, PIETERS R, NIEUWOUDT C, BORGEN AR, KYLIN H and BOUWMAN H (2009) Distribution profiles of selected organic pollutants in soils and sediments of industrial, residential and agricultural areas of South Africa. *Journal of Environmental Monitoring* 11: 1647-1657.

QUINN LP, ROOS C, PIETERS R, LØKEN K, POLDER A, SKAARE JU and BOUWMAN H (2013) Levels of PCBs in wild bird eggs: Considering toxicity through enzyme induction potential and molecular structure. *Chemosphere* 90: 1109-1116.

RAE JE and ALLEN JRL (1993) The significance of organic matter degradation in the interpretation of historical pollution trends in depth profiles of estuarine sediment. *Estuaries* 16: 678-682.

RICE DC and HAYWARD SH (1997) Effects of postnatal exposure to a PCBs mixture in monkeys on nonspatial discrimination reversal and delayed alternation performance. *Neurotoxicology* 18: 479-494.

ROESIJADI G, YOUNG JS, DRUM AS and GURTISEN JM (1984) Behavior of trace metals in *Mytilus edulis* during a reciprocal transplant field experiment. *Marine Ecology Progress Series* 18: 155-70.

ROOS C, PIETERS R, GENTHE B and BOUWMAN H (2011) *Persistent organic pollutants (POPs) in the water environment*. Water Research Commission Report No. 1561/1/11, South Africa.

SACN (SCIENTIFIC ADVISORY COMMITTEE ON NUTRITION) (2004) Committee on Toxicity. Advice on fish consumption: Benefits and Risks. Online at: http://www.sacn.gov.uk/reports/#.

SALAMA AA, MOHAMMED MAM, DUVAL B, POTTER TL and LEVIN RE (1998) Polychlorinated biphenyl concentrations in raw and cooked North Atlantic bluefish (*Pomatomus saltatrix*) fillets. *Journal of Agricultural and Food Chemistry* 46: 1359-1362.

SANGER DM, HOLLAND AF and SCOTT GI (1999) Tidal creek and salt marsh sediments in South Carolina coastal estuaries: II. Distribution of organic contaminants. *Archives of Environmental Contamination and Toxicology* 37: 458-471.

SCHIFF KC and WEISBERG SW (1999) Iron as a reference element for determining trace metal enrichment in Southern California coastal shelf sediments. *Marine Environmental Research* 48: 161-176.

SCHLENK D, SAPOZHNIKOVA Y and CLIFF G (2005) Incidence of organochlorine pesticides in muscle and liver tissues of South African great white sharks *Carcharodon carcharias*. *Marine Pollution Bulletin* 50: 208-236.

SCHNITZLER JG, THOMÉ JP, LEPAGE M and DAS K (2011) Organochlorine pesticides, polychlorinated biphenyls and trace elements in wild European sea bass (*Dicentrarchus labrax*) off European estuaries. *Science of the Total Environment* 409: 3680-3686.

SCHOOF RA, EICKHOV J, YOST LJ, CRAGIN DW, MEACHER DM and MENZEL DB (1999). Dietary exposure to inorganic arsenic. In: Chappell WR, Abernathy CO and Calderon RL (Eds), *Arsenic Exposure and Health Effects*. Elsevier, Amsterdam.

SCHROPP S and WINDOM H (1988) *A guide to the interpretation of metal concentrations in estuarine sediments*. Florida Department of Environmental Protection. Tallahassee, FL.

SCHROPP S, LEWIS FG, WINDOM HL, RYAN JD, CALDER FD and BURNEY LC (1990) Interpretation of metal concentrations in estuarine sediments of Florida using aluminum as a reference element. *Estuaries* 13: 227-235.

SCHULZ R, PEALL SKC, DABROWSKI JM and REINECKE AJ (2001) Current-use insecticides, phosphates and suspended solids in the Lourens River, Western Cape, during the first rainfall event of the wet season. *Water SA* 27: 65-70.

SENN DB, CHESNEY EJ, BLUM JD, BANK MS, MAAG EA and SHINE JP (2010) Stable isotope (N, C, Hg) study of methylmercury sources and trophic transfer in the Northern Gulf of Mexico. *Environmental Science and Technology* 44: 1630-1637.

SERICANO JL, WADE TL, JACKSON TJ, BROOKS JM, TRIPP BW, FARRINGTON JW, MEE LD, READMANN JW, VILLENEUVE J-P and GOLDBERG ED (1995) Trace organic contamination in the Americas: an overview of the US national status and trends and the International Mussel Watch Programmes. *Marine Pollution*

Bulletin 31: 214-225.

SHIM WJ, HONG SH, YIM UH, LI D and KANNAN N (2010) Occurrence and Spatial Distribution of Organic Contaminants in Sediments from Chinhae Bay, Korea. *Toxicology and Environmental Health Science* 2: 119-124.

SHISANA O, LABADARIOS D, REHLE T, SIMBAYI L, ZUMA K, DHANSAY A, REDDY P, PARKER W, HOOSAIN E, NAIDOO P, HONGORO C, MCHIZA Z, STEYN NP, DWANE N, MAKOAE M, MALULEKE T, RAMLAGAN S, ZUNGU N, EVANS MG, JACOBS L, FABER M and SANHANES-1 Team (2013) *South African National Health and Nutrition Examination Survey (SANHANES-1)*. Cape Town: HSRC Press.

SIBALI LL, OKWONKWO JO and MCCRINDLE RI (2008) Determination of selected organochlorine pesticide (OCP) compounds from the Jukskei River catchment area in Gauteng, South Africa. *Water SA* 34: 611-621.

SLOTH JJ, LARSEN EH and JULSHAMN (2005) Survey of inorganic arsenic in marine animals and marine Certified Reference Materials by anion exchange High-Performance Liquid Chromatography-Inductively Coupled Plasma Mass Spectrometry. *Journal of Agricultural and Food Chemistry* 53: 6011-6018.

SMEDES F and DE BOER J (1997) Determination of chlorobiphenyls in sediments – analytical methods. *Trends in Analytical Chemistry* 16: 503-517.

SMITH A and GANGOLLI S (2002) Organochlorine chemicals in seafood: occurrence and health concerns. *Food Chemistry and Toxicology* 40: 767-779.

SNYDER RA and RAO R (2008) *Bioaccumulation of Chemical Contaminants in Fishes of Escambia Bay*. Florida Department of Health.

SNYDER RA and KAROUNA-RENIER N (2009) *Accumulation of pollutants in fish and shellfish from the Northwest Florida Region*. Center for Environmental Diagnostics and Bioremediation, University of West Florida, Pensacola, FL.

SOCLO HH, GARRIGUES P and EWALD M (2000) Origin of polycyclic aromatic hydrocarbons (PAHs) in coastal marine sediments: case studies in Cotonou (Benin) and Aquitaine (France) areas. *Marine Pollution Bulletin* 40: 387-396.

STAHL LL, SNYDER BD, OLSEN AR and PITT JL (2009) Contaminants in fish tissue from US lakes and reservoirs: a national probabilistic study. *Environmental Monitoring and Assessment* 150: 3-19.

STEUER J,SELBIG W, HORNEWER and PREY J (1997) *Sources of contamination in an urban basin in Marquette, Michigan, and an analysis of concentrations, loads, and data quality*. US Geological Survey Water Resources Investigations Report 97-4242; US Geological Survey, Denver, CO.

STEIN ED, TIEFENTHALER LL and SCHIFF K (2006) Watershed-based sources of polycyclic aromatic hydrocarbons in urban stormwater. *Environmental Toxicology and Chemistry* 25: 373-385.

STILLMAN JE, MEYERS PA and EADIE BJ (1998) Perylene: An indicator of alteration processes or precursor materials? *Organic Geochemistry* 29: 1737-1744.

STORELLI MM, STORELLI A, GIACOMINELLI-STUFFLER R and MARCOTRIGIANO GO (2005) Mercury speciation in the muscle of two commercially important fish, hake (*Merluccius merluccius*) and striped mullet (*Mullus barbatus*) from the Mediterranean sea: estimated weekly intake. *Food Chemistry* 89: 295-300.

STUMM W and MORGAN JJ (1996) *Aquatic chemistry*. John Wiley and Sons, New York.

STUNZ G and ROBILLARD M (2011) *Contaminant level of fishes in several coastal bend estuaries: Screening investigation technical report*. Coastal Bend Bays and Estuaries Program Publication CBBEP-69.

SUCHANEK T, EAGLES-SMITH C, SLOTTON D, HARNER E, COLWELL A, ANDERSON N, MULLEN L, FLANDERS J, ADAM D and MCELROY K (2008) Spatio-temporal trends of mercury in fish from a mine-dominated ecosystem at Clear Lake, California: individual, species and population level trends. *Ecological Applications* 18: A177-A195.

SUN J-H, WANG GL, CHAI Y, ZHANG G, LI J and FENG J (2009) Distribution of polycyclic aromatic hydrocarbons (PAHs) in Henan Reach of the Yellow River, Middle China. *Ecotoxicology and Environmental Safety* 72: 1614-1624.

SWARTZ R (1999) Consensus sediment quality guidelines for polycyclic aromatic hydrocarbon mixtures. *Environmental Toxicology and Chemistry* 18: 780-787.

SYAKTI AD, ASIA L, KANZARI F, UMASANGADJI H, MALLERET L, TERNOIS Y, MILLE G and DOUMENQ P (2012) Distribution of organochlorine pesticides (OCs) and polychlorinated biphenyls (PCBs) in marine sediments directly exposed to wastewater from Cortiou, Marseille. *Environmental Science and Pollution Research* 19:1524-1535.

TAYLOR SR and MCLENNAN SM (1981) The composition and evolution of the continental crust: rare earth element evidence from sedimentary rocks. *Philosophical Transactions of the Royal Society, London* 301: 381-399.

TAO J, HUGGINS D, WELKER G, DIAS J, INGERSOLL C and MUROWCHICK J (2010) Sediment contamination of residential streams in the metropolitan Kansas City area, USA: Part I. distribution of polycyclic aromatic hydrocarbon and pesticide-related compounds. *Archives of Environmental Contamination and Toxicology* 59: 352-369.

TEPE Y (2008) Metal concentrations in eight fish species from Aegean and Mediterranean Seas. *Environmental Monitoring and Assessment* 159: 501-509.

THOMAS CA and BENDELL-YOUNG LI (1999) The significance of diagenesis versus riverine input in contributions to the sediment geochemical matrix of iron and manganese in an intertidal region. *Estuarine and Coastal Shelf Science* 48: 635-647.

THOMSEN V, SCHATZLEIN D and MERCURO D (2003) Limits of detection in spectroscopy. *Spectroscopy* 18: 112-114.

TROTTER WJ, CORNELIUSSEN PE, LASKI RR and VANNELLI JJ (1989) Levels of polychlorinated biphenyls and organochlorine pesticides in bluefish before and after cooking. *Journal of Association of Official Analytical Chemists* 72: 501-503.

TSUTSUMI T, YANAGI T, NAKAMUR M, KONO Y, UCHIBE H, IIDA T (2001) Update of daily intake of PCDDs, PCDFs, and dioxin-like PCBs from food in Japan. *Chemosphere* 45: 1129-1137.

TUREKIAN KK and WEDEPOHL KH (1961) Distribution of the elements in some major units of the earth's crust. *Geological Society of America Bulletin* 72: 175-192.

UKFSA (2005) *Survey of arsenic in fish and shellfish: Food Survey Information Sheet 82/05*. Food Standards Agency UK. Online at: tp://www.food.gov.uk/science/research/surveillance/fsis2005/fsis8205#.U1ZIm1e_uzE.

UNEP (1999) *Guidelines for the identification of PCBs and materials containing PCBs*. United Nations Environment Programme: Geneva, Switzerland.

URCAN E, HAERTEL U, STYLLOU M, HICKEL R, SCHERTHAN H and REICHL FX (2010) Real-time xCELLigence impedance analysis of the cytotoxicity of dental composite components on human gingival fibroblasts. *Dental Materials* 26: 51-58.

USA MUSSEL WATCH (2012) Data online at: http://ccma.nos.noaa.gov/about/coast/nsandt/musselwatch.aspx.

USFDA (UNITED STATES FOOD AND DRUG ADMINISTRATION) (1993) *Guidance document for arsenic in shellfish*. U.S. Department of Health and Human Services, Public Health Service, Office of Seafood (HFS-416), Washington, DC.

USEPA (UNITED STATES ENVIRONMENTAL PROTECTION AGENCY) (1996) *Calculation and evaluation of sediment effect concentrations for the amphipod Hyalella azteca and the midge Chironomus riparius*. UGreat Lakes National Program Office, Chicago, IL. EPA 905/R-96/008.

USEPA (UNITED STATES ENVIRONMENTAL PROTECTION AGENCY) (1997) *Mercury Study Report to Congress*. Online at: http://www.epa.gov/hg/report.htm.

USEPA (UNITED STATES ENVIRONMENTAL PROTECTION AGENCY) (2000a) *Guidance for assessing chemical contaminant data for use in fish advisories. Volume 1: Fish sampling and analysis*. Washington, DC. EPA 823-B-00-007.

USEPA (UNITED STATES ENVIRONMENTAL PROTECTION AGENCY) (2000b) *Guidance for assessing chemical*

contaminant data for use in fish advisories. Volume 2: Risk assessment and fish consumption limits. Washington, DC. EPA 823-B-00-007.

USEPA (UNITED STATES ENVIRONMENTAL PROTECTION AGENCY) (2003) *Technical Summary of Information Available on the Bioaccumulation of Arsenic in Aquatic Organisms*. Office of Water, Washington, DC. EPA 822-R-03-032.

USEPA (UNITED STATES ENVIRONMENTAL PROTECTION AGENCY) (2004) Technical Memorandum. Origin of 1 meal/week non-commercial fish consumption rate in National Advisory for Mercury. Online at: http://epa.gov/waterscience/fishadvice/1-meal-per-week.pdf.

USEPA (UNITED STATES ENVIRONMENTAL PROTECTION AGENCY) (2009) *Guidance for implementing the January 2001 methylmercury water quality criterion*. Office of Water, Washington, DC. EPA 823-R-09-002.

USEPA (UNITED STATES ENVIRONMENTAL PROTECTION AGENCY) (2011) *2010 biennial national listing of fish advisories*. EPA-820-F-11-014.

VAN DEN BERG M, BIRNBAUM L, BOSVELD A, BRUNSTRÖM B, COOK P, FEELEY M, GIESY JP, HANBERG A, HASEGAWA R and KENNEDY SW (1998) Toxic equivalency factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife. *Environmental Health Perspectives* 106: 775-792.

VAN METRE PC and MAHLER BJ (2010) Contribution of PAHs from coal-tar pavement sealcoat and other sources to 40 U.S. Lakes. *Science of the Total Environment* 409: 334-344.

VANE CH, HARRISON I and KIM AW (2007) Assessment of polyaromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in surface sediments of the Inner Clyde Estuary, UK. *Marine Pollution Bulletin* 54: 1287-1306.

VARANASI U, STEIN JE and NISHIMOTO M (1989) Biotransformation and disposition of PAH in fish. In: Varanasi U (Ed), *Metabolism of Polycyclic Aromatic Hydrocarbons in the Aquatic Environment.* CRC Press, Boca Raton, FL.

VARANASI U, STIEN JE, REICHERT WL, TILBURY KL and CHAN S-L (1992) Chlorinated and aromatic hydrocarbons in bottom sediments, fish and marine mammals in the US coastal waters: laboratory and field studies of metabolisms and accumulation. In: Walker C and Livingstone DR (Eds), *Persistent Pollutant in Marine Ecosystems*. Pergamon Press, Oxford.

VILLENEUVE DL, BLANKENSHIP AL and GIESY JP (2000) Derivation and application of relative potency estimates based on in vitro bioassay results. *Environmental Toxicology and Chemistry* 19: 2835-2843.

VILLENEUVE DL, RICHTER CA, BLANKENSHIP AL and GIESY JP (2009) Rainbow trout cell bioassay-derived relative potencies for halogenated aromatic hydrocarbons: Comparison and sensitivity analysis. *Environmental Toxicology and Chemistry,* 18: 879-888.

VISTICA DT, SKEHAN P, SCUDIERO D, MONKS A, PITTMAN A and BOYD MR (1991) Tetrazolium-based assays for cellular viability: a critical examination of selected parameters affecting formazan production. *Cancer Research* 51: 2515-2520.

VOSLOO R and BOUWMAN H (2005) *Survey of certain Persistent Organic Pollutants in major South African waters*. Water Research Commission Report No. 1213/1/05, South Africa.

WADE TL, SWEET ST and KLEIN AG (2008) Assessment of sediment contamination in Casco Bay, Maine, USA. *Environmental Pollution* 152: 505-521.

WAGENER A de LR, HAMACHER C, FARIAS CO, GODOY JM, SCOFIELD A de L (2010) Evaluation of tools to identify hydrocarbon sources in recent and historical sediments of a tropical bay. *Marine Chemistry* 21: 67-79.

WAGENER A de LR, MENICONI MFG, HAMACHER C, FARIAS CO, SILVA GC, GABARDO IT and SCOFIELD A de L (2012) Hydrocarbons in sediments of a chronically contaminated bay: The challenge of source assignment. *Mar Marine Pollution Bulletin* 64: 284-294.

WAKEHAM SG, SCHAFFNER C and GIGER W (1980) Polycyclic aromatic hydrocarbons in recent lake sediments I. Compounds having anthropogenic origins. *Geochimica et Cosmochimica Acta* 44: 403-413.

WANG XC, ZHANG YX and CHEN RF (2001) Distribution and partitioning of polycyclic aromatic hydrocarbons

(PAHs) in different size fractions in sediments from Boston Harbor, United States. *Marine Pollution Bulletin* 42: 1139-1149.

WANG Z, YAN W, CHI J and ZHANG (2008) Spatial and vertical distribution of organochlorine pesticides in sediments from Daya Bay, South China. *Marine Pollution Bulletin* 56: 1578-1585.

WANGERSKY PJ (1986) Biological control of trace metal residence time and speciation: A review and synthesis. *Marine Chemistry* 18: 269-297.

WDEC (WASHINGTON STATE DEPARTMENT OF ECOLOGY) (2005) *Screening survey for petroleum contamination at Cornet Bay Marina (Island County)*. Department of Ecology, Washington, Publication No. 05-03-033.

WDEC (WASHINGTON STATE DEPARTMENT OF ECOLOGY) (2012) *Port Angeles harbor sediment characterization study, Port Angeles, Washington: Sediment Investigation Report*. Toxics Cleanup Program, Washington.

WEAVER JMC (1993) *A preliminary survey of pesticide levels in groundwater from a selected area of intensive agriculture in Western Cape*. Water Research Commission Report No. 268/1/93, Pretoria, South Africa.

WEBB GA (2002) *Biology and demography of the spotted grunter* Pomadasys commersonnii *(*Haemulidae*) in South African waters*. MSc Thesis. Rhodes University, Grahamstown.

WEBSTER L, FRYER RJ, DALGARNO J, MEGGINSON C and MOFFAT CF (2001) The polycyclic aromatic hydrocarbon and geochemical biomarker composition of sediments from voes and coastal areas in the Shetland and Orkney Islands. *Journal of Environmental Monitoring* 3: 591-601.

WEDEPOHL KH (1995) The composition of the continental crust. *Geochimica et Cosmochimimica Acta* 59: 1217-1232.

WEI S, LAU RFK, FUNG CN, ZHENG GJ, LAM JCW, CONNELL DW, FANG Z, RICHARDSON BJ and LAM PKS (2006) Trace organic contamination in biota collected from the Pearl River Estuary, China: A preliminary risk assessment. *Marine Pollution Bulletin* 52: 1682-1694.

WEPENER V, SMIT N, COVACI A, DYKE S and BERVOETS L (2012) Seasonal bioaccumulation of organohalogens in tigerfish, *Hydrocynus vittatus* Castelnau, from Lake Pongolapoort, South Africa. *Bulletin of Environmental Contamination and Toxicology* 88: 277-282.

WHO (WORLD HEALTH ORGANISATION) (1993) *Chemistry of Polychlorinated Biphenyls and Terphenyls*. World Health Organization Environmental Health Criteria 140, Geneva.

WINDOM H, SCHROPP S, CALDER F, RYAN J, SMITH R, BURNEY L, LEWIS F and RAWLINSON C (1989) Natural trace metal concentrations in estuarine and coastal marine sediments of the south-eastern United States. *Environmental Science and Technology* 23: 314-320.

WU C, YE H, BAI W, LI Q, GUO D, LU G, YAN H and WANG X (2010) New potential anticancer agent of carborane derivatives: selective cellular interaction and activity of ferrocene-substituted dithio-o-carborane conjugates. *Bioconjugate Chemistry* 22: 16-25.

XUE W and WARSHAWSKY D (2005) Metabolic activation of polycyclic and heterocyclic aromatic hydrocarbons and DNA damage: a review. *Toxicology and Applied Pharmacology* 206: 73-93.

YAMAUCHI H, KAISE T and YAMAMURA Y (1986) Metabolism and excretion of orally administered arsenobetaine in the hamster. *Bulletin of Environmental Contamination and Toxicology* 36: 350-355.

YANG Y, VAN METRE PC, MAHLER BJ, WILSON JT, LIGOUIS B, RAZZAQUE MM, SCHAEFFER DJ and WERTH CJ (2010) Influence of coal-tar sealcoat and other carbonaceous materials on polycyclic aromatic hydrocarbon loading in an urban watershed. *Environmental Science and Technology* 44: 1217-1223.

YAP CK, A ISMAIL and TAN SG (2003) Background concentrations of Cd, Cu, Pb and Zn in the green-lipped mussel *Perna viridis* (Linnaeus) from Peninsular Malaysia. *Marine Pollution Bulletin* 46: 1035-1048.

YEARDLEY RB (2000) Use of small forage fish for regional streams wildlife risk assessment: Relative bioaccumulation of contaminant. *Environmental Monitoring and Assessment* 65: 559-585.

YOSHIMINE RV, CARREIRA RS, SCOFIELD AL, WAGENER ALR (2012) Regional assessment of PAHs contamination in SE Brazil using brown mussels (*Perna perna* Linnaeus 1758). *Marine Pollution Bulletin*

64: 2581-2587.

YUNKER MB and MACDONALD RW (1995) Composition and origins of polycyclic aromatic hydrocarbons in the Mackenzie River and on the Beaufort Sea shelf. *Arctic* 48: 118-129.

YUNKER MB, MACDONALD RW, VINGARZAN R, MITCHELL RH, GOYETTE D and SYLVESTRE S (2002) PAHs in the Fraser River basin: A critical appraisal of PAH ratios as indicators of PAH source and composition. *Organic Geochemistry* 33: 489-515.

ZABIK ME, BOOREN A, ZABIK MJ, WELCH R and HUMPHERY H (1996) Pesticide residues, PCBs and PAHs in baked, charbroiled, salt boiled and smoked Great Lakes lake trout. *Food Chemistry* 55: 231-239.

ZARANKO DT, GRIFFITHS RW and KAUSHIK NK (1997) Biomagnification of polychlorinated biphenyls through a riverine food web. *Environmental Toxicology and Chemistry* 16: 1463-1471.

ZHOU R, ZHU L, YANG K and CHEN Y (2006) Distribution of organochlorine pesticides in surface water and sediments from Qiantang River, East China. *Journal of Hazardous Materials* A137: 68-75.

ZHOU S-S, SHAO L-Y, YANG H-Y, WANG C and LIU W-P (2012) Residues and sources recognition of polychlorinated biphenyls in surface sediments of Jiaojiang Estuary, East China Sea. *Marine Pollution Bulletin* 64: 539-545.

ZHU J, WANG X, XU X and ABASSI YA (2006) Dynamic and label-free monitoring of natural killer cell cytotoxic activity using electronic cell sensor arrays. *Journal of Immunological Methods* 309: 25-33.

APPENDICES

APPENDIX 1

Abstract of publication on brominated flame retardants in sediment in the eThekwini area of KwaZulu-Natal.

ENVIRONMENTAL Science & Technology

Article

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Brominated Flame-Retardants in Sub-Saharan Africa: Burdens in Inland and Coastal Sediments in the eThekwini Metropolitan Municipality, South Africa

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Supporting Information

ABSTRACT: Brominated flame-retardant (BFR) additives are present in many polymeric consumer products at percent levels. High environmental concentrations have been observed near cities and polymer, textile, and electronics manufacturing centers. Most studies have focused on European, North American, and Asian locales. Releases are likely rising most dramatically in countries with weak environmental and human health regulation and enforcement, demand for electrical and electronic equipment (EEE) is escalating, and importation of waste EEE occurs. Several African countries meet these criteria, but little data are available on burdens or sources. To better understand the extent of BFR environmental dissemination in a southern African urban community, inland and coastal sediments were collected in the eThekwini metropolitan municipality, South Africa, and analyzed for polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCD), 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (TBB), 2-ethylhexyl 2,3,4,5-tretabromophalate (TBPH), 1,2-bis (2,4,6-tribromophenoxy) ethane (BTBPE), and decabromodiphenyl ethane (DBDPE). BFRs were detected in all samples (n = 45). Concentration data are presented on total organic carbon (TOC) normalized basis. ΣBFR ranged from 114 to 47 100 ng g^{-1}. Decabromodiphenyl ether was detected in 93% of samples (mean concentration 3208 ng g^{-1}) followed by TBB at 91% (mean conc. 545 ng g^{-1}). Durban Bay is strongly influenced by urban runoff and tidal hydrology, and sediments therein exhibited ΣPBDE concentrations ranging from 1850 to 25 400 ng g^{-1} (median conc. 3240 ng g^{-1}). These levels rival those in the heavily impacted Pearl River Delta, China. BFRs likely enter the South African environment during manufacture of BFR-containing products, during and following product use (i.e., after disposal and as a result of materials recycling activities), and from nonpoint sources such as atmospheric fallout and urban runoff. These results underline the need to investigate further the environmental burdens and risks associated with BFRs in developing countries.

APPENDIX 2

Global positioning system coordinates for stations where sediment was collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2011.

Station	GPS	GPS
UNKN	-29.506496	31.235281
TONG	-29.572451	31.184433
MDLO	-29.648977	31.124826
MHLA	-29.702043	31.099279
MNG1	-29.810422	31.036118
MNG2	-29.809794	31.028306
MNG3	-29.808988	31.018991
MNG4	-29.812290	31.010567
MNG5	-29.810646	31.003355
MNG6	-29.808086	30.998106
MNG7	-29.807764	30.995788
MNG8	-29.805355	30.965335
MNG9	-29.799776	30.991299
MNG10	-29.796761	30.990646
MNG11	-29.791297	30.977406
MNG12	-29.770428	31.000476
MNG13	-29.745537	31.014005
MNG14	-29.727780	31.012171
MNG15	-29.719682	31.005496
MNG16	-29.731017	31.002112
DBAY1	-29.862166	31.022651
DBAY2	-29.862030	31.025489
DBAY3	-29.904267	31.008400
DBAY4	-29.898500	31.003967
DBAY5	-29.885067	30.995733

Station	GPS	GPS
DBAY6	-29.867933	31.013467
DBAY7	-29.890450	31.027467
UMB1	-29.900318	31.002699
UMB2	-29.907525	30.986660
UMB3	-29.896653	30.983435
UMB4	-29.864558	30.964978
UMB5	-29.899331	30.926632
UMB6	-29.876873	30.961870
AMA1	-29.907286	31.007409
AMA2	-29.915351	30.995596
IVC1	-29.892044	31.027063
ISI1	-29.993596	30.948725
ISI2	-29.990735	30.949699
ISI3	-29.990272	30.941997
ISI4	-29.989070	30.941307
ISI5	-29.982485	30.931016
MBO1	-30.008269	30.930108
MBO2	-30.006370	30.925189
MBO3	-30.009471	30.906845
MBO4	-29.995241	30.922107
AMAN	-30.058709	30.881719
LOVU	-30.107196	30.848115
UMSI	-30.128929	30.844453
UMGA	-30.160155	30.822861

APPENDIX 3

Grain size composition and Total Organic Content and Total Organic Carbon fractions of sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2011.VCS = very coarse-grained sand, CS = coarse-grained sand, MS = medium-grained sand, FS = fine-grained sand, VFS = very fine-grained sand.

Station	Gravel %	VCS %	CS %	MS %	FS %	VFS %	Mud %	Sand %	Mean phi	Mean mm	Median phi	Median mm	Sorting	Skewness	Total Organic Content %	Total Organic Carbon %
UNKN	0.00	0.83	5.45	60.24	24.31	3.63	5.55	94.45	1.81	0.29	1.78	0.29	0.80	2.29	0.76	0.41
TONG	6.61	1.69	12.48	50.18	11.96	1.62	15.46	77.93	1.62	0.33	1.59	0.33	1.44	-1.12	1.84	0.30
MDLO	5.54	32.96	24.69	24.72	9.02	1.12	1.95	92.51	0.54	0.69	0.43	0.74	1.17	1.41	0.52	1.32
MHLA	0.35	2.08	17.34	40.63	31.06	3.60	4.94	94.71	1.70	0.31	1.81	0.29	0.97	0.56	0.78	0.74
MNG1	0.14	0.43	1.63	28.02	23.06	6.15	40.55	59.30	2.99	0.13	2.67	0.16	1.27	2.87	1.73	2.08
MNG2	0.00	0.07	0.74	3.22	4.76	3.42	87.80	12.20	4.43	0.05	4.43	0.05	0.61	-2.41	4.80	4.13
MNG3	0.00	0.00	0.22	6.17	31.05	8.11	54.44	45.56	3.67	0.08	4.08	0.06	1.08	-3.60	4.08	2.82
MNG4	0.00	0.06	0.45	1.85	2.94	1.66	93.04	6.96	4.46	0.05	4.46	0.05	0.50	-1.14	6.42	5.13
MNG5	1.04	0.87	1.50	10.17	26.62	8.18	51.62	47.34	3.60	0.08	4.03	0.06	1.18	-4.76	3.30	2.42
MNG6	1.86	8.09	25.89	22.34	3.29	1.79	36.73	61.40	2.12	0.23	1.50	0.35	1.87	7.79	4.01	3.93
MNG7	10.49	1.45	12.14	45.25	18.29	4.93	7.47	82.04	1.57	0.34	1.44	0.37	1.49	-1.35	1.08	5.12
MNG8	1.11	0.72	8.27	41.07	32.44	7.59	8.79	90.10	2.04	0.24	1.98	0.25	1.03	2.24	0.79	0.50
MNG9	0.16	1.15	15.63	42.98	11.11	2.94	26.03	73.81	2.35	0.20	1.70	0.31	1.51	7.49	0.83	0.65
MNG10	0.12	0.88	3.84	8.02	10.90	6.06	70.18	29.70	3.78	0.07	4.29	0.05	1.22	-7.05	3.74	2.49
MNG11	20.24	11.86	8.44	8.84	11.90	4.89	33.83	45.93	1.69	0.31	2.04	0.24	2.55	-7.40	2.30	3.77
MNG12	0.00	0.00	0.20	2.57	23.36	12.15	61.73	38.27	3.84	0.07	4.19	0.05	0.97	-3.07	3.63	2.97
MNG13	0.00	0.00	0.17	21.42	40.88	13.46	24.07	75.93	2.92	0.13	2.56	0.17	1.11	3.31	0.90	0.84
MNG14	0.00	0.64	9.49	56.98	22.08	5.75	5.05	94.95	1.77	0.29	1.64	0.32	0.88	2.64	0.36	0.26
MNG15	6.16	3.82	9.40	34.85	24.98	5.16	15.64	78.20	2.06	0.24	1.89	0.27	1.62	-0.64	0.57	1.49
MNG16	0.08	0.21	1.66	23.99	30.63	12.57	30.86	69.06	2.98	0.13	2.73	0.15	1.24	2.08	1.95	3.17
DBAY1	1.34	3.86	11.10	36.28	40.97	2.46	3.99	94.67	1.80	0.29	1.95	0.26	0.78	-2.08	1.34	0.70
DBAY2	4.33	4.49	5.49	26.20	41.83	4.74	12.93	82.74	2.02	0.25	2.14	0.23	1.23	-1.73	2.05	1.94
DBAY3	0.00	0.00	0.32	5.01	26.68	3.89	64.11	35.89	3.76	0.07	4.22	0.05	1.06	-4.01	7.71	7.48
DBAY4	0.00	0.14	0.22	4.74	30.66	7.85	56.39	43.61	3.69	0.08	4.11	0.06	1.06	-3.49	4.83	4.42
DBAY5	0.09	0.24	1.29	15.75	27.38	2.74	52.51	47.40	3.56	0.08	4.05	0.06	1.20	-4.83	2.91	3.07
DBAY6	0.17	0.17	0.65	8.66	40.29	5.33	44.74	55.10	3.25	0.11	2.99	0.13	1.12	1.90	8.84	2.00
DBAY7	0.00	0.06	0.65	19.85	41.50	4.68	33.25	66.75	2.95	0.13	2.46	0.18	1.16	4.36	1.34	2.56
AMA1	0.00	0.00	0.48	1.45	5.44	2.78	89.84	10.16	4.44	0.05	4.44	0.05	0.57	-1.85	9.79	1.42
AMA2	9.30	9.44	12.92	39.53	24.68	3.79	0.33	90.36	1.21	0.43	1.64	0.32	1.31	-6.22	0.46	1.70
IVC1	0.76	0.48	1.40	14.35	26.44	6.54	50.04	49.20	3.55	0.09	4.00	0.06	1.21	-4.85	6.32	8.87
UMB1	1.57	2.20	11.14	43.53	21.32	6.63	13.60	84.83	1.81	0.28	1.84	0.28	1.06	2.43	1.41	0.80

Station	Gravel %	VCS %	CS %	MS %	FS %	VFS %	Mud %	Sand %	Mean phi	Mean mm	Median phi	Median mm	Sorting	Skewness	Total Organic Content %	Total Organic Carbon %
UMB2	6.00	10.76	12.70	54.23	14.22	1.24	0.85	93.15	1.12	0.46	1.41	0.38	1.07	-3.82	0.44	0.05
UMB4	1.27	2.54	12.43	72.09	11.30	0.11	0.25	98.48	1.48	0.36	1.51	0.35	0.56	-0.61	0.44	0.14
UMB5	0.32	0.79	3.26	17.50	28.46	8.91	40.77	58.91	3.11	0.12	2.98	0.13	1.30	0.46	4.30	2.99
UMB6	1.34	1.78	7.26	55.70	22.75	4.97	6.20	92.46	1.82	0.28	1.76	0.29	0.93	2.14	1.07	0.42
UMB7	0.00	0.06	0.25	1.87	13.99	10.12	73.70	26.30	4.03	0.06	4.32	0.05	0.84	-2.59	9.49	0.90
ISI1	10.79	4.59	16.47	26.42	21.61	2.94	17.18	72.03	1.95	0.26	1.75	0.30	2.02	-1.40	1.80	0.87
ISI2	2.23	3.45	16.40	41.26	27.01	2.09	7.55	90.22	1.63	0.32	1.76	0.30	1.12	1.19	0.78	0.88
ISI3	3.32	31.21	29.54	7.63	9.71	2.51	16.08	80.60	1.31	0.40	0.38	0.77	1.96	14.64	1.36	1.53
IS4	0.14	1.20	3.70	25.74	36.82	2.78	29.61	70.25	2.80	0.14	2.31	0.20	1.29	4.40	2.47	9.17
ISI5	0.68	0.72	3.46	22.85	27.59	2.98	41.71	57.60	2.93	0.13	2.52	0.17	1.33	3.46	3.67	0.47
MBO1	0.47	6.31	18.96	64.12	9.03	0.09	1.02	98.51	1.27	0.42	1.33	0.40	0.70	-0.84	0.35	0.23
MBO2	1.39	9.80	28.79	41.20	14.65	2.01	2.16	96.45	1.18	0.44	1.23	0.43	0.98	-0.29	0.33	0.12
MBO3	0.17	1.99	5.19	35.62	43.74	10.04	3.25	96.58	2.18	0.22	2.11	0.23	0.66	-0.86	0.21	0.63
MBO4	10.70	15.39	36.21	26.59	5.68	2.14	3.29	86.01	0.62	0.65	0.71	0.61	1.29	-1.54	0.53	0.54
AMAN	1.36	2.78	10.17	28.48	18.77	6.19	32.25	66.39	2.62	0.16	2.31	0.20	1.58	2.50	3.22	2.16
LOVU	0.86	1.57	3.96	3.05	6.39	4.43	79.73	19.41	4.05	0.06	4.37	0.05	1.10	-7.56	3.70	2.45
UMSI	0.06	1.83	11.37	53.94	26.99	2.59	3.21	96.73	1.71	0.31	1.68	0.31	0.71	-0.19	0.20	0.15
UMGA	0.97	6.32	14.09	33.60	26.06	5.54	13.42	85.61	1.74	0.30	1.89	0.27	1.26	0.94	0.57	0.47

APPENDIX 4

Metal concentrations in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2011. Al = aluminium, Fe = iron, As = arsenic, Ba = Barium, Be = beryllium, Cd = cadmium, Co = cobalt, Cu = copper, Cr = chromium, Mn = manganese, Hg = mercury, Ni = nickel, Pb = lead, V = vanadium, Zn = zinc.

Station	Al $mg.g^{-1}$	Fe $mg.g^{-1}$	As $\mu g.g^{-1}$	Ba $\mu g.g^{-1}$	Be $\mu g.g^{-1}$	Cd $\mu g.g^{-1}$	Co $\mu g.g^{-1}$	Cu $\mu g.g^{-1}$	Cr $\mu g.g^{-1}$	Mn $\mu g.g^{-1}$	Hg $\mu g.g^{-1}$	Ni $\mu g.g^{-1}$	Pb $\mu g.g^{-1}$	V $\mu g.g^{-1}$	Zn $\mu g.g^{-1}$
UNKN	5.94	5.42	3.32	16.47	0.12	0.163	1.82	13.54	21.38	62.09	<0.03	2.19	9.17	12.80	14.91
TONG	3.65	3.24	3.20	13.23	0.10	0.143	1.08	12.22	10.88	40.63	<0.03	1.11	7.65	6.84	8.67
MDLO	13.31	14.53	4.75	60.40	0.46	0.149	3.98	25.96	40.50	128.85	<0.03	6.94	19.37	19.42	46.49
MHLA	4.34	4.71	<1.0	28.99	0.17	0.145	1.78	6.02	16.34	74.09	<0.03	2.89	4.19	7.05	10.80
MNG1	26.18	26.35	5.55	85.11	0.83	0.361	8.82	52.29	72.67	135.06	0.030	17.23	38.77	42.48	292.42
MNG2	6.34	6.31	1.01	27.78	0.18	0.238	2.02	10.25	18.90	77.05	<0.03	4.99	17.48	10.18	45.59
MNG3	35.52	36.22	5.15	95.34	1.05	0.210	13.55	79.66	96.57	504.23	<0.03	19.34	24.65	46.67	168.09
MNG4	43.84	44.74	5.55	140.69	1.29	0.292	16.26	92.62	109.78	699.69	<0.03	27.52	58.03	64.17	208.30
MNG5	36.79	37.95	7.39	131.91	0.99	0.350	15.68	70.67	84.23	587.19	<0.03	24.08	52.94	62.63	174.21
MNG6	25.26	25.73	4.35	105.96	0.73	0.346	10.58	42.18	59.69	445.62	<0.03	15.42	43.35	37.91	401.03
MNG7	17.15	17.24	3.40	72.38	0.50	0.201	7.75	21.34	47.18	286.08	<0.03	10.18	21.62	28.49	115.00
MNG8	38.03	38.52	8.35	96.74	0.91	0.213	13.77	89.36	94.04	668.32	<0.03	20.29	56.68	54.25	236.33
MNG9	16.13	16.45	2.48	62.51	0.48	0.268	8.16	25.11	41.66	292.54	<0.03	10.68	22.65	28.60	63.43
MNG10	42.62	41.70	8.68	129.66	1.40	0.555	13.95	84.88	127.35	239.38	0.070	30.17	68.75	70.98	485.28
MNG11	32.00	31.17	6.07	90.60	1.01	0.385	9.75	60.40	93.55	172.52	0.040	21.51	50.19	51.15	323.47
MNG12	50.50	50.02	10.40	194.49	1.74	0.648	18.15	112.71	147.97	403.41	0.110	37.86	86.85	81.17	688.58
MNG13	27.63	27.45	4.52	114.00	0.90	0.331	11.04	52.13	72.20	452.34	0.080	18.48	44.76	42.54	287.91
MNG14	24.15	23.75	4.05	107.99	0.74	0.372	8.39	53.81	79.33	297.79	0.040	15.71	40.77	34.28	255.62
MNG15	38.99	38.98	6.52	162.99	1.10	0.489	13.09	84.84	179.29	803.63	0.100	26.95	71.96	53.24	405.12
MNG16	6.53	6.33	<1.0	28.19	0.18	0.391	2.15	14.66	25.50	85.91	<0.03	15.63	15.86	11.33	65.59
DBAY1	7.91	7.98	2.10	39.48	0.39	0.316	3.27	144.69	50.82	75.85	0.270	9.95	64.46	13.32	455.73
DBAY2	9.12	9.42	4.23	91.55	0.57	0.436	4.02	165.54	74.30	105.74	0.190	11.33	95.40	17.38	424.92
DBAY3	20.34	21.43	6.51	104.91	1.00	2.567	22.13	269.43	392.67	249.20	0.090	81.82	160.13	43.08	813.75
DBAY4	16.85	17.37	4.82	80.83	0.89	0.410	6.79	136.51	134.17	120.16	0.230	17.49	226.12	31.75	328.53
DBAY5	26.64	27.97	9.02	157.65	1.47	0.346	11.09	342.87	355.74	328.48	0.130	36.90	106.81	50.92	356.99
DBAY6	22.27	23.03	5.83	109.71	1.02	0.751	11.12	216.18	230.91	426.43	0.060	35.69	87.95	41.61	339.88
DBAY7	0.79	0.64	1.10	11.02	0.11	0.112	0.34	7.22	7.12	46.95	<0.03	1.58	4.61	1.39	41.36
AMA1	35.45	36.31	14.26	141.45	2.06	5.631	35.92	530.33	870.69	277.30	0.180	153.74	376.11	87.56	1663.85
AMA2	12.82	12.96	1.41	67.50	0.44	1.039	6.38	43.10	92.71	199.95	<0.03	23.43	22.00	21.77	149.70
IVC1	20.27	22.26	9.49	67.10	1.64	0.581	24.46	1325.89	920.15	260.22	0.070	336.06	90.93	47.42	547.53
UMB1	10.12	9.20	2.62	30.62	0.25	0.386	4.57	48.85	57.36	125.87	<0.03	14.64	35.16	17.84	103.00

Station	Al $mg.g^{-1}$	Fe $mg.g^{-1}$	As $\mu g.g^{-1}$	Ba $\mu g.g^{-1}$	Be $\mu g.g^{-1}$	Cd $\mu g.g^{-1}$	Co $\mu g.g^{-1}$	Cu $\mu g.g^{-1}$	Cr $\mu g.g^{-1}$	Mn $\mu g.g^{-1}$	Hg $\mu g.g^{-1}$	Ni $\mu g.g^{-1}$	Pb $\mu g.g^{-1}$	V $\mu g.g^{-1}$	Zn $\mu g.g^{-1}$
UMB2	10.34	9.33	1.48	45.14	0.25	0.201	5.51	621.59	54.35	160.48	<0.03	11.15	41.38	16.27	62.60
UMB4	3.70	3.33	1.79	17.86	0.10	0.216	1.33	19.17	12.37	87.71	<0.03	5.02	17.73	7.67	30.97
UMB5	27.58	24.83	5.11	97.12	0.77	0.274	9.45	46.07	65.97	869.06	0.060	15.43	57.70	48.44	146.14
UMB6	6.22	6.51	1.76	30.94	0.19	0.175	1.64	17.13	14.62	100.49	<0.03	4.06	7.61	9.03	43.91
UMB7	10.44	10.57	3.39	38.61	0.28	0.182	5.73	25.30	26.96	194.04	<0.03	8.27	14.06	17.28	85.60
ISI1	13.55	14.75	4.75	30.51	1.02	0.170	4.63	31.35	56.48	94.73	0.030	10.36	29.35	23.52	259.95
ISI2	12.28	13.47	2.40	42.85	0.71	0.127	2.77	21.15	89.33	130.35	<0.03	7.43	24.07	11.29	194.17
ISI3	8.24	8.78	2.26	39.91	0.84	0.191	3.46	31.94	31.94	86.91	<0.03	7.66	28.94	10.83	266.67
IS4	15.38	16.97	5.56	57.85	1.00	0.260	5.62	69.07	81.89	178.59	<0.03	12.67	47.96	26.17	273.30
ISI5	27.95	29.92	7.40	153.35	1.19	0.474	8.36	102.64	138.14	283.95	0.040	23.08	89.67	46.64	490.51
MBO1	2.89	2.82	<1.0	13.58	0.16	0.088	1.49	4.11	12.58	36.22	<0.03	4.37	4.47	4.70	35.51
MBO2	4.79	4.95	<1.0	31.37	0.64	0.054	2.07	5.59	16.70	41.62	<0.03	4.00	5.50	8.64	33.52
MBO3	5.07	5.15	<1.0	24.93	0.71	0.034	2.33	3.98	14.97	58.55	<0.03	3.73	4.01	8.05	12.49
MBO4	9.54	10.09	<1.0	44.15	0.91	0.178	2.91	7.41	28.96	94.01	<0.03	5.02	5.93	13.84	39.10
AMAN	21.63	20.61	7.90	34.94	0.49	0.219	6.20	26.58	53.88	125.75	<0.03	9.55	29.58	32.74	69.57
LOVU	39.00	36.29	7.56	48.46	1.12	0.199	11.90	30.37	70.44	151.62	<0.03	16.26	42.58	58.60	65.94
UMSI	7.78	7.30	4.14	13.01	0.14	0.144	3.29	14.02	25.77	140.78	<0.03	4.46	10.46	18.94	11.02
UMGA	14.39	13.33	6.08	29.65	0.36	0.143	4.93	17.71	37.83	194.43	<0.03	7.44	18.08	25.88	19.94

APPENDIX 5

Polycyclic aromatic hydrocarbon concentrations in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2011.

Station	UNKN µg.kg^{-1}	TONG µg.kg^{-1}	MDLO µg.kg^{-1}	MHLA µg.kg^{-1}	MNG1 µg.kg^{-1}	MNG2 µg.kg^{-1}	MNG3 µg.kg^{-1}	MNG4 µg.kg^{-1}	MNG5 µg.kg^{-1}	MNG6 µg.kg^{-1}	MNG7 µg.kg^{-1}	MNG8 µg.kg^{-1}	MNG9 µg.kg^{-1}	MNG10 µg.kg^{-1}	MNG11 µg.kg^{-1}	MNG12 µg.kg^{-1}	MNG13 µg.kg^{-1}
Naphthalene	0.58	<0.1	<0.1	<0.1	3.67	6.14	4.26	31.43	7.40	4.55	16.62	0.67	2.58	3.75	11.49	5.42	1.01
2-Methyl naphthalene	0.99	<0.1	<0.1	<0.1	4.34	13.58	8.17	50.06	15.13	8.31	27.85	0.96	2.41	7.48	30.01	15.82	2.19
1-Methyl naphthalene	0.53	<0.1	<0.1	<0.1	1.71	6.28	3.03	22.27	8.60	3.61	15.16	0.49	1.40	4.34	16.07	9.34	1.36
Acenaphthene	1.22	<0.1	0.33	<0.1	1.92	6.31	4.00	25.06	5.56	3.13	25.57	0.46	0.98	3.41	19.95	9.65	1.35
Acenaphthylene	0.71	<0.1	<0.1	<0.1	1.92	7.38	3.89	14.80	4.85	2.94	7.53	0.64	0.25	3.12	12.34	4.71	0.70
Fluorene	3.36	<0.1	<0.1	<0.1	3.89	12.95	7.24	46.17	8.61	6.93	37.98	0.65	2.05	6.70	26.44	16.27	2.31
Phenanthrene	58.40	2.42	7.72	1.23	27.15	87.62	53.13	233.20	83.81	57.52	182.50	10.53	14.05	107.33	266.00	110.14	22.48
1-Methylphenanthrene	6.31	0.57	1.06	<0.1	6.86	26.07	15.48	57.33	23.42	13.41	28.91	1.82	5.17	15.32	77.66	39.32	6.15
Anthracene	7.46	0.36	1.23	0.12	6.30	19.78	12.00	45.59	12.83	11.50	31.34	1.62	1.42	20.72	43.06	17.52	3.31
Fluoranthene	102.29	5.12	20.69	1.91	60.84	161.94	113.58	393.61	118.24	90.17	209.28	24.90	35.27	174.94	320.20	138.90	29.41
Pyrene	70.60	4.32	15.78	1.85	61.26	180.03	113.15	402.51	115.17	95.63	187.87	21.93	33.22	138.61	318.99	157.20	27.75
Benz(a)anthracene	48.11	2.30	13.04	1.08	34.12	67.60	45.01	136.20	50.88	43.72	81.00	15.54	34.41	76.97	116.48	48.11	12.98
Chrysene	39.33	4.12	14.37	1.42	37.70	90.80	60.64	175.14	74.23	57.10	94.04	19.14	41.36	93.34	185.33	68.68	20.62
Benzo(b)fluoranthene	30.04	5.96	18.74	1.57	48.96	112.81	77.78	268.11	76.32	69.32	131.53	19.43	27.96	73.25	202.07	72.48	20.57
Benzo(k)fluoranthene	20.80	2.70	10.78	1.07	32.21	71.61	48.04	130.39	47.90	37.07	72.07	13.89	21.89	48.78	129.35	42.72	12.60
Benzo(e)pyrene	18.78	3.75	11.74	1.13	30.78	81.62	53.22	166.55	52.43	48.11	86.85	12.28	16.04	48.36	142.44	49.84	12.99
Benzo(a)pyrene	15.70	1.88	9.53	0.79	27.75	76.41	53.75	158.61	48.56	46.85	84.14	12.24	3.41	25.47	117.14	51.47	12.01
Perylene	8.63	10.21	106.71	2.87	51.24	115.76	67.34	310.08	53.19	58.97	183.28	12.74	1.66	3.01	27.89	47.62	11.53
Benzo(g,h,i)perylene	16.81	4.06	9.59	1.26	33.10	98.32	63.27	217.48	50.63	50.32	109.73	10.69	5.72	33.33	164.15	64.08	9.98
Indeno (1,2,3-c,d) pyrene	14.65	2.86	9.13	0.96	25.07	77.43	52.80	180.65	43.54	45.81	92.49	9.49	7.23	34.68	133.54	51.21	9.04
Dibenzo(a,h)anthracene	2.75	0.70	1.70	0.24	5.49	13.29	9.45	39.07	8.84	8.77	20.74	2.27	1.72	8.00	28.16	7.09	2.03

Station	MNG14 µg.kg^{-1}	MNG15 µg.kg^{-1}	MNG16 µg.kg^{-1}	DBAY1 µg.kg^{-1}	DBAY2 µg.kg^{-1}	DBAY3 µg.kg^{-1}	DBAY4 µg.kg^{-1}	DBAY5 µg.kg^{-1}	DBAY6 µg.kg^{-1}	DBAY7 µg.kg^{-1}	AMA1 µg.kg^{-1}	AMA2 µg.kg^{-1}	IVC1 µg.kg^{-1}	UMB1 µg.kg^{-1}	UMB2 µg.kg^{-1}	UMB4 µg.kg^{-1}
Naphthalene	2.09	2.14	6.38	25.27	34.67	111.58	31.29	25.11	18.90	2.83	93.78	2.92	34.18	5.47	3.22	<0.1
2-Methyl naphthalene	2.53	2.66	5.59	42.64	27.69	273.34	54.80	55.52	46.72	3.73	211.67	22.06	102.96	7.71	7.62	0.55
1-Methyl naphthalene	1.55	1.47	2.78	32.09	14.83	158.81	30.07	31.01	27.29	1.88	115.04	21.11	57.21	6.03	4.66	0.46
Acenaphthene	0.62	0.82	1.27	29.97	49.43	171.33	46.50	29.59	24.69	1.94	64.83	4.44	38.73	4.42	3.54	0.15
Acenaphthylene	<0.1	0.65	1.05	7.12	12.07	13.20	36.18	17.42	23.76	0.96	13.75	2.13	17.05	40.64	0.75	0.20
Fluorene	1.20	1.29	4.03	43.00	63.77	220.34	71.76	42.38	44.02	4.06	122.14	9.91	32.40	48.48	5.34	0.25
Phenanthrene	9.40	13.39	24.77	272.99	440.19	719.95	640.14	353.93	336.22	27.12	452.80	41.29	487.63	549.45	56.53	3.21
1-Methylphenanthrene	2.33	2.70	3.74	71.30	49.24	251.44	99.14	74.01	109.10	8.58	299.95	14.20	72.72	23.04	14.36	0.68
Anthracene	1.07	1.74	3.63	44.16	76.27	141.69	136.58	64.13	53.18	4.13	92.87	2.93	70.12	93.80	6.77	0.36

Station	MNG14 µg.kg^{-1}	MNG15 µg.kg^{-1}	MNG16 µg.kg^{-1}	DBAY1 µg.kg^{-1}	DBAY2 µg.kg^{-1}	DBAY3 µg.kg^{-1}	DBAY4 µg.kg^{-1}	DBAY5 µg.kg^{-1}	DBAY6 µg.kg^{-1}	DBAY7 µg.kg^{-1}	AMA1 µg.kg^{-1}	AMA2 µg.kg^{-1}	IVC1 µg.kg^{-1}	UMB1 µg.kg^{-1}	UMB2 µg.kg^{-1}	UMB4 µg.kg^{-1}
Fluoranthene	12.25	19.31	35.34	398.13	594.91	388.62	880.82	425.57	396.34	33.59	388.83	49.57	481.29	717.10	75.27	8.01
Pyrene	11.31	17.86	29.80	355.33	499.40	541.57	864.23	447.01	421.24	41.78	488.02	47.35	461.40	504.50	76.05	6.61
Benz(a)anthracene	5.94	8.42	15.11	158.35	201.81	240.01	478.50	150.63	103.24	13.28	81.79	15.41	262.58	228.30	27.10	3.62
Chrysene	8.76	14.50	23.07	160.65	152.64	169.67	158.97	150.14	138.25	20.64	130.78	20.79	142.35	225.76	32.44	5.22
Benzo(b)fluoranthene	7.77	8.90	18.02	127.40	194.92	262.27	476.05	231.27	173.89	17.29	253.82	14.34	398.40	140.83	22.50	4.47
Benzo(k)fluoranthene	5.07	6.66	11.23	106.47	139.73	207.47	347.96	147.86	98.62	11.50	153.41	8.79	296.02	116.31	17.86	3.24
Benzo(e)pyrene	5.20	7.21	11.43	86.64	129.10	197.34	363.04	161.69	122.71	11.63	199.43	10.41	278.26	83.75	17.79	3.13
Benzo(a)pyrene	4.16	3.75	10.94	92.09	147.26	198.77	369.08	168.35	115.24	11.39	170.61	7.78	329.26	112.18	15.90	2.89
Perylene	3.22	3.88	9.91	24.76	40.12	82.23	200.68	199.97	107.01	3.91	77.99	3.04	120.66	31.50	5.70	1.69
Benzo(g,h,i)perylene	4.81	5.48	9.92	76.77	173.77	309.19	496.82	220.84	183.17	16.31	333.36	9.40	389.99	67.36	15.28	2.67
Indeno (1,2,3-c,d) pyrene	4.45	4.25	8.45	73.17	144.06	187.31	387.01	174.61	121.21	10.04	193.03	6.94	327.76	73.80	13.51	3.24
Dibenzo(a,h)anthracene	0.91	0.82	1.43	14.23	29.04	40.42	79.14	37.07	30.65	2.00	47.88	2.31	84.67	12.48	2.54	<0.1

Station	UMB5 µg.kg^{-1}	UMB6 µg.kg^{-1}	UMB7 µg.kg^{-1}	ISI1 µg.kg^{-1}	ISI2 µg.kg^{-1}	ISI3 µg.kg^{-1}	IS4 µg.kg^{-1}	ISI5 µg.kg^{-1}	MBO1 µg.kg^{-1}	MBO2 µg.kg^{-1}	MBO3 µg.kg^{-1}	MBO4 µg.kg^{-1}	AMAN µg.kg^{-1}	LOVU µg.kg^{-1}	UMSI µg.kg^{-1}	UMGA µg.kg^{-1}
Naphthalene	20.40	6.09	1.14	1.65	2.16	2.89	17.35	1.99	<0.1	0.64	0.74	34.29	3.83	4.02	<0.1	0.91
2-Methyl naphthalene	34.30	4.74	2.20	4.90	3.84	7.78	34.10	2.45	0.71	1.11	0.91	48.34	3.68	2.13	0.34	1.07
1-Methyl naphthalene	22.56	2.85	1.59	3.13	2.52	5.14	21.45	1.73	<0.1	0.90	0.53	26.47	2.01	1.21	<0.1	0.64
Acenaphthene	25.22	13.64	1.11	1.78	1.55	7.27	14.49	0.82	0.54	0.55	0.41	15.87	1.02	0.81	<0.1	0.26
Acenaphthylene	3.72	0.80	4.36	2.27	1.51	3.77	51.90	0.79	<0.1	0.32	0.27	20.82	1.86	1.51	0.58	0.52
Fluorene	27.65	10.50	2.69	3.72	2.80	22.76	25.71	1.20	0.64	0.58	0.40	27.15	2.84	1.95	0.36	0.54
Phenanthrene	161.09	97.67	42.09	43.37	24.85	110.25	212.33	12.06	5.57	3.45	3.27	186.51	16.70	21.74	2.87	5.04
1-Methylphenanthrene	24.92	6.76	6.10	10.37	8.62	41.51	49.68	1.97	0.64	0.50	0.54	50.32	3.74	2.79	<0.1	0.63
Anthracene	25.54	20.20	6.69	5.59	4.24	27.24	47.46	1.61	0.84	0.52	0.50	36.80	2.43	2.40	0.88	0.63
Fluoranthene	173.15	157.04	64.16	57.81	33.88	152.46	537.41	21.47	11.28	4.39	3.90	274.96	29.71	26.19	15.93	5.99
Pyrene	141.92	126.32	63.61	52.24	33.70	161.49	453.09	17.09	9.87	4.76	3.72	285.26	26.00	19.35	14.28	5.72
Benz(a)anthracene	71.47	69.10	28.46	42.23	14.18	63.63	210.16	12.30	6.93	2.67	2.40	92.29	19.28	9.33	14.31	3.16
Chrysene	95.91	77.61	33.94	25.79	17.87	77.66	227.96	14.32	8.69	3.34	2.84	123.16	21.18	12.97	15.80	3.85
Benzo(b)fluoranthene	76.58	57.29	29.56	34.56	20.36	72.05	194.53	14.01	9.93	3.70	3.70	146.14	24.36	14.90	15.04	5.06
Benzo(k)fluoranthene	48.06	48.75	18.53	20.06	11.26	43.34	130.54	9.63	6.57	2.18	2.32	80.48	13.64	9.19	10.32	3.04
Benzo(e)pyrene	51.36	35.09	18.37	21.32	14.70	49.77	137.27	10.25	6.65	2.46	2.51	117.28	15.58	9.20	9.94	3.55
Benzo(a)pyrene	49.42	51.05	19.17	18.59	10.83	37.34	135.58	11.39	7.96	2.45	2.43	107.22	12.67	8.03	8.05	3.39
Perylene	16.14	14.81	7.79	15.42	12.16	24.43	80.60	5.72	4.29	5.32	8.33	42.33	58.26	207.66	1.67	7.30
Benzo(g,h,i)perylene	47.86	33.55	18.90	20.80	14.64	41.23	120.22	8.87	7.06	2.53	2.37	158.29	13.68	7.71	7.72	3.33
Indeno (1,2,3-c,d) pyrene	39.44	37.82	15.56	19.15	12.28	36.21	106.71	9.78	6.76	2.51	2.20	109.91	12.44	7.94	8.43	2.23
Dibenzo(a,h)anthracene	8.45	4.99	3.16	4.07	3.33	7.57	26.44	1.88	1.49	0.30	0.41	26.79	2.67	1.25	2.63	0.60

APPENDIX 6

Pesticide concentrations in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2011.

Station	UNKN µg.kg^{-1}	TONG µg.kg^{-1}	MDLO µg.kg^{-1}	MHLA µg.kg^{-1}	MNG1 µg.kg^{-1}	MNG2 µg.kg^{-1}	MNG3 µg.kg^{-1}	MNG4 µg.kg^{-1}	MNG5 µg.kg^{-1}	MNG6 µg.kg^{-1}	MNG7 µg.kg^{-1}	MNG8 µg.kg^{-1}	MNG9 µg.kg^{-1}	MNG10 µg.kg^{-1}	MNG11 µg.kg^{-1}	MNG12 µg.kg^{-1}	MNG13 µg.kg^{-1}
BHC-alpha	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
BHC-beta	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
BHC-delta	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
BHC-gamma	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Endosulfan-I	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Endosulfan-II	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Hexachlorobenzene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Heptachlor	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Heptachlor epoxide	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Aldrin	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Dieldrin	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
chlorpyrifos	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	10.86	13.00	35.65	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Endrin	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Perthane	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Oxychlordane	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Trans-chlordane	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Cis-chlordane	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Trans-nonachlor	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Cis-nonachlor	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Dicofol	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Mirex	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
2,4'-DDD	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
4,4'-DDD	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
2,4'-DDE	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
4,4'-DDE	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
2,4'-DDT	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
4,4'-DDT	0.46	<0.10	0.31	2.94	4.24	14.00	2.68	32.95	6.31	2.48	<0.10	1.12	2.17	11.83	<0.10	7.21	1.97
Parlar 26	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Parlar 50	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Parlar 62	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10

Station	MNG14 µg.kg^{-1}	MNG15 µg.kg^{-1}	MNG16 µg.kg^{-1}	DBAY1 µg.kg^{-1}	DBAY2 µg.kg^{-1}	DBAY3 µg.kg^{-1}	DBAY4 µg.kg^{-1}	DBAY5 µg.kg^{-1}	DBAY6 µg.kg^{-1}	DBAY7 µg.kg^{-1}	AMA1 µg.kg^{-1}	AMA2 µg.kg^{-1}	IVC1 µg.kg^{-1}	UMB1 µg.kg^{-1}	UMB2 µg.kg^{-1}	UMB4 µg.kg^{-1}
BHC-alpha	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
BHC-beta	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
BHC-delta	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
BHC-gamma	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Endosulfan-I	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Endosulfan-II	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Hexachlorobenzene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Heptachlor	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Heptachlor epoxide	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Aldrin	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Dieldrin	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
chlorpyrifos	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Endrin	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Perthane	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Oxychlordane	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Trans-chlordane	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	3.78	<0.10	<0.10	<0.10	<0.10
Cis-chlordane	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	1.84	<0.10	<0.10	<0.10	<0.10
Trans-nonachlor	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	1.08	<0.10	<0.10	<0.10	<0.10
Cis-nonachlor	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Dicofol	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Mirex	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
2,4'-DDD	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
4,4'-DDD	<0.10	<0.10	1.26	16.73	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
2,4'-DDE	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
4,4'-DDE	<0.10	<0.10	1.32	6.70	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	0.27	<0.10	1.01	<0.10	<0.10
2,4'-DDT	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
4,4'-DDT	<0.10	2.01	2.80	20.48	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	2.59	<0.10	<0.10
Parlar 26	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Parlar 50	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Parlar 62	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10

Station	UMB5 µg.kg^{-1}	UMB6 µg.kg^{-1}	UMB7 µg.kg^{-1}	ISI1 µg.kg^{-1}	ISI2 µg.kg^{-1}	ISI3 µg.kg^{-1}	IS4 µg.kg^{-1}	ISI5 µg.kg^{-1}	MBO1 µg.kg^{-1}	MBO2 µg.kg^{-1}	MBO3 µg.kg^{-1}	MBO4 µg.kg^{-1}	AMAN µg.kg^{-1}	LOVU µg.kg^{-1}	UMSI µg.kg^{-1}	UMGA µg.kg^{-1}
BHC-alpha	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
BHC-beta	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
BHC-delta	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
BHC-gamma	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Endosulfan-I	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Endosulfan-II	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Hexachlorobenzene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Heptachlor	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Heptachlor epoxide	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Aldrin	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Dieldrin	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
chlorpyrifos	3.88	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Endrin	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Perthane	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Oxychlordane	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Trans-chlordane	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Cis-chlordane	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Trans-nonachlor	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Cis-nonachlor	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Dicofol	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Mirex	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
2,4'-DDD	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
4,4'-DDD	11.69	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	0.41	<0.10	<0.10
2,4'-DDE	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
4,4'-DDE	11.32	<0.10	<0.10	1.14	1.46	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	0.31	0.69	<0.10	<0.10
2,4'-DDT	13.19	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
4,4'-DDT	18.25	1.04	<0.10	<0.10	<0.10	8.63	<0.10	0.68	<0.10	0.77	0.34	3.02	2.45	5.17	<0.10	0.37
Parlar 26	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Parlar 50	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Parlar 62	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10

APPENDIX 7

Polychlorinated biphenyl concentrations in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2011.

Station	UNKN µg.kg^{-1}	TONG µg.kg^{-1}	MDLO µg.kg^{-1}	MHLA µg.kg^{-1}	MNG1 µg.kg^{-1}	MNG2 µg.kg^{-1}	MNG3 µg.kg^{-1}	MNG4 µg.kg^{-1}	MNG5 µg.kg^{-1}	MNG6 µg.kg^{-1}	MNG7 µg.kg^{-1}	MNG8 µg.kg^{-1}	MNG9 µg.kg^{-1}	MNG10 µg.kg^{-1}	MNG11 µg.kg^{-1}	MNG12 µg.kg^{-1}	MNG13 µg.kg^{-1}
PCB1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB3	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB4,10	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB9,7	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB6	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB8,5	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB19	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB18	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	1.28	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB17	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB15	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB27,24	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB16,32	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	3.32	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB34	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB29	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB26	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB25	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB28,31	<0.1	<0.1	<0.1	<0.1	0.84	1.21	4.21	<0.1	<0.1	<0.1	2.69	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB33,20	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB53	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB51	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB22	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	1.09	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB45	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB46	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB69	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB52	<0.1	<0.1	<0.1	<0.1	1.13	1.59	1.67	6.87	0.92	1.05	3.19	<0.1	<0.1	0.52	<0.1	1.68	<0.1
PCB49	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	1.76	<0.1	<0.1	0.27	<0.1	0.49	<0.1
PCB47,48,75	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB35	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB44	<0.1	<0.1	<0.1	<0.1	<0.1	0.73	0.77	2.48	<0.1	<0.1	2.07	<0.1	<0.1	<0.1	<0.1	0.69	<0.1
PCB37	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB42,59	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB41,64	<0.1	<0.1	<0.1	<0.1	1.47	<0.1	1.87	<0.1	<0.1	<0.1	3.21	<0.1	<0.1	0.58	<0.1	<0.1	<0.1
PCB40	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

Station	UNKN µg.kg^{-1}	TONG µg.kg^{-1}	MDLO µg.kg^{-1}	MHLA µg.kg^{-1}	MNG1 µg.kg^{-1}	MNG2 µg.kg^{-1}	MNG3 µg.kg^{-1}	MNG4 µg.kg^{-1}	MNG5 µg.kg^{-1}	MNG6 µg.kg^{-1}	MNG7 µg.kg^{-1}	MNG8 µg.kg^{-1}	MNG9 µg.kg^{-1}	MNG10 µg.kg^{-1}	MNG11 µg.kg^{-1}	MNG12 µg.kg^{-1}	MNG13 µg.kg^{-1}
PCB67	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB100	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB63	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB74	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB66,70,95	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB91	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB56,60	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB92	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB84	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB101,90	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.83	<0.1	<0.1	<0.1
PCB99	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB119	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB83	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB97	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB87,115	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB85	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB136	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB110	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	1.38	<0.1	<0.1	<0.1
PCB77	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB82	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB151	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB135	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB107	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB123	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB149	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	1.02	<0.1	<0.1	1.00	<0.1	<0.1	<0.1
PCB118	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB134	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB131	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB122	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB146	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB153,132	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB105	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB141	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB179	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB137	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB130	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB176	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

Station	UNKN µg.kg^{-1}	TONG µg.kg^{-1}	MDLO µg.kg^{-1}	MHLA µg.kg^{-1}	MNG1 µg.kg^{-1}	MNG2 µg.kg^{-1}	MNG3 µg.kg^{-1}	MNG4 µg.kg^{-1}	MNG5 µg.kg^{-1}	MNG6 µg.kg^{-1}	MNG7 µg.kg^{-1}	MNG8 µg.kg^{-1}	MNG9 µg.kg^{-1}	MNG10 µg.kg^{-1}	MNG11 µg.kg^{-1}	MNG12 µg.kg^{-1}	MNG13 µg.kg^{-1}
PCB138,158	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	2.00	<0.1	<0.1	2.00	<0.1	<0.1	<0.1
PCB129	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB178	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB175	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB187	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB183	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB128	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB167	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB185	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB174	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB177	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB202	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB171	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB156	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB157	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB173	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB201	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB172	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB197	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB180,193	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB191	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB200	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB170,190	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB199	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB203,196	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB189	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB208	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB195	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB207	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB194	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB205	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB206	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB209	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

Station	MNG14	MNG15	MNG16	DBAY1	DBAY2	DBAY3	DBAY4	DBAY5	DBAY6	DBAY7	AMA1	AMA2	IVC1	UMB1	UMB2	UMB4

	µg.kg^{-1}	µg.kg^{-1}	µg.kg^{-1}	µg.kg^{-1}	µg.kg^{-1}	µg.kg^{-1}	µg.kg^{-1}	µg.kg^{-1}	µg.kg^{-1}	µg.kg^{-1}	µg.kg^{-1}	µg.kg^{-1}	µg.kg^{-1}	µg.kg^{-1}	µg.kg^{-1}	µg.kg^{-1}
PCB1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB3	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB4,10	<0.1	<0.1	<0.1	<0.1	<0.1	2.98	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB9,7	<0.1	<0.1	<0.1	<0.1	<0.1	1.20	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB6	<0.1	<0.1	<0.1	<0.1	<0.1	2.27	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB8,5	<0.1	<0.1	<0.1	<0.1	<0.1	15.08	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.83	<0.1	<0.1
PCB19	<0.1	<0.1	<0.1	<0.1	<0.1	0.93	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB18	<0.1	<0.1	<0.1	<0.1	<0.1	26.53	<0.1	<0.1	1.38	<0.1	<0.1	0.34	<0.1	<0.1	<0.1	<0.1
PCB17	<0.1	<0.1	<0.1	<0.1	<0.1	12.64	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB15	<0.1	<0.1	<0.1	<0.1	<0.1	2.50	<0.1	<0.1	2.09	0.58	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB27,24	<0.1	<0.1	<0.1	<0.1	<0.1	2.24	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB16,32	<0.1	<0.1	<0.1	<0.1	<0.1	18.93	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	1.35	<0.1	<0.1
PCB34	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB29	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB26	<0.1	<0.1	<0.1	<0.1	<0.1	4.54	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB25	<0.1	<0.1	<0.1	<0.1	<0.1	1.88	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB28,31	<0.1	<0.1	<0.1	<0.1	<0.1	62.22	<0.1	<0.1	<0.1	1.36	<0.1	0.97	<0.1	2.25	<0.1	<0.1
PCB33,20	<0.1	<0.1	<0.1	<0.1	<0.1	42.86	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	1.46	<0.1	<0.1
PCB53	<0.1	<0.1	<0.1	<0.1	<0.1	2.91	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB51	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB22	<0.1	<0.1	<0.1	<0.1	<0.1	12.35	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.39	<0.1	<0.1
PCB45	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB46	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB69	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB52	<0.1	<0.1	<0.1	<0.1	0.45	18.02	<0.1	5.86	2.50	0.62	<0.1	0.80	<0.1	0.76	<0.1	<0.1
PCB49	<0.1	<0.1	<0.1	<0.1	<0.1	15.07	<0.1	1.74	<0.1	<0.1	<0.1	0.32	<0.1	0.51	<0.1	<0.1
PCB47,48,75	<0.1	<0.1	<0.1	<0.1	<0.1	11.66	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB35	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.84	<0.1	<0.1	<0.1	<0.1
PCB44	<0.1	<0.1	<0.1	<0.1	<0.1	17.81	<0.1	3.96	<0.1	0.97	<0.1	<0.1	<0.1	0.64	<0.1	<0.1
PCB37	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB42,59	<0.1	<0.1	<0.1	<0.1	<0.1	5.44	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB41,64	<0.1	<0.1	<0.1	<0.1	<0.1	30.26	<0.1	6.13	<0.1	0.67	<0.1	<0.1	<0.1	1.26	<0.1	<0.1
PCB40	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB67	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB100	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB63	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	3.58	<0.1	<0.1	<0.1	<0.1
PCB74	<0.1	<0.1	<0.1	<0.1	<0.1	11.43	<0.1	1.06	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

Station	MNG14 µg.kg^{-1}	MNG15 µg.kg^{-1}	MNG16 µg.kg^{-1}	DBAY1 µg.kg^{-1}	DBAY2 µg.kg^{-1}	DBAY3 µg.kg^{-1}	DBAY4 µg.kg^{-1}	DBAY5 µg.kg^{-1}	DBAY6 µg.kg^{-1}	DBAY7 µg.kg^{-1}	AMA1 µg.kg^{-1}	AMA2 µg.kg^{-1}	IVC1 µg.kg^{-1}	UMB1 µg.kg^{-1}	UMB2 µg.kg^{-1}	UMB4 µg.kg^{-1}
PCB66,70,95	<0.1	<0.1	<0.1	<0.1	<0.1	51.82	<0.1	16.55	<0.1	0.85	<0.1	0.79	<0.1	<0.1	<0.1	<0.1
PCB91	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB56,60	<0.1	<0.1	<0.1	<0.1	<0.1	20.07	<0.1	<0.1	<0.1	<0.1	<0.1	1.78	<0.1	<0.1	<0.1	<0.1
PCB92	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	6.39	<0.1	<0.1	<0.1	<0.1
PCB84	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	25.04	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB101,90	<0.1	<0.1	<0.1	<0.1	1.61	7.15	<0.1	13.34	<0.1	0.40	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB99	<0.1	<0.1	<0.1	<0.1	<0.1	3.17	<0.1	7.06	<0.1	<0.1	<0.1	0.68	<0.1	<0.1	<0.1	<0.1
PCB119	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	1.45	<0.1	<0.1	<0.1	<0.1
PCB83	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB97	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB87,115	<0.1	<0.1	<0.1	<0.1	<0.1	3.38	<0.1	2.18	<0.1	<0.1	<0.1	4.79	<0.1	<0.1	<0.1	<0.1
PCB85	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB136	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB110	<0.1	<0.1	<0.1	<0.1	0.85	10.96	<0.1	14.88	<0.1	<0.1	<0.1	5.31	<0.1	<0.1	<0.1	<0.1
PCB77	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	4.38	<0.1	<0.1	<0.1	<0.1
PCB82	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB151	<0.1	<0.1	<0.1	<0.1	0.81	<0.1	<0.1	2.00	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB135	<0.1	<0.1	<0.1	<0.1	0.76	<0.1	<0.1	1.69	<0.1	<0.1	<0.1	17.29	<0.1	<0.1	<0.1	<0.1
PCB107	<0.1	<0.1	0.21	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	5.08	<0.1	<0.1	<0.1	<0.1
PCB123	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	1.11	<0.1	<0.1	<0.1	<0.1
PCB149	<0.1	<0.1	<0.1	<0.1	5.36	5.49	<0.1	16.40	<0.1	<0.1	<0.1	<0.1	<0.1	0.28	<0.1	<0.1
PCB118	<0.1	<0.1	<0.1	<0.1	<0.1	12.66	<0.1	20.82	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB134	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	2.88	<0.1	<0.1	<0.1	<0.1
PCB131	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	15.30	<0.1	<0.1	<0.1	<0.1
PCB122	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	1.29	<0.1	<0.1	<0.1	<0.1
PCB146	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	7.84	<0.1	<0.1	<0.1	<0.1
PCB153,132	<0.1	<0.1	<0.1	<0.1	4.18	5.66	<0.1	14.51	<0.1	<0.1	<0.1	3.11	<0.1	<0.1	<0.1	<0.1
PCB105	<0.1	<0.1	<0.1	<0.1	<0.1	5.46	<0.1	10.15	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB141	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB179	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.86	<0.1	<0.1	<0.1	<0.1
PCB137	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	33.58	<0.1	<0.1	<0.1	<0.1
PCB130	<0.1	<0.1	0.36	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB176	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	1.45	<0.1	<0.1	<0.1	<0.1
PCB138,158	<0.1	<0.1	<0.1	<0.1	8.39	11.99	4.42	32.48	1.53	<0.1	<0.1	<0.1	<0.1	0.74	<0.1	<0.1
PCB129	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	7.06	<0.1	<0.1	<0.1	<0.1
PCB178	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	4.08	<0.1	<0.1	<0.1	<0.1
PCB175	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	3.44	<0.1	<0.1	<0.1	<0.1

Station	MNG14 µg.kg^{-1}	MNG15 µg.kg^{-1}	MNG16 µg.kg^{-1}	DBAY1 µg.kg^{-1}	DBAY2 µg.kg^{-1}	DBAY3 µg.kg^{-1}	DBAY4 µg.kg^{-1}	DBAY5 µg.kg^{-1}	DBAY6 µg.kg^{-1}	DBAY7 µg.kg^{-1}	AMA1 µg.kg^{-1}	AMA2 µg.kg^{-1}	IVC1 µg.kg^{-1}	UMB1 µg.kg^{-1}	UMB2 µg.kg^{-1}	UMB4 µg.kg^{-1}
PCB187	<0.1	<0.1	<0.1	<0.1	2.51	<0.1	<0.1	1.83	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB183	<0.1	<0.1	<0.1	<0.1	1.02	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB128	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	7.06	<0.1	<0.1	<0.1	<0.1
PCB167	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	4.16	<0.1	<0.1	<0.1	<0.1
PCB185	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB174	<0.1	<0.1	<0.1	<0.1	1.34	<0.1	<0.1	2.16	<0.1	<0.1	<0.1	2.39	<0.1	<0.1	<0.1	<0.1
PCB177	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	2.75	<0.1	<0.1	<0.1	<0.1
PCB202	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB171	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB156	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB157	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB173	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB201	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	30.22	<0.1	<0.1	<0.1	<0.1
PCB172	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB197	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB180,193	<0.1	<0.1	<0.1	<0.1	8.29	<0.1	<0.1	12.68	<0.1	<0.1	<0.1	11.75	<0.1	<0.1	<0.1	<0.1
PCB191	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	2.18	<0.1	<0.1	<0.1	<0.1
PCB200	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	1.97	<0.1	<0.1	<0.1	<0.1
PCB170,190	<0.1	<0.1	<0.1	<0.1	1.34	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB199	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB203,196	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB189	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB208	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB195	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB207	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB194	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB205	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB206	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB209	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

Station	UMB5 µg.kg^{-1}	UMB6 µg.kg^{-1}	UMB7 µg.kg^{-1}	ISI1 µg.kg^{-1}	ISI2 µg.kg^{-1}	ISI3 µg.kg^{-1}	IS4 µg.kg^{-1}	ISI5 µg.kg^{-1}	MBO1 µg.kg^{-1}	MBO2 µg.kg^{-1}	MBO3 µg.kg^{-1}	MBO4 µg.kg^{-1}	AMAN µg.kg^{-1}	LOVU µg.kg^{-1}	UMSI µg.kg^{-1}	UMGA µg.kg^{-1}
PCB1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB3	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB4,10	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB9,7	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

Station	UMB5 µg.kg^{-1}	UMB6 µg.kg^{-1}	UMB7 µg.kg^{-1}	ISI1 µg.kg^{-1}	ISI2 µg.kg^{-1}	ISI3 µg.kg^{-1}	IS4 µg.kg^{-1}	ISI5 µg.kg^{-1}	MBO1 µg.kg^{-1}	MBO2 µg.kg^{-1}	MBO3 µg.kg^{-1}	MBO4 µg.kg^{-1}	AMAN µg.kg^{-1}	LOVU µg.kg^{-1}	UMSI µg.kg^{-1}	UMGA µg.kg^{-1}
PCB6	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB8,5	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB19	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB18	<0.1	<0.1	<0.1	<0.1	<0.1	1.57	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB17	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB15	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB27,24	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB16,32	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB34	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB29	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB26	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB25	<0.1	<0.1	<0.1	0.88	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB28,31	0.95	<0.1	<0.1	<0.1	0.89	8.36	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB33,20	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB53	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB51	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB22	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB45	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB46	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB69	<0.1	<0.1	<0.1	0.39	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB52	0.39	<0.1	<0.1	<0.1	0.34	3.47	1.41	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB49	0.23	<0.1	<0.1	<0.1	0.22	2.95	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB47,48,75	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB35	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB44	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB37	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB42,59	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB41,64	<0.1	<0.1	<0.1	<0.1	<0.1	6.06	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB40	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB67	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB100	<0.1	<0.1	<0.1	0.28	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB63	<0.1	<0.1	<0.1	1.54	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB74	<0.1	<0.1	<0.1	<0.1	<0.1	1.84	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB66,70,95	<0.1	<0.1	<0.1	<0.1	1.28	9.19	3.50	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB91	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB56,60	<0.1	<0.1	<0.1	<0.1	<0.1	5.17	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB92	<0.1	<0.1	<0.1	0.55	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

Station	UMB5 µg.kg^{-1}	UMB6 µg.kg^{-1}	UMB7 µg.kg^{-1}	ISI1 µg.kg^{-1}	ISI2 µg.kg^{-1}	ISI3 µg.kg^{-1}	IS4 µg.kg^{-1}	ISI5 µg.kg^{-1}	MBO1 µg.kg^{-1}	MBO2 µg.kg^{-1}	MBO3 µg.kg^{-1}	MBO4 µg.kg^{-1}	AMAN µg.kg^{-1}	LOVU µg.kg^{-1}	UMSI µg.kg^{-1}	UMGA µg.kg^{-1}
PCB84	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB101,90	<0.1	<0.1	<0.1	<0.1	0.91	4.42	1.55	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB99	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB119	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB83	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB97	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB87,115	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB85	<0.1	<0.1	<0.1	0.82	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB136	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB110	<0.1	<0.1	<0.1	<0.1	0.75	5.69	3.27	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB77	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB82	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB151	<0.1	<0.1	<0.1	<0.1	1.10	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB135	<0.1	<0.1	<0.1	<0.1	0.49	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB107	<0.1	<0.1	<0.1	0.73	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB123	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB149	0.19	<0.1	<0.1	<0.1	4.51	4.31	2.73	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB118	<0.1	<0.1	<0.1	<0.1	2.46	<0.1	<0.1	<0.1	7.18	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB134	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB131	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB122	<0.1	<0.1	<0.1	0.64	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB146	<0.1	<0.1	<0.1	<0.1	0.67	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB153,132	<0.1	<0.1	<0.1	<0.1	3.99	3.82	2.05	<0.1	0.36	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB105	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.26	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB141	<0.1	<0.1	<0.1	<0.1	1.98	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB179	<0.1	<0.1	<0.1	<0.1	1.42	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB137	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB130	<0.1	<0.1	<0.1	1.75	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB176	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB138,158	0.57	<0.1	<0.1	<0.1	8.00	8.62	5.41	<0.1	1.23	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB129	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB178	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB175	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB187	<0.1	<0.1	<0.1	<0.1	3.37	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB183	<0.1	<0.1	<0.1	<0.1	1.40	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB128	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB167	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

Station	UMB5 µg.kg^{-1}	UMB6 µg.kg^{-1}	UMB7 µg.kg^{-1}	ISI1 µg.kg^{-1}	ISI2 µg.kg^{-1}	ISI3 µg.kg^{-1}	IS4 µg.kg^{-1}	ISI5 µg.kg^{-1}	MBO1 µg.kg^{-1}	MBO2 µg.kg^{-1}	MBO3 µg.kg^{-1}	MBO4 µg.kg^{-1}	AMAN µg.kg^{-1}	LOVU µg.kg^{-1}	UMSI µg.kg^{-1}	UMGA µg.kg^{-1}
PCB185	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB174	<0.1	<0.1	<0.1	<0.1	2.92	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB177	<0.1	<0.1	<0.1	<0.1	2.08	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB202	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB171	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB156	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB157	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB173	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB201	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB172	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB197	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB180,193	<0.1	<0.1	<0.1	<0.1	11.51	3.39	3.59	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB191	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB200	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB170,190	<0.1	<0.1	<0.1	<0.1	3.27	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB199	<0.1	<0.1	<0.1	<0.1	0.93	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB203,196	<0.1	<0.1	<0.1	<0.1	1.04	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB189	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB208	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB195	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB207	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB194	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB205	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB206	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB209	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

APPENDIX 8

Global positioning system coordinates for stations where sediment was collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2012.

Station	GPS	GPS
MNG1	-29.810827°	31.036663°
MNG2	-29.809222°	31.024610°
MNG3	-29.809608°	31.015888°
MNG4	-29.810958°	31.004637°
MNG5	-29.809332°	31.002467°
MNG6	-29.813513°	31.000474°
MNG7	-29.803705°	30.992446°
MNG8	-29.803871°	30.981006°
MNG9	-29.805335°	30.965476°
MNG10	-29.803213°	30.963909°
MNG11	-29.796191°	30.982485°
MNG12	-29.787850°	30.994672°
MNG13	-29.769305°	31.004396°
MNG14	-29.760932°	31.019063°
MNG15	-29.750444°	31.011757°
MNG17	-29.727788°	31.012117°
MNG18	-29.717373°	31.000009°
MNG19	-29.734737°	30.997561°
MNG20	-29.732059°	30.984093°
MNG21	-29.750353°	30.889851°
MNG22	-29.715479°	30.868902°
IVC1	-29.893865°	31.027479°
IVC2	-29.891078°	31.023584°
DBAY1	-29.889428°	31.027570°
DBAY2	-29.881731°	31.025629°
DBAY3	-29.862121°	31.025517°
DBAY4	-29.862393°	31.022675°

Station	GPS	GPS
DBAY5	-29.867239°	31.012785°
DBAY6	-29.875042°	31.008823°
DBAY7	-29.885427°	30.996161°
DBAY8	-29.891083°	31.007284°
DBAY9	-29.898226°	31.004033°
BC1	-29.897692°	31.002107°
DBAY10	-29.904127°	31.008510°
AMA1	-29.914428°	30.996488°
AMA2	-29.920118°	30.982036°
AMA3	-29.932339°	30.973067°
UMB1	-29.896466°	30.980838°
UMB2	-29.876889°	30.961892°
UMB3	-29.864604°	30.965267°
UMB4	-29.862057°	30.967785°
UMB5	-29.848904°	30.953237°
UMB7	-29.845020°	30.890498°
UMB8	-29.835270°	30.878018°
UMB/UMH	-29.900388°	31.002754°
UMH1	-29.910192°	30.979529°
UMH3	-29.897690°	30.901502°
UMH5	-29.879753°	30.883957°
UMH6	-29.863055°	30.867171°
ISI2	-29.993577°	30.948891°
ISI4	-29.990284°	30.942038°
ISI5	-29.989035°	30.941322°
ISI7	-29.997749°	30.937549°
ISI8	-29.982424°	30.931091°

APPENDIX 9

Grain size composition and Total Organic Content and Total Organic Carbon fractions of sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2012.VCS = very coarse-grained sand, CS = coarse-grained sand, MS = medium-grained sand, FS = fine-grained sand, VFS = very fine-grained sand.

Station	Gravel %	VCS %	CS %	MS %	FS %	VFS %	Mud %	Sand %	Mean phi	Mean mm	Median phi	Median mm	Sorting	Skewness	Total Organic Content %	Total Organic Carbon %
MNG1	0.22	0.76	2.76	47.89	34.87	5.45	8.05	91.73	2.13	0.23	1.98	0.25	0.84	2.77	0.48	1.95
MNG2	0.00	0.15	0.97	49.33	26.57	3.52	19.46	80.54	2.58	0.17	1.99	0.25	1.18	5.79	1.42	1.13
MNG3	0.11	0.34	1.85	46.11	43.42	5.33	2.84	97.05	2.07	0.24	2.02	0.25	0.46	-0.05	0.50	0.40
MNG4	4.42	15.83	40.13	18.90	3.69	0.55	16.48	79.10	1.53	0.35	0.77	0.59	1.91	11.13	1.34	1.71
MNG5	0.00	12.95	57.22	25.01	3.00	0.34	1.48	98.52	0.71	0.61	0.68	0.62	0.69	0.32	0.31	0.25
MNG6	0.03	0.34	5.27	43.56	28.21	2.37	20.22	79.75	2.53	0.17	2.02	0.25	1.29	5.34	2.17	2.75
MNG7	1.10	1.42	2.41	1.84	2.73	3.88	86.62	12.28	4.42	0.05	4.42	0.05	0.79	-5.60	3.51	2.99
MNG8	3.83	6.23	20.15	52.64	11.69	3.44	2.02	94.15	1.29	0.41	1.29	0.41	0.95	-0.79	0.14	0.32
MNG9	0.32	5.58	56.85	35.42	1.64	0.16	0.03	99.65	0.83	0.56	0.83	0.56	0.58	0.08	0.15	0.16
MNG10	0.00	10.55	44.76	34.72	6.33	2.15	1.49	98.51	0.93	0.52	0.91	0.53	0.84	0.75	0.18	0.19
MNG11	2.20	1.72	6.97	38.91	21.16	5.56	23.48	74.32	2.50	0.18	2.01	0.25	1.48	4.64	1.72	2.60
MNG12	0.00	0.12	2.42	18.24	20.81	6.05	52.36	47.64	3.51	0.09	4.05	0.06	1.28	-5.97	2.39	1.84
MNG13	0.79	2.42	13.28	45.04	15.06	4.27	19.14	80.07	2.30	0.20	1.77	0.29	1.49	5.76	0.71	0.91
MNG14	1.43	1.43	10.59	52.39	29.37	1.89	2.90	95.67	1.71	0.31	1.72	0.30	0.71	-0.03	0.36	0.38
MNG15	2.60	3.92	20.13	55.68	11.94	3.42	2.31	95.09	1.35	0.39	1.33	0.40	0.84	-0.10	0.33	0.37
MNG17	0.00	0.68	19.16	45.09	22.23	6.42	6.42	93.58	1.73	0.30	1.52	0.35	1.04	3.77	0.40	0.40
MNG18	0.00	0.06	0.12	0.70	7.78	12.14	79.20	20.80	3.91	0.07	4.37	0.05	0.91	-2.93	5.18	5.89
MNG19	5.07	4.19	15.72	19.06	7.84	4.29	43.83	51.10	2.61	0.16	2.65	0.16	1.92	-4.45	3.46	3.76
MNG20	0.52	1.34	9.11	27.65	19.11	8.90	33.37	66.11	2.71	0.15	2.45	0.18	1.49	2.37	0.53	0.76
MNG21	0.18	0.95	7.26	52.83	19.09	4.94	14.75	85.07	1.80	0.29	1.76	0.29	0.94	3.70	1.57	1.01
MNG22	0.05	7.30	34.28	42.58	14.16	1.18	0.45	99.50	1.15	0.45	1.16	0.45	0.82	-0.09	0.16	0.11
IVC1	0.13	0.45	1.70	22.92	22.02	7.03	45.75	54.12	3.03	0.12	2.70	0.15	1.28	2.83	5.08	2.03
IVC2	7.10	3.70	8.28	59.73	18.36	0.93	1.90	91.00	1.49	0.36	1.61	0.33	1.02	-4.99	0.50	7.07
DBAY1	0.10	0.17	0.34	11.20	41.80	4.16	42.23	57.67	3.17	0.11	2.82	0.14	1.13	2.79	3.64	1.97
DBAY2	1.38	1.26	4.25	24.69	33.65	5.08	29.69	68.93	2.80	0.14	2.36	0.19	1.35	3.49	1.13	0.96
DBAY3	2.50	3.78	7.26	15.12	31.00	3.89	36.45	61.05	2.76	0.15	2.47	0.18	1.61	0.53	5.47	5.33
DBAY4	4.04	5.69	9.48	39.24	35.07	2.26	4.22	91.74	1.67	0.32	1.85	0.28	0.95	-3.77	1.91	1.35
DBAY5	13.10	16.61	28.91	26.06	12.08	1.17	2.07	84.83	0.63	0.64	0.71	0.61	1.37	-1.72	1.37	1.22
DBAY6	0.00	0.12	0.40	1.33	14.32	5.31	78.52	21.48	4.05	0.06	4.36	0.05	0.86	-2.88	1.48	2.45
DBAY7	12.13	18.37	21.65	17.18	15.06	2.27	13.34	74.53	1.02	0.49	0.89	0.54	1.89	4.24	2.98	3.17
DBAY8	1.72	2.65	7.05	13.96	21.48	9.36	43.78	54.50	2.95	0.13	2.78	0.15	1.53	-0.57	3.26	2.46

Station	Gravel %	VCS %	CS %	MS %	FS %	VFS %	Mud %	Sand %	Mean phi	Mean mm	Median phi	Median mm	Sorting	Skewness	Total Organic Content %	Total Organic Carbon %
DBAY9	0.00	0.06	0.13	0.89	5.08	12.01	81.83	18.17	4.09	0.06	4.39	0.05	0.75	-1.86	2.71	2.97
BC1	5.87	2.97	4.86	30.68	40.21	4.23	11.18	82.95	2.08	0.24	2.09	0.24	1.33	-2.63	2.40	6.84
DBAY10	0.00	0.00	0.33	1.97	9.86	2.71	85.13	14.87	4.41	0.05	4.41	0.05	0.61	-2.24	2.32	3.11
AMA1	12.77	2.93	3.99	21.79	45.40	5.21	7.91	79.32	1.69	0.31	2.12	0.23	1.65	-7.69	1.55	1.45
AMA2	0.00	5.53	12.38	41.22	32.20	3.49	5.18	94.82	1.72	0.30	1.85	0.28	1.02	0.26	1.07	2.34
AMA3	3.43	5.43	11.57	50.42	27.97	0.71	0.47	96.10	1.55	0.34	1.71	0.30	0.86	-2.74	0.19	0.60
UMB1	1.25	2.65	16.65	58.26	16.77	3.26	1.16	97.59	1.51	0.35	1.52	0.35	0.77	0.02	0.19	0.34
UMB2	1.58	4.61	24.55	48.95	13.16	3.21	3.94	94.48	1.38	0.38	1.36	0.39	0.83	-0.46	0.66	0.67
UMB3	0.07	1.75	26.80	54.34	10.92	2.22	3.90	96.03	1.36	0.39	1.33	0.40	0.71	0.37	0.52	0.61
UMB4	0.00	9.03	24.62	33.55	22.75	4.03	6.02	93.98	1.44	0.37	1.52	0.35	1.21	1.60	0.66	0.79
UMB5	0.00	6.60	31.44	44.93	13.28	2.44	1.31	98.69	1.24	0.42	1.23	0.43	0.85	0.35	0.25	0.33
UMB7	1.12	5.64	29.50	53.70	8.45	0.94	0.65	98.23	1.18	0.44	1.21	0.43	0.73	-0.40	0.19	0.18
UMB8	14.99	17.13	36.27	29.60	1.56	0.07	0.38	84.63	0.34	0.79	0.56	0.68	1.16	-3.22	0.18	1.41
UMB/ UMH	0.64	6.51	34.50	44.38	10.62	0.77	2.58	96.78	1.15	0.45	1.18	0.44	0.81	-0.25	0.39	0.54
UMH1	0.32	2.78	7.60	63.08	23.17	1.86	1.19	98.49	1.69	0.31	1.69	0.31	0.65	-0.31	0.17	0.22
UMH3	0.24	1.61	26.45	60.75	9.09	0.86	1.00	98.76	1.29	0.41	1.28	0.41	0.62	0.12	0.22	0.28
UMH5	0.00	3.09	21.38	56.83	11.53	2.22	4.95	95.05	1.41	0.38	1.40	0.38	0.93	2.35	0.72	1.03
UMH6	5.02	15.57	29.24	34.17	9.49	2.67	3.84	91.14	0.93	0.53	1.00	0.50	1.10	-1.00	0.31	0.27
ISI2	1.58	7.29	23.27	26.31	18.98	2.65	19.92	78.50	2.07	0.24	1.75	0.30	1.75	4.27	0.71	2.50
ISI4	0.00	0.00	1.79	6.32	17.58	3.85	70.46	29.54	3.78	0.07	4.29	0.05	1.12	-5.13	12.16	6.36
ISI5	0.00	0.97	5.81	34.08	38.87	4.54	15.73	84.27	2.43	0.19	2.14	0.23	1.09	3.10	1.53	2.36
ISI7	0.00	1.17	6.21	44.87	40.94	2.25	4.56	95.44	1.97	0.26	1.97	0.26	0.58	-0.33	0.92	1.29
ISI8	0.37	0.43	1.58	12.19	19.74	6.95	58.74	40.89	3.64	0.08	4.15	0.06	1.21	-5.60	4.74	4.07

APPENDIX 10

Metal concentrations in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2012. Al = aluminium, Fe = iron, As = arsenic, Ba = Barium, Be = beryllium, Cd = cadmium, Co = cobalt, Cu = copper, Cr = chromium, Mn = manganese, Hg = mercury, Ni = nickel, Pb = lead, V = vanadium, Zn = zinc.

Station	Al $mg.g^{-1}$	Fe $mg.g^{-1}$	As $\mu g.g^{-1}$	Ba $\mu g.g^{-1}$	Be $\mu g.g^{-1}$	Cd $\mu g.g^{-1}$	Co $\mu g.g^{-1}$	Cu $\mu g.g^{-1}$	Cr $\mu g.g^{-1}$	Mn $\mu g.g^{-1}$	Hg $\mu g.g^{-1}$	Ni $\mu g.g^{-1}$	Pb $\mu g.g^{-1}$	V $\mu g.g^{-1}$	Zn $\mu g.g^{-1}$
MNG1	33.26	33.61	5.60	63.38	0.92	0.09	11.07	87.29	88.91	463.93	<0.03	18.00	46.20	61.25	155.55
MNG2	14.64	12.07	3.69	30.46	0.37	0.24	4.97	23.59	33.70	86.20	<0.03	8.68	18.34	20.95	76.89
MNG3	5.33	6.80	<1	15.91	0.15	0.21	2.94	27.02	34.48	105.60	<0.03	4.55	15.72	15.17	37.37
MNG4	7.38	6.00	<1	23.27	0.22	0.18	3.31	16.08	16.22	100.88	<0.03	4.66	7.49	10.15	37.73
MNG5	3.80	3.39	<1	11.86	0.14	0.20	2.06	4.97	8.30	35.49	<0.03	2.82	4.95	5.50	12.02
MNG6	8.21	8.52	1.43	33.32	0.21	0.34	3.99	28.70	36.87	279.68	<0.03	6.19	21.66	15.05	50.37
MNG7	61.99	44.72	10.45	241.95	1.72	0.26	24.00	75.03	112.15	1565.48	<0.03	34.04	97.81	71.57	493.77
MNG8	6.19	6.59	<1	22.76	0.20	0.19	3.56	8.70	15.33	110.78	<0.03	4.73	8.63	10.94	21.73
MNG9	0.62	0.51	<1	2.64	0.02	0.08	<1	<1	1.75	29.08	<0.03	0.76	<1	1.09	<1
MNG10	5.09	7.28	<1	19.46	0.19	0.17	3.40	5.75	17.09	201.38	<0.03	5.27	7.52	12.21	8.03
MNG11	29.03	27.84	6.76	97.65	0.78	0.23	12.91	58.54	75.33	403.68	<0.03	20.04	41.35	53.39	160.20
MNG12	23.01	24.24	<1	121.65	0.91	0.19	9.19	33.82	61.17	354.54	<0.03	18.67	28.57	34.83	179.24
MNG13	11.71	11.83	3.06	49.22	0.36	0.21	6.92	17.97	30.11	235.84	<0.03	9.08	13.19	18.87	85.52
MNG14	5.83	6.71	<1	23.41	0.19	0.17	3.81	15.79	24.45	170.04	<0.03	5.81	7.00	12.40	45.20
MNG15	4.94	5.90	<1	20.20	0.17	0.18	3.33	6.09	17.12	77.85	<0.03	3.91	8.15	10.89	59.48
MNG17	7.90	9.47	1.65	34.53	0.28	0.21	5.41	11.32	24.90	213.14	<0.03	6.58	12.06	17.18	81.68
MNG18	36.42	42.43	5.99	89.80	0.84	1.00	11.46	130.48	267.65	263.14	<0.03	31.11	118.69	72.76	5531.55
MNG19	25.83	32.63	5.33	102.65	0.80	0.27	9.59	1453.48	92.34	395.04	<0.03	19.51	32.35	56.23	124.70
MNG20	18.05	14.61	<1	69.55	0.50	0.16	9.51	49.49	46.11	428.24	<0.03	13.38	22.80	28.54	83.15
MNG21	7.08	4.42	<1	23.37	0.16	0.22	2.35	4.12	22.26	72.58	<0.03	3.17	8.12	9.37	9.60
MNG22	3.91	3.71	<1	22.83	0.14	0.09	2.62	1.95	8.97	170.34	<0.03	2.20	3.70	7.99	8.01
IVC1	18.17	26.92	8.97	48.66	0.64	0.58	19.00	911.24	474.62	310.96	<0.03	256.59	82.81	43.66	386.13
IVC2	4.23	5.87	3.84	14.94	0.15	0.37	3.32	43.21	62.86	131.36	<0.03	14.27	12.76	9.62	38.82
DBAY1	20.93	21.54	8.22	49.65	0.61	0.19	9.22	62.05	56.51	271.21	0.04	17.83	37.69	39.78	86.67
DBAY2	14.24	15.25	4.38	79.31	0.45	0.16	5.38	35.82	36.65	196.91	<0.03	11.86	33.87	27.34	60.06
DBAY3	13.45	14.47	2.54	44.47	0.30	0.50	7.37	212.12	38.09	98.71	0.59	13.25	186.38	20.84	747.75
DBAY4	6.21	6.55	<1	20.51	0.16	0.39	3.43	204.22	21.49	66.24	0.04	8.71	91.58	10.61	277.44
DBAY5	9.67	10.32	<1	23.32	0.25	0.30	6.56	126.82	32.14	142.91	<0.03	11.85	55.61	15.65	82.32
DBAY6	37.19	41.60	9.10	106.36	1.23	0.45	14.50	162.22	95.59	405.51	0.08	33.08	83.91	72.34	217.92
DBAY7	17.51	18.24	13.28	61.06	0.55	0.58	16.12	84.86	265.26	335.31	<0.03	53.49	99.18	27.76	189.30
DBAY8	15.10	16.39	<1	48.45	0.52	0.51	7.63	112.32	47.66	202.71	<0.03	22.22	45.52	28.46	120.42

Station	Al $mg.g^{-1}$	Fe $mg.g^{-1}$	As $\mu g.g^{-1}$	Ba $\mu g.g^{-1}$	Be $\mu g.g^{-1}$	Cd $\mu g.g^{-1}$	Co $\mu g.g^{-1}$	Cu $\mu g.g^{-1}$	Cr $\mu g.g^{-1}$	Mn $\mu g.g^{-1}$	Hg $\mu g.g^{-1}$	Ni $\mu g.g^{-1}$	Pb $\mu g.g^{-1}$	V $\mu g.g^{-1}$	Zn $\mu g.g^{-1}$
DBAY9	30.05	33.77	5.94	97.41	1.10	0.61	12.38	136.22	89.43	261.81	<0.03	31.12	82.13	50.04	199.80
BC1	10.12	10.21	1.98	64.66	0.46	0.81	7.90	91.13	61.71	142.21	<0.03	16.00	74.09	14.72	145.98
DBAY10	45.91	47.44	10.46	136.06	1.28	0.54	16.42	923.34	167.75	366.31	0.24	43.52	124.08	76.15	426.57
AMA1	5.09	6.95	4.22	27.46	0.18	0.37	6.05	70.21	79.27	124.46	<0.03	14.93	46.91	15.08	148.51
AMA2	38.65	40.52	8.77	120.26	1.11	0.62	16.51	748.54	148.76	450.33	<0.03	103.05	211.37	64.40	295.95
AMA3	4.11	6.58	2.41	31.63	0.16	0.17	3.80	79.54	42.41	154.53	<0.03	9.55	34.04	10.00	112.71
UMB1	3.28	4.65	2.86	15.93	0.15	0.19	2.14	15.10	18.74	107.91	<0.03	5.17	9.08	7.48	20.69
UMB2	6.58	6.62	2.93	24.06	0.25	0.27	3.78	15.82	31.65	136.26	<0.03	27.67	11.61	12.83	49.51
UMB3	4.77	4.77	2.18	20.20	0.18	0.09	2.39	7.52	13.92	150.66	<0.03	3.51	7.30	8.35	16.37
UMB4	8.34	11.64	4.23	35.58	0.31	0.09	4.62	20.81	37.13	160.66	<0.03	9.15	28.03	18.21	43.07
UMB5	4.10	4.65	2.31	14.46	0.16	0.23	1.72	69.78	14.66	64.03	<0.03	3.00	7.74	8.83	15.33
UMB7	3.13	2.82	3.43	13.10	0.13	0.19	1.12	3.66	7.41	31.04	<0.03	2.05	6.40	4.82	20.26
UMB8	4.35	5.16	2.12	18.33	0.21	0.07	2.48	9.75	19.80	61.17	<0.03	4.20	5.55	9.72	32.73
UMB/ UMH	3.45	3.41	1.93	10.41	0.14	0.08	1.83	23.93	23.19	250.06	<0.03	4.76	5.68	6.09	16.59
UMH1	2.77	2.43	<1	13.23	0.09	0.18	1.54	7.92	11.49	56.26	<0.03	3.10	6.19	4.31	8.80
UMH3	2.72	2.18	<1	12.03	0.09	0.05	<1	1.89	4.51	39.59	<0.03	0.87	5.81	3.39	11.44
UMH5	2.70	1.96	<1	13.19	0.09	0.20	<1	3.54	5.03	20.82	<0.03	1.28	4.36	3.19	18.18
UMH6	3.56	2.87	<1	34.84	0.13	0.14	1.04	2.33	9.15	53.08	0.04	1.56	10.29	4.26	36.88
ISI2	12.18	10.17	2.16	20.59	0.30	0.11	4.66	20.54	32.12	81.74	<0.03	5.93	16.75	17.91	90.45
ISI4	29.39	30.84	5.37	109.38	0.71	0.39	11.01	186.29	165.01	272.63	<0.03	31.36	133.47	48.97	920.55
ISI5	9.93	9.33	3.69	23.89	0.25	0.14	3.85	33.71	42.47	134.63	<0.03	5.91	28.39	17.15	89.55
ISI7	5.59	8.12	2.89	49.30	0.18	0.30	3.57	30.40	41.58	118.73	<0.03	15.19	26.00	11.80	220.23
ISI8	5.49	8.02	3.74	49.07	0.17	0.36	3.79	30.51	42.28	119.13	<0.03	15.19	26.20	12.02	221.31

APPENDIX 11

Polycyclic aromatic hydrocarbon concentrations in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2012.

Station	MNG1 µg.kg^{-1}	MNG2 µg.kg^{-1}	MNG3 µg.kg^{-1}	MNG4 µg.kg^{-1}	MNG5 µg.kg^{-1}	MNG6 µg.kg^{-1}	MNG7 µg.kg^{-1}	MNG8 µg.kg^{-1}	MNG9 µg.kg^{-1}	MNG10 µg.kg^{-1}	MNG11 µg.kg^{-1}	MNG12 µg.kg^{-1}	MNG13 µg.kg^{-1}	MNG14 µg.kg^{-1}
Naphthalene	6.80	8.30	<1	6.40	3.60	15.40	27.40	5.60	3.00	3.10	21.90	11.10	9.00	5.30
2-Methyl naphthalene	8.00	6.80	2.70	5.50	2.80	20.80	22.70	4.10	2.50	1.90	19.70	7.90	7.90	4.00
1-Methyl naphthalene	8.00	4.80	2.10	5.20	2.30	12.80	15.10	2.70	1.20	1.70	11.60	7.00	4.70	2.40
Acenaphthene	1.30	<1	<1	<1	<1	<1	4.80	<1	<1	1.00	9.90	2.20	1.90	<1
Acenaphthylene	2.50	3.30	1.60	3.10	1.60	<1	12.50	1.90	1.80	1.30	8.80	7.70	4.10	2.30
Fluorene	3.30	3.20	2.70	4.60	1.50	<1	15.10	1.40	1.20	1.00	11.90	5.10	3.80	2.10
Phenanthrene	18.60	22.50	26.50	20.20	8.70	79.30	60.00	14.80	8.70	8.70	84.50	29.70	19.80	15.80
1-Methylphenanthrene	4.80	5.00	4.70	1.00	2.20	22.40	17.30	4.30	2.60	2.80	17.60	7.40	5.70	4.70
Anthracene	7.10	9.10	8.20	12.40	3.70	<1	26.20	6.60	4.40	5.20	34.70	13.30	9.40	8.60
Fluoranthene	15.10	26.30	17.50	23.10	7.20	102.90	69.60	13.80	3.70	4.10	110.00	32.40	17.10	14.90
Pyrene	12.00	24.10	16.40	24.40	6.30	107.10	66.20	11.30	3.60	3.80	85.90	27.10	17.00	11.80
Benz(a)anthracene	4.40	10.90	4.40	9.70	1.90	40.50	22.50	4.80	1.50	<1	36.40	10.40	5.60	7.20
Chrysene	6.80	14.10	9.20	15.20	2.60	67.40	36.60	6.70	1.90	1.20	55.20	16.60	9.70	8.50
Benzo(b)fluoranthene	4.80	11.10	5.50	11.20	2.00	41.80	29.80	4.40	1.70	<1	36.80	12.80	6.70	7.40
Benzo(k)fluoranthene	3.30	5.70	2.40	4.70	<1	19.50	12.40	2.40	1.20	<1	15.00	7.00	3.20	4.50
Benzo(e)pyrene	4.50	9.10	4.10	9.30	2.00	42.70	20.30	3.30	1.30	<1	27.60	9.80	5.70	5.60
Benzo(a)pyrene	36.60	4.80	2.20	4.80	<1	33.80	11.90	1.60	1.00	<1	21.60	5.50	2.60	2.40
Perylene	6.50	20.90	4.40	19.90	4.20	<1	253.00	5.60	1.40	2.20	17.60	26.50	14.80	5.50
Benzo(g,h,i)perylene	7.80	18.10	13.90	31.20	2.70	30.70	51.30	7.30	2.60	1.70	67.30	25.90	12.10	8.70
Indeno (1,2,3-c,d) pyrene	7.10	17.40	9.50	16.00	<1	<1	34.90	4.90	2.60	<1	49.20	14.40	10.10	7.90
Dibenzo(a,h)anthracene	2.60	3.60	2.70	5.40	<1	<1	11.40	1.50	<1	<1	12.70	3.40	2.90	3.80

Station	MNG15 µg.kg^{-1}	MNG17 µg.kg^{-1}	MNG18 µg.kg^{-1}	MNG19 µg.kg^{-1}	MNG20 µg.kg^{-1}	MNG21 µg.kg^{-1}	MNG22 µg.kg^{-1}	IVC1 µg.kg^{-1}	IVC2 µg.kg^{-1}	DBAY1 µg.kg^{-1}	DBAY2 µg.kg^{-1}	DBAY3 µg.kg^{-1}	DBAY4 µg.kg^{-1}	DBAY5 µg.kg^{-1}
Naphthalene	8.10	7.30	49.90	27.50	4.70	4.40	2.50	153.40	21.10	32.80	11.40	121.20	56.50	21.50
2-Methyl naphthalene	9.20	5.70	207.10	19.80	3.10	2.60	1.90	259.20	52.90	54.80	53.40	101.30	40.40	27.20
1-Methyl naphthalene	5.00	3.80	145.60	16.60	3.60	2.30	2.00	115.70	36.90	23.30	21.40	56.00	24.00	20.20
Acenaphthene	<1	1.40	<1	7.70	<1	<1	<1	34.20	<1	3.20	2.20	62.80	18.00	9.20
Acenaphthylene	1.60	2.60	<1	4.80	2.30	2.80	<1	15.00	<1	2.50	<1	16.60	2.60	5.40
Fluorene	2.60	3.50	<1	16.30	1.90	1.80	1.30	78.00	10.50	19.40	26.00	109.70	48.30	30.10
Phenanthrene	26.20	17.90	545.50	98.10	10.40	10.60	8.30	515.50	131.40	107.70	115.40	618.50	179.20	331.30
1-Methylphenanthrene	5.40	8.30	398.30	1.00	3.80	2.50	2.20	120.00	104.70	26.90	18.70	<1	<1	74.10
Anthracene	2.00	7.80	<1	29.30	7.30	5.40	6.30	87.50	8.80	12.90	<1	75.00	17.50	60.20

Fluoranthene	11.10	10.80	442.80	92.30	11.40	8.90	7.60	766.30	63.30	89.90	51.00	1266.40	318.40	737.80
Pyrene	7.80	12.30	435.50	67.30	9.90	6.40	3.50	768.90	100.60	91.80	54.40	1100.30	264.40	561.20
Benz(a)anthracene	2.90	3.70	92.80	28.60	3.20	1.90	<1	391.30	19.80	37.10	18.80	315.40	81.50	269.70
Chrysene	5.80	6.00	196.50	39.10	5.00	3.70	<1	452.70	57.40	49.90	28.50	406.40	117.80	314.00
Benzo(b)fluoranthene	3.00	3.60	60.30	22.40	3.60	4.30	<1	207.60	15.30	24.60	13.80	162.50	46.50	125.60
Benzo(k)fluoranthene	1.70	2.30	23.40	11.20	1.40	2.40	<1	161.00	8.80	20.80	10.80	160.10	44.10	116.60
Benzo(e)pyrene	2.70	3.30	39.30	20.60	2.20	3.00	<1	154.00	15.30	16.30	9.80	126.40	34.50	93.90
Benzo(a)pyrene	<1	1.60	30.70	10.80	1.40	1.70	<1	128.80	6.80	13.80	6.70	132.20	29.90	91.00
Perylene	<1	8.90	1.00	19.70	6.70	2.50	<1	39.10	2.20	12.30	11.60	35.00	8.00	22.90
Benzo(g,h,i)perylene	3.40	8.10	18.70	38.70	3.90	4.70	<1	62.10	4.20	7.50	4.50	69.40	16.20	35.70
Indeno (1,2,3-c,d) pyrene	3.00	5.60	<1	19.20	4.00	3.40	<1	57.50	3.10	6.30	4.80	60.90	17.60	38.30
Dibenzo(a,h)anthracene	<1	1.50	<1	8.90	1.20	1.50	<1	20.70	<1	3.40	1.90	20.30	6.50	12.60

Station	**DBAY6** $\mu g.kg^{-1}$	**DBAY7** $\mu g.kg^{-1}$	**DBAY8** $\mu g.kg^{-1}$	**DBAY9** $\mu g.kg^{-1}$	**BC1** $\mu g.kg^{-1}$	**DBAY10** $\mu g.kg^{-1}$	**AMA1** $\mu g.kg^{-1}$	**AMA2** $\mu g.kg^{-1}$	**AMA3** $\mu g.kg^{-1}$	**UMB1** $\mu g.kg^{-1}$	**UMB2** $\mu g.kg^{-1}$	**UMB3** $\mu g.kg^{-1}$	**UMB4** $\mu g.kg^{-1}$	**UMB5** $\mu g.kg^{-1}$
Naphthalene	24.90	40.40	23.90	11.00	308.20	29.00	50.70	132.90	<1	12.20	7.50	4.80	<1	<1
2-Methyl naphthalene	36.10	70.10	52.80	22.70	626.40	51.90	98.90	77.70	<1	27.40	5.10	3.90	<1	<1
1-Methyl naphthalene	18.50	37.50	22.50	11.50	309.10	21.90	57.80	42.30	<1	17.60	4.40	3.80	<1	<1
Acenaphthene	4.50	30.80	3.60	<1	27.30	4.40	12.20	4.90	<1	2.00	<1	<1	<1	<1
Acenaphthylene	3.10	4.70	3.20	4.80	20.80	1.90	2.20	4.10	<1	3.80	3.90	1.20	<1	<1
Fluorene	16.10	59.60	28.60	14.20	112.40	20.90	40.00	35.60	<1	6.90	3.00	2.10	<1	<1
Phenanthrene	111.30	266.80	89.10	114.80	797.80	98.00	233.10	157.50	<1	37.10	19.40	13.40	<1	<1
1-Methylphenanthrene	24.70	41.80	<1	<1	199.50	<1	112.30	60.40	<1	11.60	4.40	3.40	<1	<1
Anthracene	17.20	42.40	15.40	22.30	121.10	19.70	19.90	15.00	<1	13.20	8.90	5.30	<1	<1
Fluoranthene	159.10	472.20	139.80	247.70	789.20	152.90	220.90	106.50	39.30	26.30	23.70	8.90	50.40	34.00
Pyrene	150.10	477.40	154.10	216.20	777.10	190.20	209.70	124.90	34.60	25.10	19.90	6.70	41.50	24.60
Benz(a)anthracene	66.50	167.30	51.10	105.30	355.90	55.20	47.70	28.70	12.00	7.90	7.00	2.90	16.20	10.30
Chrysene	96.00	199.50	70.00	155.30	583.40	75.10	97.70	53.70	22.60	14.10	11.40	3.10	28.20	13.10
Benzo(b)fluoranthene	61.10	153.70	48.80	82.70	449.50	32.50	33.00	19.90	8.70	6.50	5.80	2.10	16.70	7.50
Benzo(k)fluoranthene	53.00	134.40	40.90	86.00	245.90	25.80	28.00	13.50	6.30	3.50	4.40	1.20	11.20	5.00
Benzo(e)pyrene	45.60	110.20	39.80	74.50	370.70	25.90	23.90	23.10	7.30	6.00	6.00	1.90	12.50	6.10
Benzo(a)pyrene	34.80	108.00	31.50	57.40	252.40	18.80	15.70	10.80	4.70	2.30	2.90	<1	8.30	4.20
Perylene	77.40	116.40	98.30	45.90	74.50	7.20	7.60	4.50	2.30	3.60	6.40	1.90	3.80	2.60
Benzo(g,h,i)perylene	19.20	59.40	17.00	36.50	157.20	11.60	8.30	13.40	3.80	11.40	14.30	7.10	5.10	2.10
Indeno (1,2,3-c,d) pyrene	19.20	62.10	16.30	42.30	142.20	7.60	7.20	5.10	2.70	10.80	11.80	5.20	4.30	2.30
Dibenzo(a,h)anthracene	6.90	18.20	6.00	12.30	45.90	4.10	2.80	1.60	<1	3.20	3.90	<1	1.90	<1

Station	UMB7 µg.kg^{-1}	UMB8 µg.kg^{-1}	UMB/UMH µg.kg^{-1}	UMH1 µg.kg^{-1}	UMH3 µg.kg^{-1}	UMH5 µg.kg^{-1}	UMH6 µg.kg^{-1}	ISI2 µg.kg^{-1}	ISI4 µg.kg^{-1}	ISI5 µg.kg^{-1}	ISI7 µg.kg^{-1}	ISI8 µg.kg^{-1}
Naphthalene	<1	5.70	5.00	4.30	2.40	6.40	3.80	19.20	10.20	22.80	20.00	53.90
2-Methyl naphthalene	<1	11.10	6.80	4.20	2.10	6.20	2.50	35.90	27.00	25.20	20.30	70.00
1-Methyl naphthalene	<1	3.90	7.00	2.90	1.60	4.40	2.00	23.70	13.20	14.90	13.50	43.80
Acenaphthene	<1	<1	1.10	1.70	<1	<1	1.30	2.90	1.10	9.60	4.50	12.50
Acenaphthylene	<1	<1	2.10	1.20	1.20	2.40	1.20	4.30	<1	29.00	8.20	17.20
Fluorene	<1	<1	3.20	1.80	1.40	3.70	14.50	6.50	5.80	17.10	10.20	26.70
Phenanthrene	<1	39.30	17.80	17.10	9.50	14.90	9.70	55.60	52.60	178.00	69.40	150.00
1-Methylphenanthrene	<1	8.20	4.20	3.70	2.30	4.70	2.90	9.80	17.00	21.50	20.30	40.80
Anthracene	<1	8.00	8.50	2.90	3.80	9.70	2.60	14.50	1.00	82.60	27.60	52.60
Fluoranthene	23.50	81.00	18.90	18.70	6.30	13.70	6.60	40.20	46.70	420.00	119.00	197.00
Pyrene	19.00	59.60	16.10	13.20	6.20	16.60	5.50	36.90	41.50	309.00	103.00	191.00
Benz(a)anthracene	9.20	22.40	5.80	3.40	2.30	4.50	1.20	14.30	18.00	171.00	37.00	79.50
Chrysene	13.20	29.90	8.90	5.30	2.90	7.50	2.20	21.80	26.30	210.00	76.20	132.00
Benzo(b)fluoranthene	6.60	13.30	5.10	4.70	2.20	5.00	2.20	16.90	19.00	129.00	46.00	91.90
Benzo(k)fluoranthene	5.50	9.30	3.20	2.40	1.40	2.40	1.00	6.90	9.40	72.70	27.90	56.30
Benzo(e)pyrene	6.40	10.40	4.40	4.10	2.40	4.90	1.50	13.40	16.60	94.30	33.00	78.90
Benzo(a)pyrene	2.30	4.50	2.40	<1	<1	2.00	<1	6.90	10.00	81.20	18.60	46.60
Perylene	1.90	2.80	7.90	<1	3.90	4.20	<1	18.10	7.60	125.00	17.00	44.00
Benzo(g,h,i)perylene	2.10	1.40	9.70	5.20	3.40	6.80	2.60	33.10	6.40	129.00	62.10	121.00
Indeno (1,2,3-c,d) pyrene	2.00	1.30	12.70	6.40	2.80	6.60	3.30	24.60	7.40	150.00	54.60	113.00
Dibenzo(a,h)anthracene	<1	<1	<1	<1	<1	1.80	<1	7.30	<1	44.00	13.60	27.40

APPENDIX 12

Pesticide concentrations in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2012.

Station	MNG1 µg.kg^{-1}	MNG2 µg.kg^{-1}	MNG3 µg.kg^{-1}	MNG4 µg.kg^{-1}	MNG5 µg.kg^{-1}	MNG6 µg.kg^{-1}	MNG7 µg.kg^{-1}	MNG8 µg.kg^{-1}	MNG9 µg.kg^{-1}	MNG10 µg.kg^{-1}	MNG11 µg.kg^{-1}	MNG12 µg.kg^{-1}	MNG13 µg.kg^{-1}	MNG14 µg.kg^{-1}
BHC-alpha	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
BHC-beta	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
BHC-delta	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
BHC-gamma	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Endosulfan-I	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Endosulfan-II	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Endosulfan sulfate	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Hexachlorobenzene	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Heptachlor	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Heptachlor epoxide	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Aldrin	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Dieldrin	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Endrin	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Endrin aldehyde	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Endrin ketone	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Perthane	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Oxychlordane	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Chlordane-alpha	<1	<1	<1	<1	<1	2.8	1.5	<1	<1	<1	<1	<1	<1	1.2
Chlordane-gamma	<1	<1	<1	<1	<1	3	1.2	<1	<1	<1	1.8	<1	<1	1.8
cis-Nonachlor	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
trans-Nonachlor	<1	<1	<1	<1	<1	1.5	<1	<1	<1	<1	<1	<1	<1	1.0
Mirex	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
2,4'-DDD	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
4,4'-DDD	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
2,4'-DDE	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
4,4'-DDE	2.2	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
4,4'-DDT	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
2,4'-DDT	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Methoxychlor	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Toxaphene	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1

Station	MNG15	MNG17	MNG18	MNG19	MNG20	MNG21	MNG22	IVC1	IVC2	DBAY1	DBAY2	DBAY3	DBAY4	DBAY5

	µg.kg^{-1}	µg.kg^{-1}	µg.kg^{-1}	µg.kg^{-1}	µg.kg^{-1}	µg.kg^{-1}	µg.kg^{-1}	µg.kg^{-1}	µg.kg^{-1}	µg.kg^{-1}	µg.kg^{-1}	µg.kg^{-1}	µg.kg^{-1}	µg.kg^{-1}
BHC-alpha	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
BHC-beta	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
BHC-delta	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
BHC-gamma	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Endosulfan-I	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Endosulfan-II	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	43.9	<1
Endosulfan sulfate	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Hexachlorobenzene	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Heptachlor	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Heptachlor epoxide	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Aldrin	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Dieldrin	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Endrin	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Endrin aldehyde	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Endrin ketone	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Perthane	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Oxychlordane	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Chlordane-alpha	<1	<1	<1	2.3	<1	<1	<1	<1	<1	<1	<1	<1	<1	3
Chlordane-gamma	<1	<1	<1	2.7	<1	<1	<1	<1	<1	<1	<1	<1	<1	4.4
cis-Nonachlor	<1	<1	<1	<1	<1	<1	<1	4.7	<1	<1	<1	<1	<1	<1
trans-Nonachlor	<1	<1	<1	1.7	<1	<1	<1	11.2	<1	<1	<1	<1	<1	2.2
Mirex	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
2,4'-DDD	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
4,4'-DDD	<1	<1	<1	6.2	<1	<1	<1	74.5	<1	<1	<1	31.3	19.1	<1
2,4'-DDE	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
4,4'-DDE	<1	<1	<1	31.4	<1	<1	<1	30.4	<1	<1	<1	<1	<1	<1
4,4'-DDT	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
2,4'-DDT	<1	<1	<1	<1	<1	<1	<1	<1	37.8	<1	<1	<1	<1	<1
Methoxychlor	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Toxaphene	<1	<1	11.41	<1	<1	<1	<1	<1	<1	32.03	21.85	111.87	<1	29.09

Station	**DBAY6** µg.kg^{-1}	**DBAY7** µg.kg^{-1}	**DBAY8** µg.kg^{-1}	**DBAY9** µg.kg^{-1}	**BC1** µg.kg^{-1}	**DBAY10** µg.kg^{-1}	**AMA1** µg.kg^{-1}	**AMA2** µg.kg^{-1}	**AMA3** µg.kg^{-1}	**UMB1** µg.kg^{-1}	**UMB2** µg.kg^{-1}	**UMB3** µg.kg^{-1}	**UMB4** µg.kg^{-1}	**UMB5** µg.kg^{-1}
BHC-alpha	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1

Station	DBAY6 µg.kg^{-1}	DBAY7 µg.kg^{-1}	DBAY8 µg.kg^{-1}	DBAY9 µg.kg^{-1}	BC1 µg.kg^{-1}	DBAY10 µg.kg^{-1}	AMA1 µg.kg^{-1}	AMA2 µg.kg^{-1}	AMA3 µg.kg^{-1}	UMB1 µg.kg^{-1}	UMB2 µg.kg^{-1}	UMB3 µg.kg^{-1}	UMB4 µg.kg^{-1}	UMB5 µg.kg^{-1}
BHC-beta	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
BHC-delta	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
BHC-gamma	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Endosulfan-I	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Endosulfan-II	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Endosulfan sulfate	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Hexachlorobenzene	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Heptachlor	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Heptachlor epoxide	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Aldrin	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Dieldrin	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Endrin	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Endrin aldehyde	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Endrin ketone	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Perthane	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Oxychlordane	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Chlordane-alpha	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Chlordane-gamma	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
cis-Nonachlor	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
trans-Nonachlor	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Mirex	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
2,4'-DDD	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
4,4'-DDD	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
2,4'-DDE	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
4,4'-DDE	<1	<1	<1	<1	<1	<1	373.9	364.5	<1	<1	<1	<1	<1	<1
4,4'-DDT	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
2,4'-DDT	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Methoxychlor	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Toxaphene	91.03	143.88	17.72	13.72	21.02	27.42	<1	<1	<1	<1	<1	<1	<1	<1

Station	UMB7 µg.kg^{-1}	UMB8 µg.kg^{-1}	UMB/ UMH µg.kg^{-1}	UMH1 µg.kg^{-1}	UMH3 µg.kg^{-1}	UMH5 µg.kg^{-1}	UMH6 µg.kg^{-1}	ISI2 µg.kg^{-1}	ISI4 µg.kg^{-1}	ISI5 µg.kg^{-1}	ISI7 µg.kg^{-1}	ISI8 µg.kg^{-1}

Station	UMB7	UMB8	UMB/ UMH	UMH1	UMH3	UMH5	UMH6	ISI2	ISI4	ISI5	ISI7	ISI8
	µg.kg^{-1}	µg.kg^{-1}	µg.kg^{-1}	µg.kg^{-1}	µg.kg^{-1}	µg.kg^{-1}	µg.kg^{-1}	µg.kg^{-1}	µg.kg^{-1}	µg.kg^{-1}	µg.kg^{-1}	µg.kg^{-1}
BHC-alpha	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
BHC-beta	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
BHC-delta	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
BHC-gamma	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Endosulfan-I	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Endosulfan-II	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Endosulfan sulfate	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Hexachlorobenzene	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Heptachlor	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Heptachlor epoxide	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Aldrin	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Dieldrin	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Endrin	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Endrin aldehyde	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Endrin ketone	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Perthane	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Oxychlordane	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Chlordane-alpha	<1	<1	<1	<1	<1	<1	<1	<1	<1	1.8	<1	3.7
Chlordane-gamma	<1	<1	<1	<1	<1	<1	<1	<1	<1	2.3	<1	3
cis-Nonachlor	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
trans-Nonachlor	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	1.9
Mirex	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
2,4'-DDD	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
4,4'-DDD	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
2,4'-DDE	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
4,4'-DDE	<1	<1	<1	<1	<1	<1	<1	<1	<1	6.8	<1	4.5
4,4'-DDT	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
2,4'-DDT	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Methoxychlor	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Toxaphene	<1	<1	<1	<1	<1	<1	<1	<1	<1	213.92	<1	17.88

APPENDIX 13

Polychlorinated biphenyl concentrations in sediment collected in rivers, estuaries and canals in the eThekwini area of KwaZulu-Natal in 2012.

Station	PCB1 µg.kg^{-1}	PCB8 µg.kg^{-1}	PCB18 µg.kg^{-1}	PCB28 µg.kg^{-1}	PCB44 µg.kg^{-1}	PCB52 µg.kg^{-1}	PCB66 µg.kg^{-1}	PCB77 µg.kg^{-1}	PCB101 µg.kg^{-1}	PCB105 µg.kg^{-1}	PCB118 µg.kg^{-1}	PCB126 µg.kg^{-1}	PCB128 µg.kg^{-1}	PCB138 µg.kg^{-1}	PCB153 µg.kg^{-1}	PCB169 µg.kg^{-1}	PCB170 µg.kg^{-1}	PCB180 µg.kg^{-1}	PCB187 µg.kg^{-1}	PCB195 µg.kg^{-1}	PCB206 µg.kg^{-1}	PCB209 µg.kg^{-1}
MNG1	<5	<5	<5	<5	<5	<5	<5	<1	<5	<2	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
MNG2	<5	<5	<5	<5	<5	<5	<5	<1	<5	<2	<1	<1	<1	2.00	<1	<1	<1	<1	<1	<1	<1	<1
MNG3	<5	<5	<5	<5	<5	<5	<5	<1	<5	<2	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
MNG4	<5	<5	<5	<5	<5	<5	<5	<1	<5	<2	<1	<1	<1	2.00	<1	<1	<1	<1	<1	<1	<1	<1
MNG5	<5	<5	<5	<5	<5	<5	<5	<1	<5	<2	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
MNG6	<5	<5	<5	<5	<5	<5	<5	<5	<5	<2	<1	<1	<1	1.08	<1	<1	<1	<1	<1	<1	<1	<1
MNG7	<5	<5	<5	<5	<5	<5	<5	<1	11.90	<2	<1	<1	<1	1.61	<1	<1	<1	<1	<1	<1	<1	<1
MNG8	<5	<5	<5	<5	<5	<5	<5	<1	<5	<2	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
MNG9	<5	<5	<5	<5	<5	<5	<5	<1	<5	<2	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
MNG10	<5	<5	<5	<5	<5	<5	<5	<1	<5	<2	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
MNG11	<5	<5	<5	<5	<5	<5	<5	<1	<5	<2	<1	<1	<1	3.00	2.00	<1	<1	1.00	<1	<1	<1	<1
MNG12	<5	<5	<5	<5	<5	<5	<5	<1	<5	<2	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
MNG13	<5	<5	<5	<5	<5	<5	<5	<1	<5	<2	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
MNG14	<5	<5	<5	<5	<5	<5	<5	<1	<5	<2	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
MNG15	<5	<5	<5	<5	<5	<5	<5	<1	<5	<2	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
MNG17	<5	<5	<5	<5	<5	<5	<5	<1	<5	<2	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
MNG18	<5	<5	<5	<5	<5	<5	<5	3.00	<5	<2	<1	<1	<1	2.00	<1	<1	<1	<1	<1	<1	<1	<1
MNG19	<5	<5	<5	<5	<5	<5	<5	<1	<5	<2	<1	<1	<1	1.25	<1	<1	<1	<1	<1	<1	<1	<1
MNG20	<5	<5	<5	<5	<5	<5	<5	<1	<5	<2	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
MNG21	<5	<5	<5	<5	<5	<5	<5	<1	<5	<2	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
MNG22	<5	<5	<5	<5	<5	<5	<5	<1	<5	<2	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
IVC1	<5	<5	<5	<5	<5	<5	<5	<1	<5	<2	2.26	<1	1.10	7.37	4.74	<1	2.25	3.47	<1	<1	<1	<1
IVC2	<5	<5	<5	<5	<5	<5	<5	<1	<5	<2	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
DBAY1	<5	<5	<5	<5	<5	<5	<5	<1	<5	<2	2.00	<1	<1	9.00	6.00	<1	2.00	4.00	2.00	<1	1.00	<1
DBAY2	<5	<5	<5	<5	<5	<5	<5	<1	<5	<2	<1	<1	<1	7.00	5.00	<1	2.00	4.00	2.00	<1	<1	<1
DBAY3	<5	<5	<5	<5	<5	<5	<5	1.26	8.79	5.36	4.73	<1	2.82	29.40	17.80	<1	9.94	18.50	9.24	1.69	2.86	1.44
DBAY4	<5	<5	<5	<5	<5	<5	<5	<1	<5	<2	1.68	<1	<1	8.89	5.84	<1	3.31	6.00	3.21	<1	<1	<1
DBAY5	<5	<5	<5	<5	<5	<5	<5	<1	<5	<2	2.00	<1	<1	3.00	2.00	<1	<1	1.00	<1	<1	<1	<1
DBAY6	<5	<5	<5	<5	<5	<5	<5	<1	<5	<2	2.00	<1	<1	9.00	5.00	<1	2.00	4.00	2.00	<1	1.00	<1
DBAY7	<5	<5	<5	<5	<5	<5	<5	<1	9.09	5.70	7.69	<1	2.26	26.70	20.00	<1	7.81	14.34	8.19	1.33	2.56	<1
DBAY8	<5	<5	<5	<5	<5	<5	<5	<1	<5	2.17	2.19	<1	1.44	7.68	4.31	<1	2.18	3.31	2.10	<1	<1	<1
DBAY9	<5	<5	<5	<5	<5	<5	<5	<1	<5	<2	<1	<1	<1	3.00	2.00	<1	<1	1.00	<1	<1	<1	<1
BC1	<5	<5	<5	<5	<5	<5	<5	<1	<5	<2	1.33	<1	<1	2.88	2.12	<1	1.02	1.68	1.05	<1	<1	<1
DBAY10	<5	<5	<5	<5	<5	<5	<5	<1	<5	2.52	3.07	<1	<1	10.70	6.95	<1	3.26	5.36	2.70	<1	<1	<1

Station	PCB1 µg.kg^{-1}	PCB8 µg.kg^{-1}	PCB18 µg.kg^{-1}	PCB28 µg.kg^{-1}	PCB44 µg.kg^{-1}	PCB52 µg.kg^{-1}	PCB66 µg.kg^{-1}	PCB77 µg.kg^{-1}	PCB101 µg.kg^{-1}	PCB105 µg.kg^{-1}	PCB118 µg.kg^{-1}	PCB126 µg.kg^{-1}	PCB128 µg.kg^{-1}	PCB138 µg.kg^{-1}	PCB153 µg.kg^{-1}	PCB169 µg.kg^{-1}	PCB170 µg.kg^{-1}	PCB180 µg.kg^{-1}	PCB187 µg.kg^{-1}	PCB195 µg.kg^{-1}	PCB206 µg.kg^{-1}	PCB209 µg.kg^{-1}
AMA1	<5	<5	<5	<5	<5	<5	<5	<1	<5	<2	1.17	<1	<1	4.25	2.58	<1	1.59	2.40	1.42	<1	<1	<1
AMA2	<5	<5	<5	<10	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
AMA3	<5	<5	<5	<5	<5	<5	<5	<1	<5	<2	<1	<1	<1	2.00	<1	<1	<1	<1	<1	<1	<1	<1
UMB1	<5	<5	<5	<5	<5	<5	<5	<1	<5	<2	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
UMB2	<5	<5	<5	<5	<5	<5	<5	<1	<5	<2	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
UMB3	<5	<5	<5	<5	<5	<5	<5	<1	<5	<2	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
UMB4	<5	<5	<5	<5	<5	<5	<5	<1	<5	<2	<1	<1	<1	1.00	<1	<1	<1	<1	<1	<1	<1	<1
UMB5	<5	<5	<5	<5	<5	<5	<5	<1	<5	<2	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
UMB7	<5	<5	<5	<5	<5	<5	<5	<1	<5	<2	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
UMB8	<5	<5	<5	<5	<5	<5	<5	<1	<5	<2	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
UMB/ UMH	<5	<5	<5	<5	<5	<5	<5	<1	<5	<2	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
UMH1	<5	<5	<5	<5	<5	<5	<5	<1	<5	<2	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
UMH3	<5	<5	<5	<5	<5	<5	<5	<1	<5	<2	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
UMH5	<5	<5	<5	<5	<5	<5	<5	<1	<5	<2	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
UMH6	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
ISI2	<5	<5	<5	<5	<5	<5	<5	<1	<5	<2	<1	<1	<1	1.00	<1	<1	<1	<1	<1	<1	<1	<1
ISI4	<5	<5	<5	<5	<5	<5	<5	<1	<1	6.11	9.08	<1	2.55	23.80	13.80	<1	4.99	7.57	3.37	<1	<1	<1
ISI5	<5	<5	<5	<5	<5	<5	<5	<1	<5	<2	1.44	<1	<1	2.21	2.14	<1	<1	1.17	<1	<1	<1	<1
ISI7	<5	<5	<5	<5	<5	<5	<5	<1	<5	<2	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
ISI8	<5	<5	<5	<5	<5	<5	<5	<1	6.10	3.14	3.09	<1	1.27	15.17	10.00	<1	4.11	9.12	5.31	<1	<1	<1

APPENDIX 14

Total length, moisture content and metal concentrations (dry weight) in fish caught in Durban Bay and the uMngeni and Isipingo River estuaries in 2013. Al = aluminium, Fe = iron, As = arsenic (In = inorganic), Cd = cadmium, Cr = chromium, Cu = copper, Pb = lead, Mn = manganese, Hg = mercury, Ni = nickel, Se = selenium, Zn = zinc.

System	Species	Total length mm	Moisture %	Al mg.kg^{-1}	As mg.kg^{-1}	As In mg.kg^{-1}	Cd mg.kg^{-1}	Cr mg.kg^{-1}	Cu mg.kg^{-1}	Fe mg.kg^{-1}	Pb mg.kg^{-1}	Mn mg.kg^{-1}	Hg mg.kg^{-1}	Ni mg.kg^{-1}	Se mg.kg^{-1}	Zn mg.kg^{-1}
DBN	*Sphyraena jello*	528.0	79.51	0.6	2.5	<0.05	<0.01	0.2	0.6	11.0	0.0	0.4	0.9	2.6	1.4	20.0
DBN	*Sphyraena jello*	617.0	77.25	1.2	0.9	<0.05	<0.01	0.2	1.1	15.0	0.1	0.4	0.4	1.3	1.4	20.0
DBN	*Valamugil buchanani*	410.0	76.20	6.1	1.6	<0.05	<0.01	1.0	1.7	43.0	0.2	0.7	0.1	1.3	1.3	32.0
DBN	*Myxus capensis*	367.0	80.86	1.3	1.2	<0.05	<0.01	0.1	1.4	28.0	0.1	0.5	0.1	0.4	1.1	38.0
DBN	*Myxus capensis*	318.0	79.36	7.7	1.3	<0.05	<0.01	0.1	2.0	33.0	0.2	0.6	0.2	0.1	1.5	51.0
DBN	*Myxus capensis*	254.0	79.69	25.0	1.7	<0.05	<0.01	0.1	1.6	46.0	0.2	0.6	0.3	0.1	1.6	43.0
DBN	*Myxus capensis*	416.0	74.46	4.5	1.2	<0.05	<0.01	0.4	1.7	32.0	0.1	0.5	0.1	4.8	4.2	25.0
DBN	*Liza dumerilii*	266.0	78.04	1.7	1.1	<0.05	<0.01	0.1	0.8	9.8	0.2	0.3	0.6	1.1	1.6	18.0
DBN	*Liza dumerilii*	264.0	78.90	0.8	1.0	<0.05	<0.01	0.1	1.6	27.0	0.1	0.5	0.0	0.1	1.8	33.0
DBN	*Liza tricuspidens*	248.0	75.88	1.2	1.1	<0.05	<0.01	0.2	0.9	11.0	0.2	0.4	0.5	1.2	1.6	20.0
DBN	*Mugil cephalus*	353.0	77.86	0.9	2.1	<0.05	<0.01	0.1	0.7	16.0	0.1	0.4	0.0	0.1	1.1	17.0
DBN	*Mugil cephalus*	496.0	76.58	0.9	1.5	<0.05	<0.01	0.1	1.1	22.0	0.1	0.3	0.0	0.1	1.0	20.0
DBN	*Pseudorhombus arsius*	158.6	79.83	2.5	4.1	<0.05	<0.01	0.1	0.6	8.3	0.0	0.6	0.4	0.1	2.1	20.0
DBN	*Sillago sihama*	192.0	78.83	1.0	32.0	<0.05	<0.01	0.2	0.6	5.2	0.1	0.3	0.5	0.6	2.5	22.0
DBN	*Sillago sihama*	13.4	77.98	1.3	24.0	<0.05	<0.01	0.1	0.9	5.2	0.0	0.6	2.1	0.1	2.8	27.0
DBN	*Sillago sihama*	-	77.26	3.3	0.8	<0.05	<0.01	0.3	2.3	24.0	0.2	0.5	0.4	0.3	2.3	36.0
DBN	*Ambassis gymnocephalus*	-	76.42	22.0	1.7	<0.05	1.1	0.3	2.1	60.0	0.6	8.0	0.1	0.3	1.4	110.0
DBN	*Ambassis gymnocephalus*	-	77.01	29.0	1.7	<0.05	0.8	0.3	2.2	67.0	0.5	8.8	0.1	0.2	1.4	110.0
DBN	*Pomadasys commersonnii*	445.0	78.41	12.0	3.6	<0.05	0.1	0.3	1.5	38.0	0.3	0.4	0.7	0.1	1.7	24.0
DBN	*Pomadasys commersonnii*	470.0	78.45	2.1	4.2	<0.05	<0.01	0.2	1.7	29.0	0.0	0.4	1.1	0.1	2.5	26.0
DBN	*Pomadasys commersonnii*	522.0	79.30	2.5	4.9	<0.05	<0.01	0.1	1.5	30.0	0.0	0.3	1.5	0.1	2.3	27.0
DBN	*Pomadasys commersonnii*	475.0	78.75	2.1	2.8	<0.05	<0.01	0.1	1.2	31.0	0.0	0.3	0.2	0.1	1.3	24.0
DBN	*Pomadasys commersonnii*	434.0	77.89	1.2	4.0	<0.05	<0.01	0.1	1.4	27.0	0.0	0.3	0.8	0.1	1.7	25.0
DBN	*Pomadasys commersonnii*	410.0	78.49	4.0	4.0	<0.05	<0.01	0.1	1.7	32.0	0.1	0.5	0.9	0.1	1.5	23.0
DBN	*Pomadasys commersonnii*	425.0	77.45	2.4	3.7	<0.05	<0.01	0.1	3.0	30.0	0.0	0.4	0.2	0.1	2.7	30.0
DBN	*Pomadasys commersonnii*	570.0	78.12	0.6	3.4	<0.05	<0.01	0.1	1.4	26.0	0.1	0.4	0.6	0.0	1.9	28.0
DBN	*Pomadasys commersonnii*	44.0	77.04	2.0	6.3	<0.05	<0.01	0.3	1.7	32.0	0.1	0.4	0.8	0.1	1.8	27.0
DBN	*Pomadasys commersonnii*	433.0	78.00	1.0	6.7	<0.05	<0.01	<0.05	1.4	20.0	0.0	0.3	1.4	0.1	2.5	28.0
DBN	*Platycephalus indicus*	317.0	76.81	0.7	3.6	<0.05	<0.01	0.1	0.8	5.4	0.1	0.3	0.4	0.1	1.9	34.0
DBN	*Perna perna* DBN1	96.3	84.37	580.0	11.0	0.4	0.3	2.8	52.0	880.0	10.0	45.0	0.2	1.9	4.7	290.0

System	Species	Total length mm	Moisture %	Al mg.kg^{-1}	As mg.kg^{-1}	As In mg.kg^{-1}	Cd mg.kg^{-1}	Cr mg.kg^{-1}	Cu mg.kg^{-1}	Fe mg.kg^{-1}	Pb mg.kg^{-1}	Mn mg.kg^{-1}	Hg mg.kg^{-1}	Ni mg.kg^{-1}	Se mg.kg^{-1}	Zn mg.kg^{-1}
DBN	*Perna perna* DBN2	67.6	80.25	560.0	10.0	0.4	0.3	2.2	44.0	810.0	7.6	85.0	0.2	1.8	4.0	250.0
DBN	*Perna perna* DBN3	95.4	78.86	600.0	8.4	0.4	0.4	2.6	29.0	860.0	7.1	56.0	0.2	2.1	4.1	220.0
DBN	*Perna perna* DBN4	104.2	80.84	230.0	8.2	0.2	0.2	1.0	15.0	390.0	3.2	28.0	0.1	0.9	3.0	150.0
DBN	*Perna perna* DBN5	89.8	80.10	720.0	7.6	0.4	0.3	3.1	50.0	1080.0	8.8	73.0	0.2	2.2	3.9	300.0
DBN	*Perna perna* DBN6	78.3	84.94	440.0	8.4	0.4	0.2	1.9	28.0	620.0	6.0	49.0	0.1	1.5	4.4	190.0
DBN	*Perna perna* DBN7	77.3	84.09	140.0	7.9	0.1	0.1	0.7	16.0	230.0	3.8	40.0	0.1	0.9	3.2	150.0
DBN	*Perna perna* DBN8	81.1	78.56	170.0	6.2	0.1	0.1	0.9	28.0	270.0	4.3	28.0	0.1	0.7	2.9	140.0
DBN	*Perna perna* DBN9	66.3	80.25	130.0	7.6	0.1	0.2	1.1	13.0	240.0	3.2	36.0	0.1	1.0	3.3	140.0
DBN	*Perna perna* DBN10	57.7	81.87	330.0	6.5	0.2	0.2	1.6	26.0	530.0	6.2	56.0	0.1	1.5	3.7	280.0
DBN	*Perna perna* DBN11	58.1	81.78	93.0	6.4	0.1	0.1	0.6	13.0	190.0	2.8	41.0	0.0	0.8	2.9	150.0
ISI	*Myxus capensis*	313.5	74.27	1.4	0.7	<0.05	0.0	0.1	1.0	14.0	0.2	0.5	0.0	0.1	1.2	43.0
ISI	*Ambassis natalensis*	-	73.73	64.0	1.9	<0.05	0.1	0.3	2.7	200.0	0.5	9.2	0.1	0.2	2.0	140.0
ISI	*Oreochromus mossambicus*	276.0	78.54	0.9	0.6	<0.05	<0.01	0.1	0.8	14.0	0.1	0.6	0.0	0.1	2.5	31.0
ISI	*Oreochromus mossambicus*	248.5	79.54	1.7	0.7	<0.05	<0.01	0.1	0.9	13.0	0.1	0.7	0.0	0.2	2.9	30.0
ISI	*Oreochromus mossambicus*	229.0	72.66	1.4	0.5	<0.05	<0.01	0.1	1.0	15.0	0.1	0.7	0.0	0.1	2.6	33.0
ISI	*Oreochromus mossambicus*	207.3	79.69	1.4	0.6	<0.05	<0.01	0.1	1.0	18.0	0.1	0.7	0.0	0.1	2.4	32.0
MNG	*Valamugil cunnesius*	209.3	72.69	1.7	1.0	<0.05	<0.01	0.1	1.9	22.0	0.2	0.3	0.0	0.2	1.3	32.0
MNG	*Valamugil cunnesius*	202.3	70.49	1.1	1.0	<0.05	<0.01	0.1	1.9	24.0	0.2	0.3	0.0	0.1	1.4	36.0
MNG	*Liza dumerilii*	254.0	78.56	23.0	1.4	<0.05	<0.01	0.1	3.9	43.0	0.2	0.6	0.0	0.3	2.5	32.0
MNG	*Liza macrolepis*	340.0	79.36	8.0	1.1	<0.05	<0.01	0.1	2.8	29.0	0.2	0.4	0.1	0.3	2.6	33.0
MNG	*Liza macrolepis*	199.4	77.99	5.5	0.7	<0.05	<0.01	0.1	2.1	24.0	0.2	0.6	0.0	0.2	2.4	35.0
MNG	*Liza tricuspidens*	542.0	78.59	4.2	1.9	<0.05	<0.01	0.2	1.3	24.0	0.1	0.6	0.2	0.1	0.7	39.0
MNG	*Mugil cephalus*	494.0	74.95	1.6	1.9	<0.05	<0.01	0.1	1.5	25.0	0.1	0.6	0.0	0.1	2.2	15.0
MNG	*Gerres methueni*	220.7	76.74	1.8	1.0	<0.05	<0.01	0.2	2.1	20.0	0.1	0.5	0.3	0.2	2.4	34.0
MNG	*Ambassis natalensis*	-	73.17	23.0	2.3	<0.05	0.3	0.2	2.2	100.0	0.2	12.0	0.1	0.2	2.3	120.0
MNG	*Oreochromus mossambicus*	268.5	77.14	1.5	0.7	<0.05	<0.01	0.1	1.0	17.0	0.2	0.7	0.0	0.1	2.8	27.0
MNG	*Oreochromus mossambicus*	244.0	77.59	0.6	0.4	<0.05	<0.01	0.1	1.1	12.0	0.1	0.7	0.0	0.1	2.4	26.0
MNG	*Oreochromus mossambicus*	270.5	77.28	13.0	2.0	<0.05	<0.01	0.2	2.1	41.0	0.2	2.3	0.1	0.1	2.1	33.0
MNG	*Oreochromus mossambicus*	193.3	78.91	2.0	0.6	<0.05	<0.01	0.1	1.3	16.0	0.1	1.0	0.1	0.1	2.5	32.0

APPENDIX 15

Polycyclic aromatic hydrocarbon concentrations (dry weight) in fish caught in Durban Bay and the uMngeni and Isipingo River estuaries in 2013. Nap = naphthalene, Acen = acenapththylene, Acent = acenaphthene, Flu = fluorine, Phen = phenanthrene, Ant = anthracene, Fluo = fluoranthene, Pyr = pyrene, Benz = benz(a)anthracene, Chry = chrysene, Ben-flu = benzo(b,k)fluoranthene, Ben-pyr = Benzo(a)pyrene, Ind = Indeno(1,2,3-c,d)pyrene, Dib = dibenzo(a,h)anthracene, Ben-p = benzo(g,h,i)perylene.

System	Species	Nap mg.kg^{-1}	Acen mg.kg^{-1}	Acent mg.kg^{-1}	Flu mg.kg^{-1}	Phen mg.kg^{-1}	Ant mg.kg^{-1}	Fluo mg.kg^{-1}	Pyr mg.kg^{-1}	Benz mg.kg^{-1}	Chry mg.kg^{-1}	Ben -flu mg.kg^{-1}	Ben-pyr mg.kg^{-1}	Ind mg.kg^{-1}	Dib mg.kg^{-1}	Ben-p mg.kg^{-1}
DBN	*Sphyraena jello*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Sphyraena jello*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Valamugil buchanani*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Myxus capensis*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.011	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Myxus capensis*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	0.019
DBN	*Myxus capensis*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.015	0.01	<0.01	<0.01	<0.01	0.02
DBN	*Myxus capensis*	0.063	<0.01	<0.01	0.019	0.034	<0.01	0.011	0.019	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Liza dumerilii*	0.011	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Liza dumerilii*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.018	0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Liza tricuspidens*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Mugil cephalus*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	0.016
DBN	*Mugil cephalus*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	0.027	0.013
DBN	*Pseudorhombus arsius*	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.012	0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Sillago sihama*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Sillago sihama*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.014	0.01	<0.01	<0.01	<0.01	0.013
DBN	*Sillago sihama*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.011	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Ambassis gymnocephalus*	<0.01	<0.01	<0.01	0.017	<0.01	<0.01	<0.01	0.012	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Ambassis gymnocephalus*	<0.01	<0.01	<0.01	0.014	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Pomadasys commersonnii*	0.011	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Pomadasys commersonnii*	0.012	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Pomadasys commersonnii*	0.012	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Pomadasys commersonnii*	0.010	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Pomadasys commersonnii*	0.011	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Pomadasys commersonnii*	0.013	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Pomadasys commersonnii*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Pomadasys commersonnii*	0.010	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Pomadasys commersonnii*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Pomadasys commersonnii*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Platycephalus indicus*	0.012	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Perna perna* DBN1	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.021	0.044	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01

System	Species	Nap $mg.kg^{-1}$	Acen $mg.kg^{-1}$	Acent $mg.kg^{-1}$	Flu $mg.kg^{-1}$	Phen $mg.kg^{-1}$	Ant $mg.kg^{-1}$	Fluo $mg.kg^{-1}$	Pyr $mg.kg^{-1}$	Benz $mg.kg^{-1}$	Chry $mg.kg^{-1}$	Ben -flu $mg.kg^{-1}$	Ben-pyr $mg.kg^{-1}$	Ind $mg.kg^{-1}$	Dib $mg.kg^{-1}$	Ben-p $mg.kg^{-1}$
DBN	*Perna perna* DBN2	<0.01	<0.01	<0.01	<0.01	0.021	<0.01	0.025	0.056	<0.01	0.028	0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Perna perna* DBN3	<0.01	<0.01	<0.01	<0.01	0.014	<0.01	0.017	0.052	<0.01	0.025	0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Perna perna* DBN4	0.027	<0.01	<0.01	<0.01	0.04	<0.01	0.03	0.061	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Perna perna* DBN5	0.029	<0.01	<0.01	<0.01	0.022	<0.01	0.015	0.027	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Perna perna* DBN6	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.014	0.032	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Perna perna* DBN7	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.022	0.044	<0.01	0.031	0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Perna perna* DBN8	<0.01	<0.01	<0.01	<0.01	0.019	<0.01	0.026	0.045	<0.01	0.016	0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Perna perna* DBN9	0.019	0.019	<0.01	<0.01	0.021	<0.01	<0.01	0.022	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Perna perna* DBN10	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.036	0.071	<0.01	0.069	0.02	<0.01	<0.01	<0.01	<0.01
DBN	*Perna perna* DBN11	<0.01	<0.01	<0.01	<0.01	0.046	<0.01	<0.01	<0.01	<0.01	0.044	0.01	<0.01	<0.01	<0.01	<0.01
ISI	*Myxus capensis*	<0.01	<0.01	<0.01	0.021	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
ISI	*Ambassis natalensis*	0.012	<0.01	<0.01	0.022	0.016	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
ISI	*Oreochromus mossambicus*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
ISI	*Oreochromus mossambicus*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
ISI	*Oreochromus mossambicus*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.013	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
ISI	*Oreochromus mossambicus*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.012	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
MNG	*Valamugil cunnesius*	<0.01	<0.01	0.045	0.016	0.016	<0.01	0.015	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
MNG	*Valamugil cunnesius*	<0.01	<0.01	<0.01	0.02	0.021	0.012	0.016	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
MNG	*Liza dumerilii*	<0.01	<0.01	<0.01	<0.01	0.011	<0.01	<0.01	0.011	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
MNG	*Liza macrolepis*	0.018	<0.01	<0.01	<0.01	0.012	<0.01	<0.01	0.011	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
MNG	*Liza macrolepis*	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	0.012	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
MNG	*Liza tricuspidens*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
MNG	*Mugil cephalus*	<0.01	<0.01	<0.01	<0.01	0.013	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
MNG	*Gerres methueni*	0.015	<0.01	<0.01	<0.01	0.015	<0.01	<0.01	0.012	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
MNG	*Ambassis natalensis*	0.021	<0.01	<0.01	0.033	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
MNG	*Oreochromus mossambicus*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
MNG	*Oreochromus mossambicus*	<0.01	<0.01	0.033	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.019	0.01	<0.01	<0.01	<0.01	<0.01
MNG	*Oreochromus mossambicus*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.013	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
MNG	*Oreochromus mossambicus*	0.021	<0.01	<0.01	<0.01	0.025	<0.01	<0.01	0.018	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01

APPENDIX 16

Organochlorine pesticide concentrations (dry weight) in fish and mussels collected in Durban Bay and the uMngeni and Isipingo River estuaries in 2013.

System	Species	HCB $mg.kg^{-1}$	Heptachlor $mg.kg^{-1}$	Heptachlor epoxide $mg.kg^{-1}$	Aldrin $mg.kg^{-1}$	BHC-gamma $mg.kg^{-1}$	BHC-alpha $mg.kg^{-1}$	BHC-beta $mg.kg^{-1}$	BHC-delta $mg.kg^{-1}$	Chlordane-trans $mg.kg^{-1}$	Chlordane-cis $mg.kg^{-1}$	Oxy-Chlordane $mg.kg^{-1}$
DBN	*Sphyraena jello*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Sphyraena jello*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Valamugil buchanani*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Myxus capensis*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Myxus capensis*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Myxus capensis*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Myxus capensis*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Liza dumerilii*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Liza dumerilii*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Liza tricuspidens*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Mugil cephalus*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Mugil cephalus*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Pseudorhombus arsius*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Sillago sihama*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Sillago sihama*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Sillago sihama*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Ambassis gymnocephalus*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Ambassis gymnocephalus*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Pomadasys commersonnii*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Pomadasys commersonnii*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Pomadasys commersonnii*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Pomadasys commersonnii*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Pomadasys commersonnii*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Pomadasys commersonnii*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Pomadasys commersonnii*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Pomadasys commersonnii*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Pomadasys commersonnii*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Pomadasys commersonnii*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Platycephalus indicus*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Perna perna* DBN1	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Perna perna* DBN2	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Perna perna* DBN3	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Perna perna* DBN4	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

System	Species	HCB mg.kg^{-1}	Heptachlor mg.kg^{-1}	Heptachlor epoxide mg.kg^{-1}	Aldrin mg.kg^{-1}	BHC-gamma mg.kg^{-1}	BHC-alpha mg.kg^{-1}	BHC-beta mg.kg^{-1}	BHC-delta mg.kg^{-1}	Chlordane-trans mg.kg^{-1}	Chlordane-cis mg.kg^{-1}	Oxy-Chlordane mg.kg^{-1}
DBN	*Perna perna* DBN5	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Perna perna* DBN6	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Perna perna* DBN7	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Perna perna* DBN8	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Perna perna* DBN9	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Perna perna* DBN10	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Perna perna* DBN11	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ISI	*Myxus capensis*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ISI	*Ambassis natalensis*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ISI	*Oreochromus mossambicus*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ISI	*Oreochromus mossambicus*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ISI	*Oreochromus mossambicus*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ISI	*Oreochromus mossambicus*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
MNG	*Valamugil cunnesius*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
MNG	*Valamugil cunnesius*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
MNG	*Liza dumerilii*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
MNG	*Liza macrolepis*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
MNG	*Liza macrolepis*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
MNG	*Liza tricuspidens*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
MNG	*Mugil cephalus*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
MNG	*Gerres methueni*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
MNG	*Ambassis natalensis*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
MNG	*Oreochromus mossambicus*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
MNG	*Oreochromus mossambicus*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
MNG	*Oreochromus mossambicus*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
MNG	*Oreochromus mossambicus*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

System	Species	Dieldrin mg.kg^{-1}	4'4'-DDE mg.kg^{-1}	4'4'-DDD mg.kg^{-1}	4'4'-DDT mg.kg^{-1}	Endrin mg.kg^{-1}	Endrin Aldehyde mg.kg^{-1}	Endrin Ketone mg.kg^{-1}	Endosulfan I mg.kg^{-1}	Endosulfan II mg.kg^{-1}	Endosulfan Sulfate mg.kg^{-1}	Methoxy-chlor mg.kg^{-1}
DBN	*Sphyraena jello*	<0.01	0.017	0.018	0.019	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Sphyraena jello*	<0.01	0.042	0.021	0.015	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Valamugil buchanani*	<0.01	0.019	0.015	0.014	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Myxus capensis*	<0.01	0.011	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Myxus capensis*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Myxus capensis*	<0.01	0.013	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

System	Species	Dieldrin mg.kg^{-1}	4’4’-DDE mg.kg^{-1}	4’4’-DDD mg.kg^{-1}	4’4’-DDT mg.kg^{-1}	Endrin mg.kg^{-1}	Endrin Aldehyde mg.kg^{-1}	Endrin Ketone mg.kg^{-1}	Endosulfan I mg.kg^{-1}	Endosulfan II mg.kg^{-1}	Endosulfan Sulfate mg.kg^{-1}	Methoxy-chlor mg.kg^{-1}
DBN	*Myxus capensis*	<0.01	0.036	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Liza dumerilii*	<0.01	0.035	0.012	0.014	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Liza dumerilii*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Liza tricuspidens*	<0.01	0.036	0.013	0.013	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Mugil cephalus*	<0.01	0.014	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Mugil cephalus*	<0.01	0.032	0.011	0.017	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Pseudorhombus arsius*	<0.01	0.011	<0.01	0.015	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Sillago sihama*	<0.01	<0.01	<0.01	0.016	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Sillago sihama*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Sillago sihama*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Ambassis gymnocephalus*	<0.01	0.047	0.016	0.016	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Ambassis gymnocephalus*	<0.01	0.032	0.012	0.034	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Pomadasys commersonnii*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Pomadasys commersonnii*	0.014	0.015	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Pomadasys commersonnii*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Pomadasys commersonnii*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Pomadasys commersonnii*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Pomadasys commersonnii*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Pomadasys commersonnii*	<0.01	0.027	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Pomadasys commersonnii*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Pomadasys commersonnii*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Pomadasys commersonnii*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Platycephalus indicus*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Perna perna* DBN1	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Perna perna* DBN2	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Perna perna* DBN3	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Perna perna* DBN4	<0.01	<0.01	<0.01	0.015	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Perna perna* DBN5	<0.01	<0.01	<0.01	0.012	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Perna perna* DBN6	<0.01	0.011	<0.01	0.012	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Perna perna* DBN7	<0.01	<0.01	<0.01	0.015	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Perna perna* DBN8	<0.01	<0.01	<0.01	0.011	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Perna perna* DBN9	<0.01	0.013	<0.01	0.012	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Perna perna* DBN10	<0.01	0.012	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DBN	*Perna perna* DBN11	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ISI	*Myxus capensis*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ISI	*Ambassis natalensis*	<0.01	<0.01	<0.01	0.012	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

System	Species	Dieldrin mg.kg^{-1}	4'4'-DDE mg.kg^{-1}	4'4'-DDD mg.kg^{-1}	4'4'-DDT mg.kg^{-1}	Endrin mg.kg^{-1}	Endrin Aldehyde mg.kg^{-1}	Endrin Ketone mg.kg^{-1}	Endosulfan I mg.kg^{-1}	Endosulfan II mg.kg^{-1}	Endosulfan Sulfate mg.kg^{-1}	Methoxy-chlor mg.kg^{-1}
ISI	*Oreochromus mossambicus*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ISI	*Oreochromus mossambicus*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ISI	*Oreochromus mossambicus*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ISI	*Oreochromus mossambicus*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
MNG	*Valamugil cunnesius*	<0.01	0.027	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
MNG	*Valamugil cunnesius*	<0.01	0.028	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
MNG	*Liza dumerilii*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
MNG	*Liza macrolepis*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
MNG	*Liza macrolepis*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
MNG	*Liza tricuspidens*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
MNG	*Mugil cephalus*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
MNG	*Gerres methueni*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
MNG	*Ambassis natalensis*	<0.01	0.021	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
MNG	*Oreochromus mossambicus*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
MNG	*Oreochromus mossambicus*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
MNG	*Oreochromus mossambicus*	<0.01	0.015	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
MNG	*Oreochromus mossambicus*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

APPENDIX 17

Polychlorinated biphenyl concentrations (dry weight) in fish caught in Durban Bay and the uMngeni and Isipingo River estuaries in 2013.

System	Species	PCB8 µg.kg^{-1}	PCB18 µg.kg^{-1}	PCB28 µg.kg^{-1}	PCB44 µg.kg^{-1}	PCB52 µg.kg^{-1}	PCB66 µg.kg^{-1}	PCB77 µg.kg^{-1}	PCB101 µg.kg^{-1}	PCB105 µg.kg^{-1}	PCB118 µg.kg^{-1}	PCB126 µg.kg^{-1}
DBN	*Sphyraena jello*	<2	<2	<2	<2	<2	<2	<2	<2	<2	5	5.3
DBN	*Sphyraena jello*	<2	<2	<2	<2	4.6	<2	<2	2.5	<2	7	6.3
DBN	*Valamugil buchanani*	<2	<2	<2	<2	4.7	<2	<2	3	<2	4.9	5.1
DBN	*Myxus capensis*	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
DBN	*Myxus capensis*	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
DBN	*Myxus capensis*	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
DBN	*Myxus capensis*	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
DBN	*Liza dumerilii*	<2	<2	<2	<2	5.1	<2	<2	2.9	<2	7.7	5.6
DBN	*Liza dumerilii*	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
DBN	*Liza tricuspidens*	<2	<2	<2	<2	4.7	<2	<2	5.3	<2	7.6	6.6
DBN	*Mugil cephalus*	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
DBN	*Mugil cephalus*	<2	<2	<2	<2	<2	<2	<2	<2	<2	2.9	<2
DBN	*Pseudorhombus arsius*	<2	<2	<2	<2	<2	<2	<2	<2	<2	3.5	2.8
DBN	*Sillago sihama*	<2	<2	<2	<2	<2	<2	<2	3.3	<2	3.3	4.6
DBN	*Sillago sihama*	<2	<2	<2	<2	<2	<2	<2	2.9	<2	2.6	3.8
DBN	*Sillago sihama*	<2	<2	<2	<2	5.7	<2	<2	<2	<2	<2	<2
DBN	*Ambassis gymnocephalus*	<2	<2	<2	<2	<2	<2	<2	4.1	<2	11	6.7
DBN	*Ambassis gymnocephalus*	<2	<2	<2	<2	2.3	<2	<2	4.3	<2	10	6.4
DBN	*Pomadasys commersonnii*	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	2.8
DBN	*Pomadasys commersonnii*	<2	<2	<2	<2	<2	<2	<2	<2	<2	2.4	6.2
DBN	*Pomadasys commersonnii*	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	2.7
DBN	*Pomadasys commersonnii*	<2	<2	<2	<2	<2	<2	<2	<2	<2	2.3	<2
DBN	*Pomadasys commersonnii*	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
DBN	*Pomadasys commersonnii*	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
DBN	*Pomadasys commersonnii*	<2	<2	<2	<2	<2	<2	<2	2.3	<2	3.3	4.2
DBN	*Pomadasys commersonnii*	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
DBN	*Pomadasys commersonnii*	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	2.1
DBN	*Pomadasys commersonnii*	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	4.3
DBN	*Platycephalus indicus*	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
DBN	*Perna perna* DBN1	<2	<2	<2	<2	4.6	<2	<2	<2	<2	3.7	<2
DBN	*Perna perna* DBN2	<2	<2	<2	<2	4.4	<2	<2	<2	<2	3.1	2.5
DBN	*Perna perna* DBN3	<2	<2	<2	<2	4.3	<2	<2	<2	<2	3.8	2.8
DBN	*Perna perna* DBN4	<2	<2	<2	<2	<2	<2	<2	<2	<2	3.4	2.6
DBN	*Perna perna* DBN5	<2	<2	<2	<2	3	<2	<2	<2	<2	3.3	3

System	Species	PCB8 µg.kg^{-1}	PCB18 µg.kg^{-1}	PCB28 µg.kg^{-1}	PCB44 µg.kg^{-1}	PCB52 µg.kg^{-1}	PCB66 µg.kg^{-1}	PCB77 µg.kg^{-1}	PCB101 µg.kg^{-1}	PCB105 µg.kg^{-1}	PCB118 µg.kg^{-1}	PCB126 µg.kg^{-1}
DBN	*Perna perna* DBN6	<2	<2	<2	<2	<2	<2	<2	<2	<2	2.6	2.5
DBN	*Perna perna* DBN7	<2	<2	<2	<2	<2	<2	<2	<2	<2	3.5	3.4
DBN	*Perna perna* DBN8	<2	<2	<2	<2	<2	<2	<2	<2	<2	2.9	3.7
DBN	*Perna perna* DBN9	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
DBN	*Perna perna* DBN10	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
DBN	*Perna perna* DBN11	<2	<2	<2	<2	<2	<2	<2	<2	<2	2.8	2.3
ISI	*Myxus capensis*	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
ISI	*Ambassis natalensis*	<2	<2	5.7	3.2	9	<2	<2	6.9	<2	13	3.2
ISI	*Oreochromus mossambicus*	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
ISI	*Oreochromus mossambicus*	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
ISI	*Oreochromus mossambicus*	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
ISI	*Oreochromus mossambicus*	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
MNG	*Valamugil cunnesius*	<2	<2	4.3	<2	6.5	<2	<2	<2	<2	5	<2
MNG	*Valamugil cunnesius*	<2	<2	4.6	<2	7	<2	<2	<2	<2	4.8	<2
MNG	*Liza dumerilii*	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
MNG	*Liza macrolepis*	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
MNG	*Liza macrolepis*	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
MNG	*Liza tricuspidens*	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
MNG	*Mugil cephalus*	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
MNG	*Gerres methueni*	<2	<2	<2	<2	<2	<2	<2	<2	<2	2.3	<2
MNG	*Ambassis natalensis*	<2	<2	<2	<2	3.5	<2	<2	<2	<2	4.1	<2
MNG	*Oreochromus mossambicus*	<2	<2	<2	<2	9.1	<2	<2	<2	<2	<2	<2
MNG	*Oreochromus mossambicus*	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
MNG	*Oreochromus mossambicus*	<2	<2	<2	<2	<2	<2	<2	<2	<2	5.1	3
MNG	*Oreochromus mossambicus*	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2

System	Species	PCB126 µg.kg^{-1}	PCB128 µg.kg^{-1}	PCB138 µg.kg^{-1}	PCB153 µg.kg^{-1}	PCB169 µg.kg^{-1}	PCB170 µg.kg^{-1}	PCB180 µg.kg^{-1}	PCB187 µg.kg^{-1}	PCB195 µg.kg^{-1}	PCB206 µg.kg^{-1}	PCB209 µg.kg^{-1}
DBN	*Sphyraena jello*	<2	15	23	<2	5	9	<2	<2	<2	<2	<2
DBN	*Sphyraena jello*	<2	18	28	<2	5.6	9.9	<2	<2	<2	<2	<2
DBN	*Valamugil buchanani*	<2	11	17	<2	4.8	6.4	<2	<2	<2	<2	<2
DBN	*Myxus capensis*	<2	<2	2.6	<2	<2	<2	<2	<2	<2	<2	<2
DBN	*Myxus capensis*	<2	<2	2.6	<2	<2	<2	<2	<2	<2	<2	<2
DBN	*Myxus capensis*	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
DBN	*Myxus capensis*	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
DBN	*Liza dumerilii*	2.2	18	29	<2	6.1	11	<2	<2	<2	<2	2.2
DBN	*Liza dumerilii*	<2	2	3.5	<2	<21	2.4	<2	<2	<2	<2	<21

System	Species	PCB126 µg.kg^{-1}	PCB128 µg.kg^{-1}	PCB138 µg.kg^{-1}	PCB153 µg.kg^{-1}	PCB169 µg.kg^{-1}	PCB170 µg.kg^{-1}	PCB180 µg.kg^{-1}	PCB187 µg.kg^{-1}	PCB195 µg.kg^{-1}	PCB206 µg.kg^{-1}	PCB209 µg.kg^{-1}
DBN	*Liza tricuspidens*	2.1	20	31	<2	6.2	11	<2	<2	<2	<2	2.1
DBN	*Mugil cephalus*	<2	2.5	3.1	<2	<2	<2	<2	<2	<2	<2	<2
DBN	*Mugil cephalus*	<2	11	9.1	<2	3	4.4	<2	<2	2.2	1	<2
DBN	*Pseudorhombus arsius*	<2	8.6	13	<2	3.1	5.1	<2	<2	<2	<2	<2
DBN	*Sillago sihama*	<2	11	14	<2	3.7	5.9	<2	<2	<2	<2	<2
DBN	*Sillago sihama*	<2	7.6	12	<2	3.9	6.5	<2	<2	<2	<2	<2
DBN	*Sillago sihama*	<2	2	2.9	<2	1	1	<2	<2	<2	<2	<2
DBN	*Ambassis gymnocephalus*	<2	24	37	<2	7.4	13	<2	<2	<2	<2	<2
DBN	*Ambassis gymnocephalus*	<2	24	32	<2	6.4	12	<2	<2	<2	<2	<2
DBN	*Pomadasys commersonnii*	<2	5.1	9.9	<2	1	1	<2	<2	<2	<2	<2
DBN	*Pomadasys commersonnii*	<2	14	20	<2	5.4	2.8	<2	<2	<2	<2	<2
DBN	*Pomadasys commersonnii*	<2	5.1	11	<2	<2	<2	<2	<2	<2	<2	<2
DBN	*Pomadasys commersonnii*	<2	4	5.5	<2	<2	<2	<2	<2	<2	<2	<2
DBN	*Pomadasys commersonnii*	<2	4.2	8.2	<2	<2	<2	<2	<2	<2	<2	<2
DBN	*Pomadasys commersonnii*	<2	<2	2.6	<2	<2	<2	<2	<2	<2	<2	<2
DBN	*Pomadasys commersonnii*	<2	12	15	<2	3.4	3.9	<2	<2	<2	<2	<2
DBN	*Pomadasys commersonnii*	<2	3.9	13	<2	<2	<2	<2	<2	<2	<2	<2
DBN	*Pomadasys commersonnii*	<2	5	9.2	<2	<2	<2	<2	<2	<2	<2	<2
DBN	*Pomadasys commersonnii*	<2	7.5	13	<2	3.5	2.5	<2	<2	<2	<2	<2
DBN	*Platycephalus indicus*	<2	2.1	3	<2	<2	<2	<2	<2	<2	<2	<2
DBN	*Perna perna* DBN1	<2	7.4	9.1	<2	<2	2.3	<2	<2	<2	<2	<2
DBN	*Perna perna* DBN2	<2	7.8	9.3	<2	<2	2.6	<2	<2	<2	<2	<2
DBN	*Perna perna* DBN3	<2	9.8	11	<2	<2	3.2	<2	<2	<2	<2	<2
DBN	*Perna perna* DBN4	<2	9.1	9	<2	<2	3.1	<2	<2	<2	<2	<2
DBN	*Perna perna* DBN5	<2	9.8	11	<2	<2	2.9	<2	<2	<2	<2	<2
DBN	*Perna perna* DBN6	<2	5.7	7.7	<2	<2	2.9	<2	<2	<2	<2	<2
DBN	*Perna perna* DBN7	<2	7.9	9.9	<2	<2	3.5	<2	<2	<2	<2	<2
DBN	*Perna perna* DBN8	<2	9.1	12	<2	<2	3.6	<2	<2	<2	<2	<2
DBN	*Perna perna* DBN9	<2	4	5.6	<2	<2	2.1	<2	<2	<2	<2	<2
DBN	*Perna perna* DBN10	<2	3.9	6.7	<2	<2	2.2	<2	<2	<2	<2	<2
DBN	*Perna perna* DBN11	<2	5.7	7.5	<2	<2	2.6	<2	<2	<2	<2	<2
ISI	*Myxus capensis*	<2	<2	4.5	<2	<2	<2	<2	<2	<2	<2	<2
ISI	*Ambassis natalensis*	2.2	22	22	<2	4.8	6.8	<2	<2	<2	<2	2.2
ISI	*Oreochromus mossambicus*	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
ISI	*Oreochromus mossambicus*	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
ISI	*Oreochromus mossambicus*	<2	2.2	3	<2	<2	<2	<2	<2	<2	<2	<2
ISI	*Oreochromus mossambicus*	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2

System	Species	PCB126 µg.kg^{-1}	PCB128 µg.kg^{-1}	PCB138 µg.kg^{-1}	PCB153 µg.kg^{-1}	PCB169 µg.kg^{-1}	PCB170 µg.kg^{-1}	PCB180 µg.kg^{-1}	PCB187 µg.kg^{-1}	PCB195 µg.kg^{-1}	PCB206 µg.kg^{-1}	PCB209 µg.kg^{-1}
MNG	*Valamugil cunnesius*	<2	6.5	8	<2	<2	3.4	<2	<2	<2	<2	<2
MNG	*Valamugil cunnesius*	<2	6.8	8.5	<2	<2	3.3	<2	<2	<2	<2	<2
MNG	*Liza dumerilii*	<2	2.2	2.7	<2	<2	<2	<2	<2	<2	<2	<2
MNG	*Liza macrolepis*	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
MNG	*Liza macrolepis*	<2	<2	2.4	<2	<2	<2	<2	<2	<2	<2	<2
MNG	*Liza tricuspidens*	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
MNG	*Mugil cephalus*	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
MNG	*Gerres methueni*	<2	4.7	4.5	<2	<2	<2	<2	<2	<2	<2	<2
MNG	*Ambassis natalensis*	<2	7	8.3	<2	<2	<2	<2	<2	<2	<2	<2
MNG	*Oreochromus mossambicus*	<2	2.3	4.3	<2	<2	<2	<2	<2	<2	<2	<2
MNG	*Oreochromus mossambicus*	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
MNG	*Oreochromus mossambicus*	<2	12	14	<2	2.4	5.3	<2	<2	<2	<2	<2
MNG	*Oreochromus mossambicus*	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2