

An assessment of the degree of mercury (Hg) bio-transformation in two river systems following discharges from a mercury recovery plant

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Abstract

Numerous reports in the media, between 1986 to 1990, have referred to discharges of Hg waste from Thor Chemicals in Kwa Zulu Natal, South Africa into two river systems. A study conducted in 1990 found that Thor Chemicals was the source of this pollution and that excessive levels of Hg were detected immediately below the plant. No other studies have been conducted since then. This study, which includes the area directly below Thor Chemicals to the top end of Inanda Dam, shows that Hg levels in sediment below the plant were of a similar magnitude to those detected 8 years previously. However, sediment and algae levels further downstream were considerably lower. A 98% increase in Hg sediment levels is noted at a sample site 10 kilometres downstream from the chemical plant. This may suggest that a degree of bio magnification may have taken place, although other factors could also be responsible for this increase. Despite Hg levels in fish collected from Inanda Dam being below statutory levels, there is a concern that the fish eating population and high risk groups may be exposed to excessive levels of Hg in their diet. Hg levels in the fish obtained from Inanda Dam indicate that consumption levels should be restricted from 16 to 3 fish meals in a month. In consideration that fish are the staple diet of the community residing in the area it is recommended that a risk assessment be conducted on the fish eating population of the region.

Introduction

The debate surrounding Hg pollution of the river system below Thor Chemicals in Kwa Zulu Natal, South Africa has been of concern to the people of the region for several years. Thor Chemicals have been processing waste Hg for approximately 12 years. The plant began to receive considerable media attention in 1989. This was centred around the apparent discharges of spent Hg waste into the Mngceweni River, situated directly below the plant (Clarke, 1994; Nichols, 1995). Reports published in the media stated that drums containing spent Hg were emptied into this river in early April 1990. At the time, Green Peace expressed concern about the probability of these contaminants rapidly being converted into methylmercury (MeHg) in the environment and posing a threat to the community living down-stream. An investigation conducted by this group revealed that the Hg levels a few hundred metres from the boundary of the Thor Chemicals plant were 8 600 times higher in the soil and the sediment than the United States limit for toxic waste (Clarke, 1994). No scientific assessment of Hg pollution has been carried out to date, other than a study conducted by Johnston et al. (1991) in 1990, in an area restricted to within 10 km of the plant. Johnston et al. (1991) obtained sediment and soil samples from the vicinity of Thor Chemicals, situated at the head of the Mngceweni River and a marshland area at the confluence of this river and at the permanent settlement of Fredville, which is situated within the Mngceweni River valley. The results indicated that Hg contamination had taken place directly below Thor Chemicals. Johnston et al. (1991) pointed out the 50 mg/l of Hg found in the river bed of the Mngceweni River could be quantified as chemical waste. The Thor Chemicals plant

was identified as the point source of Hg pollution. Since then, Thor Chemicals has attracted considerable public attention, culminating in certain matters concerning this plant being discussed in the South African Parliament.

In order to clarify some of these issues this study aimed to quantify the extent to which Hg has become mobilised in the study area and to identify possible pathways of exposure to the community. Samples of sediment, algae and fish were collected from an area located between Thor Chemicals and Inanda Dam (Fig. 1). Concentrations of Hg in these samples were determined and compared with levels detected in the control area and were compared to the results as obtained by Johnston et al. (1991) study. Hg concentrations in fish were also compared to MeHg consumption levels set by various regulatory agencies. These media were chosen for the following reasons:

Contaminated sediments at the bottom of surface waters serve as an important Hg reservoir, with sediment-bound Hg recycling back into the aquatic ecosystem for decades or longer (Jackson, 1993). The WHO (1989) has referred to several studies that demonstrate the methylation of inorganic Hg in the sediment of lakes and rivers which is a key step in the transport of Hg in the aquatic food chain. Studies have indicated that the mobilisation of the Hg from the sediment is influenced by a low pH (5.8 to 5.4) which may allow the Hg to be taken up by higher trophic levels in the aquatic system (Panda et al., 1990).

Temperature is also considered to play an important part in the methylation of Hg, particularly at high levels, possibly due to increased microbial activity (Jackson, 1993; Park et al., 1997). These two parameters, pH and temperature, are considered to be important factors when determining the state of Hg in sediment within a river system (Jackson, 1993).

The capacity for algae to bio-concentrate Hg was demonstrated by Bailey and Stokes (1985) who found that Hg levels increased 1 000 to 10 000 in concentration within the algae in water systems.

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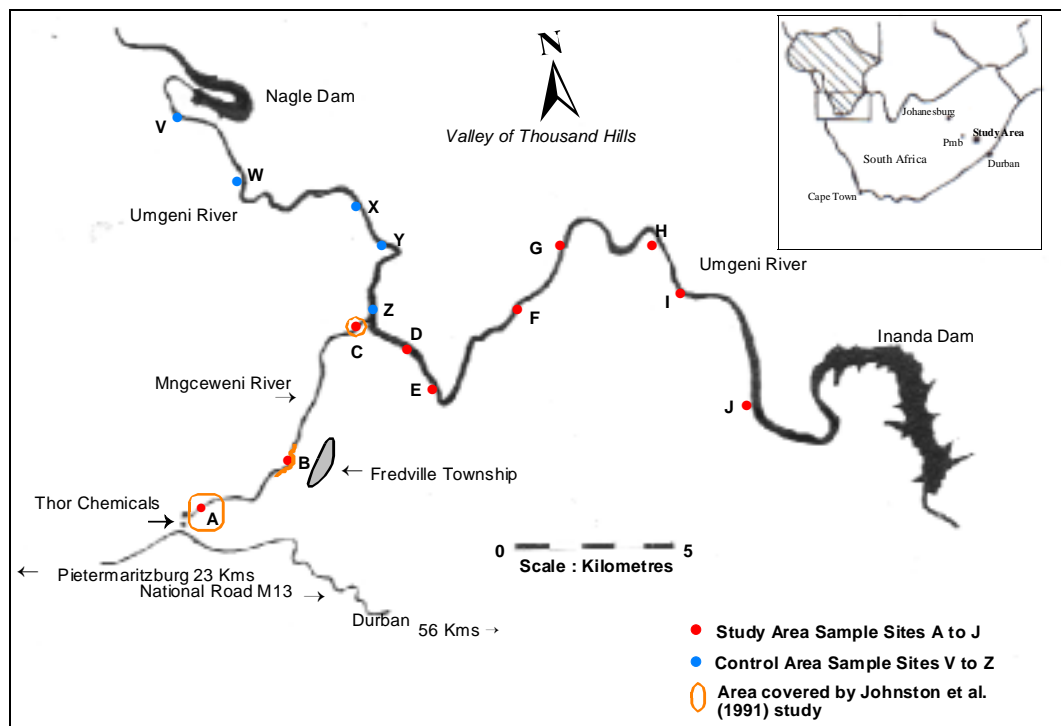


Figure 1
Sketch study area and control area indicating locality of sample Sites (A to Z) in relation to Thor Chemicals in The Valley of a Thousand Hills, KwaZulu-Natal

Likewise the US Geological Surveys National Water-Quality Assessment Program has indicated the appropriateness of algae as an indicator of Hg pollution and provided methodological procedures for the collection and analysis of Hg in algae (Porter et al., 1993). In terms of this study, algae were the most common aquatic plants found in the two river systems.

It has been shown that elevated Hg levels in fish are common throughout the USA (USEPA, 1997). In fact, Hg in fish is considered to be the single greatest public health concern associated with Hg pollution. This even applies to fish far removed from the source of the pollution and nearly 100% of the Hg found in fish muscle tissue is MeHg. MeHg appears to be primarily passed to planktivores and piscivorous fish via their diet particularly in the larger, longer lived fish species located at the upper end of the food chain (Holsbeek et al., 1996; Ikingura and Anagi, 1996). Carp (*Cyprinus carpio limaeus*) and sharp-toothed catfish (*Clarias gariepinus*) were chosen for examination as they are considered to be the most abundant species of fish found in the study area. The species of carp found in the eastern area of South Africa are omnivorous fish and consume a wide range of plant and animal matter whereas sharp-toothed catfish are piscivores and prey on a wide range of aquatic fauna (Skelton, 1993). A recent Hg update report published in 1999 by the US EPA (1999) asserts that humans are most likely to be exposed to MeHg through fish consumption. This particularly applies to subsistence fishermen that routinely consume large amounts of locally caught fish. Sensitive population groups such as pregnant women, nursing mothers and their children must be considered as particularly vulnerable (Harada, 1995; Rice, 1995). The USEPA (1999) further states that exposure to MeHg is dependent on either the quantity of fish consumed, or the level of MeHg present. Adults that consume approximately 50 g of fish per day containing between 0.1 to 0.15 ppm Hg are at risk of slightly exceeding the reference dose (RfD) to levels reaching twice the RfD. Those that consume levels of 0.5 ppm

Hg but ate less than 10 g of fish per day, are likely to experience Hg exposure near the RfD. Those who, however, consumed 40 to 70 g of fish a day are likely to exceed the RfD by as much as six times.

Methods

Sediment and algae

Ten sample sites were selected from within the study area from which sediment and algae samples were obtained. These sites extended along the Mngceweni and Umgeni Rivers at intervals ranging from between 3 and 5 km from each other. The first sample site was located directly below Thor Chemicals and the final sample was taken at the top end of Inanda Dam approximately 35 km downstream (Fig. 1). The length of the sampling site was determined by the stream's geomorphology in terms of the extent and access to the sediment bed and availability of algae in the sampling zone. The sample point was visually examined to identify areas of the river bed that appeared to include only fine grained sediments that had high organic content. Such sediments would include those that contain clay and silt particles, as these properties are considered to be natural accumulators of Hg (Shelton and Capel, 1994). The methodology as defined in the US Geological Survey National Water Quality Guidelines for collecting stream bed sediments was used (Shelton and Capel, 1994). At each sample site, 5 to 8 subsamples were collected to make one single sample which was considered to be representative of the entire sample site (Shelton and Capel, 1994). This single sample was obtained by coning the sediment samples whereby the subsamples were homogenised and combined to form a composite sample.

The collection of algae only took place after the sediment subsamples had been obtained in order to reduce stirring or contamination of the sediment within the river. Algae samples were collected

from within the sampling site area and the number of samples obtained depended on access and availability of the algae. The procedures as recommended in the US Geological Survey for collecting algae samples were adopted (Porter et al., 1993). As for the sediment samples, subsamples of algae were collected at each site and were also composited through the coning method. Temperature and pH readings of the river water were also taken at each point from where sediment and algae samples were obtained using a Beckman 200 pH meter which was calibrated on the day that measurements were taken.

Fish

Since Inanda Dam is deemed to be the major receiver of sediment deposition from the study area, (situated approximately 35 km downstream from Thor Chemicals), the sampling of large fish from this source was considered to be of great importance. Catfish and carp ranging between 3 to 5 kg in mass, or between 30 cm to 40 cm in length, were caught from Inanda Dam.

Laboratory analysis

All samples were transported to a South African accredited laboratory immediately after collection, or frozen at -15°C until they could be taken to the laboratory. Both sediment and algae samples were required to be coned within the laboratory to comply with the recommendations as given by Shelton and Capel (1994). Muscle tissue from the area adjacent to the dorsal fin of the fish was selected for analysis because the affinity of mercury to be absorbed into fish muscle (WHO, 1989).

Duplicate samples of the specimens were analysed and the final result was calculated from the mean of the two results. In order to detect Hg levels, all forms of Hg, including organic derivatives, were oxidised to ionic mercury by acidic potassium permanganate. Inorganic mercury was rapidly reduced by sodium borohydride in an acidic solution to form mercury vapor. The vapor was purged continuously with argon into an unheated quartz tube in the light path of an atomic spectrometer where absorbance is determined at 253.7 nm. The Hg values were given in $\mu\text{g}/\text{l}$. In order to compare values to regulatory standards and to the Johnston et al. (1991) study these values were converted to $\mu\text{g}/\text{g}$.

Results and discussion

Sediment and algae

The levels of Hg within the sediment at Site A, located at the source of the Mngceweni River directly below Thor Chemicals (Fig. 1), were found to be the most meaningful. Hg concentrations at this site were considerably higher ($54 \mu\text{g}/\text{g}$) than all the other Hg levels detected in the sediment at the remainder of the sample sites in the study area. Hg levels within detectable limits were only found at 5 sample sites, being A, B, C, E, H. A mean value of $0.41 \mu\text{g}/\text{g}$ Hg was calculated, with a standard deviation of 0.3 (Fig. 1). Site A was excluded as it was considered to be an outlier. The remainder of the sample site results downstream of Site A can be regarded as having a 99% reduction in Hg concentrations. Hg levels in sediment below detectable limits were recorded at sample sites, D, F, G, I and J, all of which are on the Umgeni River. This suggests that once the Mngceweni River enters the Umgeni River, which is directly below sample site C, a substantial dilution of Hg concentration in the sediment has occurred. The Mngceweni River is a small river in comparison to the Umgeni River which has a large catchment area

and therefore a higher volume and flow rate, which will increase as the Umgeni River flows further downstream towards the Inanda Dam.

When comparing Hg in sediment levels from this study to those obtained by Johnston et al. (1991), eight years previously, an interesting scenario appears. The Hg level in sediment measured at Sample Site A in 1998 ($56 \mu\text{g}/\text{g}$) compares well with Hg in sediment taken from the same area by Johnston et al. (1991). This indicates that there has been a slight increase (8.8%) in the amount of Hg below Thor Chemicals. The fact that the Hg level at this site is still high may support the theory that Hg can exist in stream sediments for decades (US EPA, 1997). The retention of the Hg in the sediment could also be due to the relatively high pH (7.0) recorded in the river water. A pH of this magnitude may be impeding the leaching of the Hg from the sediment. However, the possibility that continuous seepage of Hg effluent from the slimes dams situated within the factory complex of Thor Chemicals, into the Mngceweni River, cannot be discounted as a cause for the steady levels of Hg in the sediment over this period. In consideration of the high temperature recorded in the river water at Site A (27.8°C) and that the study area is in a subtropical region, it is highly probable that the majority of the Hg has methylated to the more toxic form of MeHg. This is a matter of concern if the Hg becomes available to be taken up by aquatic organisms which may eventually lead to elevated MeHg levels in the larger fish species.

Of particular interest is the level of Hg in the sediment at sample Site C. When comparing the values of the Johnston et al. (1991) study to the results obtained in 1998 from the same area, the mean value of Hg in the sediment increased from $0.017 \mu\text{g}/\text{g}$ in 1991 to $0.860 \mu\text{g}/\text{g}$ in 1998. This is an increase of 98.11% in Hg concentration in the sediment at this site over a period of eight years.

This may support the theory that some of the Hg is being assimilated into the sediment due to microbial activity, although several other factors could be responsible for the increased Hg values at this site (Jackson, 1993). There may have been differences in the analytical procedures used in the two studies, that possible further discharges could have occurred in the intervening eight years from Thor Chemicals or that this particular site could be acting as a natural sink for Hg deposition. Notwithstanding these findings, the Hg level at Site C is low and of a similar magnitude to the Hg levels recorded in the remainder of the Sites B to J. Other than sample site A, which was considered as an outlier, no significant difference was found in Hg levels in sediment between the study area and the control area at the 95% confidence level ($p=0.53$). Despite the fact that algae are considered to be a good indicator of Hg pollution, the Hg levels in the algae samples were all below detectable limits. A confounding factor was that only small amounts of algae were available to be collected. As a result there were insufficient algae available for the atomic absorption spectrometer to perform accurate readings to determine if there was any trend towards the mobilisation or bio-magnification of Hg in algae.

Fish

Hg concentration in the fish samples was compared for the study area (Inanda Dam) and control area (Nagle Dam) in order to investigate whether Hg being discharged from Thor Chemicals into the two river systems is having any effect on the fish population in Inanda Dam. Using the Two Sample t Test it was established that there was statistically no significant difference between the fish caught in the two dams, where a 'p' value of 0.08 was found (a p value of 0.05 or less was considered to indicate a significant difference). Nevertheless, despite the statistics, recognition has to

Hg concentration (µg/g) in fish from Inanda	Number of samples with related Hg levels	Number of recommended fish meals per month *
0.05	1	16
0.07 to 0.08	2	12
0.12	1	8
0.19 to .21	5	4
0.25	1	3

* Average adult based on weight of 72 kg consuming 227 g of fish calculated over 30.44 d (1 month)

be given to the fact that there is a 1 in 12 probability of a difference, when defining the result of this p value (0.08) further. Despite this uncertainty, it is important to note that all actual concentrations of Hg in fish in Inanda Dam were found to be within detectable limits, whereas in Nagle Dam only 40% of the Hg levels in fish were within detectable limits.

This suggests that a degree of bio-accumulation may be taking place within the Inanda Dam, possibly due to discharges from Thor Chemicals. Although the Hg levels in the fish samples comply with the South African Foodstuffs, Cosmetics and Disinfectants Regulations and the US Food and Drugs Agency Requirements for Hg in fish, being 0.5 mg/l and 1 ppm respectively (FCD Reg, 1994; US EPA, 1997) there is a need to quantify the consumption levels of Hg in the fish eating population residing in the study area. Of particular concern are the effects of Hg contaminated fish being consumed by high-risk groups such as pregnant women and children (US EPA, 1999) and in particular infants who are considered to be of greater risk (Rice, 1995). When comparing consumption levels as opposed to action levels, as stated above, the scenario emerges to be considerably different. Table 1 illustrates the US EPA recommended number of fish meals permitted in a month in terms of Hg levels in carp and catfish as found in Inanda Dam (US EPA, 1999).

Although all the Hg levels in the fish were below the action levels, as stated above, it can be seen that 60% of the fish sampled contained sufficiently elevated Hg levels to restrict a diet of fish from Inanda Dam to three to four fish meals in a month. If the assumption were made that fish were consumed on a daily basis then the community should be restricted to half their usual fish consumption.

In order to determine the possible risk to the residents residing in the study area it would be necessary to carry out a risk assessment. The aim being to establish the risk of exposure by investigating the general population and in particular the sensitive population groups (US EPA, 1999).

When comparing the concentration of Hg in similar size carp and catfish, in the study area an interesting trend emerges between the mean Hg concentration of 2.38 µg/l for the catfish and the mean value of 1.16 µg/l for carp. The mean concentration of Hg for catfish is twice that of the carp. This implies that the catfish are storing greater amounts of Hg. The Two Sample t Test confirms that there is a significant difference between the Hg concentrations in catfish and the carp in the study area at the 95% confidence level (p=0.014). The higher concentrations of Hg in the catfish may be explained by the fact that they are bottom feeders and may ingest sediment and Hg

while feeding and that they are also predators and could be ingesting Hg from other organisms as well, unlike the carp that are predominantly omnivores only (Skelton, 1993; Hg from the sediment is influenced by a low pH (5.8 to 5.4) which may allow the Hg to be taken up by higher trophic levels in the aquatic system (Panda et al., 1990); Hollsbeek et al., 1996).

Recommendations and conclusion

It is evident that extensive Hg pollution occurred eight years ago in the region directly below Thor Chemicals (Johnston et al., 1991). This study also indicated that the area is still contaminated and could remain a source of potential bio-accumulation and mobilisation of Hg into the ecosystem for many years to come. It must, nevertheless, be emphasised that the bulk of the Hg pollution appears to be contained in the immediate vicinity of Thor Chemicals and for as long as this scenario continues it is unlikely to be of any danger to those residing in the study area. However, in view of the recommended US EPA consumption levels for Hg in fish, and in particular where catfish may be consumed on a regular basis, a risk assessment study needs to be conducted on the fish-eating population.

The contaminated zone around Thor Chemicals should be clearly identified and fenced off, in order to restrict access. Some form of environmental remediation, needs to be considered, such as the design of suitably constructed wetlands. Physical removal should not be considered as this may dislodge the contaminated sediment generating pollution further downstream where there are settled human populations.

The community, government agencies, such as the South African Department of Water Affairs and Forestry, Department of Health, Thor Chemicals and other interested parties will be informed of the outcome of this research and for the need of a risk assessment study.

The appointed Catchment Management Agency should be encouraged to monitor fish Hg levels in the Inanda Dam in the future as a routine precaution. In the event of the contaminated sediment being mobilised, the logical end-point of sediment transportation would be the Inanda Dam.

In addition regular monitoring of the sediment along the length of the Mngcewewni River needs to be carried out to rule out increases in Hg levels or confirm that there is a pollution problem.

A suitable method for the disposal of remaining stockpiles of Hg waste by Thor Chemicals must be sought. Keeping Hg waste on the premises for extended periods of time is deemed to be more hazardous than the controlled recycling thereof.

Should development take place within the vicinity of Thor, in particular Fredville Township, special attention should be given of the utilisation of groundwater in the area and a hydrological survey should be conducted to assess groundwater impact from Thor Chemicals.

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References

- BAILEY RC and STOKES PM (1985) Evaluation of filamentous algae as biomonitors of metal accumulation in soft water lakes: A multivariate approach, aquatic toxicology and hazard assessment. *Proc. 7th Symp., Am. Soc. for Testing Materials*, Philadelphia. 5-26.
- CLARKE L (1994) Comment: Thor Chemicals under scrutiny. *Daily News* 23 March.
- FCD (1994) South African Food, Cosmetic And Disinfectants Act, No 54 of 1971: Regulation R1518 of 1994.
- HARADA M (1995) Minamata disease: Methylmercury poisoning in Japan caused by environmental pollution. *Critical Rev. in Toxicol.* **25** (1) 1-24.
- HOLSBEEK L, DAS HK and D JOIRIS CR (1996) Mercury speciation and accumulation in Bangladesh fresh water and andraomonous fish. *Sci. of the Total Environ.* **198** 201-210.
- IKINGURA JR and AKAGI H (1996) Monitoring of fish and human exposure to mercury due to gold mining in the Lake Victoria gold fields, Tanzania. *Sci. of the Total Environ.* **191** 59-68.
- JACKSON TA (1993) Effects of environmental and primary production on the distribution and methylation of mercury in a chain of highly eutrophic riverine lakes. *Water Pollution Res. Council J.* **28** (1) 177-216.
- JOHNSTON P, STRINGER R, FRENCH M C and VALLETTE J (1991) Contamination of soils in the vicinity of a mercury recovery plant. *Bull. of Environ. Contamination and Toxicol.* **46** 74-78.
- NICHOLS (1995) Thor fined after pleading guilty. *Natal Witness* (18 January) 5.
- PARK JG and CURTIS LR (1997) Mercury distribution in sediments and bio-accumulation by fish in two Oregon reservoirs: Point-source and non point-source impacted systems. *Arch. of Environ. Contaminants and Toxicol.* **33** 423-429.
- PANDA KK, LENKA M and PANDA B (1990) Monitoring and assessment of mercury pollution in the vicinity of a chloroalkali plant I, Distribution, availability and genotoxicity of sediment mercury in the Rushikula Estuary, India. *Sci of the Total Environ.* **96** 281-296.
- PORTER SD, CUFFNEY T, GURTZ EG AND MEADOR MR (1993) Methods of Collecting Algae Samples as part of the National Water Quality Assessment Programme. US Geological Survey Open-File Report 93-409, Sacramento, California. 30.
- RICE DC (1995) Neurotoxicity of lead, methylmercury and PCB's in relation to the Great Lakes. *Environ. Health Perspectives.* **103** (9) 71-78.
- SHELTON LR and CAPEL PD (1994) Guideline for collecting and processing samples of stream bed sediment for analysis of trace elements and organic contaminants for the National Water-Quality Assessment Programme. US Geological Survey Open-File Report 94-458, Sacramento, California. 1-27.
- SKELTON PH (1993) *A Complete Guide to the Freshwater Fishes of Southern Africa*. Southern Life Book Publishers, Halfway House, South Africa. 388 pp.
- US EPA (1997) Office of Air Quality Planning and Standards Office of Research and Development, US Environmental Protection Agency. Mercury Study Report to Congress. Vol 1 Executive Summary, EPA-452/R-97-003, December 1997. 1-40.
- US EPA (1999) Mercury Update: Impact on fish advisories [On-line]. Available from: www.epa.gov/OST/fish/mercury.html 1999. [Accessed 17 November, 1999].
- WHO (1989) Environmental Health Criteria 86. Mercury-Environmental Aspects, WHO Geneva. 14-34.