

Application of the equilibrium partitioning method to derive copper and zinc quality criteria for water and sediment: A South African perspective

V Wepener^{1*}, JHJ van Vuren² and HH du Preez²

¹Coastal Research Unit of Zululand, Department of Zoology, University of Zululand, P/Bag X1001, KwaDlangezwa 3886, South Africa

²Department of Zoology, Rand Afrikaans University, PO Box 526, Auckland Park 2006, South Africa

Abstract

This paper presents the use of an equilibrium partitioning (EP) method to derive generic quality criteria. Quality criteria for dissolved concentrations in water, total water concentrations and total sediment concentrations were derived from direct-effect data (aquatic toxicity data) and product standard data (human consumption standards). Both sets of data were obtained from physico-chemical and bioaccumulation field measurements in the Olifants and Selati Rivers, South African water quality guidelines and South African product standards. Emphasis is laid on the relation between effect and local physico-chemical data. Examples have been given for copper and zinc. Even with the acknowledged shortcomings of the EP methods the derived quality criteria for water and sediments were comparable to quality criteria from other countries.

Introduction

Environmental risk assessment and water quality management are becoming increasingly important issues, particularly in view of the large numbers of contaminants entering the aquatic environment that are harmful to the functioning of an ecosystem (Van Leeuwen, 1990). The water quality in South African rivers is gradually deteriorating and the social and economical changes taking place affect the way in which water quality has to be managed.

In South Africa water quality management is defined as the effort to control the physical, chemical and biological characteristics of water in such a way that the fitness-for-use, by recognised water users, is unimpaired (Moore et al., 1991). Prior to 1990 the Department of Water Affairs and Forestry (DWAF) controlled water quality and water pollution from point sources by requiring effluent to meet either uniform effluent standards (UES) or special effluent standards, which were set at technologically and economically feasible levels (Van der Merwe and Grobler, 1990). A new era in water quality management was entered with the promulgation of the new National Water Act (Act 36 of 1998). The central departure of the Act is the concept of resource use being dependent on resource protection. It also recognises that water quality should be extended to resource quality and include the quantity and quality of the water itself, the instream and riparian habitat (therefore the geomorphological structure of the system), the instream biota, and the associated riparian biota.

The aquatic environment differs from the other recognised water users (domestic, agricultural, recreational and industrial) in that aquatic ecosystems are essential to maintain the biological integrity necessary to ensure the sustained fitness-for-use of the water resources not only for the aquatic environment itself but also for the other user sectors. It is not a simple task to set water quality management objectives for the aquatic environment, since aquatic ecosystems may differ considerably from each other and have unique properties dictated by the natural conditions prevailing in a

specific system. In addition change is an important characteristic of aquatic ecosystems since species composition, rate processes, as well as degree of complexity and many other community characteristics change over time (Chapman, 1991). It is for this reason that general water quality guidelines cannot be regarded as blanket values because they may be over- or under-protective (Moore et al., 1991). Water quality standards or guidelines must therefore be aimed at taking regional differences into account.

At present water quality guidelines are based on the overly simplistic and entrenched philosophy that emphasises only dissolved chemicals and the water column. Very little attention has been paid to developing criteria for sediment bound chemicals. In environmental chemistry the term equilibrium partitioning refers to the relationship between the concentration of a substance in the water column and the concentration in the non-water phase, which is in contact with the water. The equilibrium partitioning (EP) method was found to be a relatively simple and applicative method to derive quality criteria (Shea, 1988).

The EP method models the co-occurrence of chemicals in water and sediments as a state of thermodynamic equilibrium, which can be regarded as a sorption equilibrium. If a direct relationship can be formulated for a chemical, it is possible to estimate quality criteria for sediments from the quality criteria of water, which in turn, are derived from toxicity tests (Van der Kooij et al., 1991). The EP approach requires four major assumptions:

- Partitioning of chemicals (i.e. metal concentrations) between the overlying water and interstitial water is stable at equilibrium.
- The sensitivities of benthic species and species tested to derive water quality criteria, predominantly water column species, are similar.
- The levels of protection afforded by water quality criteria are appropriate for benthic organisms.
- Exposures are similar regardless of feeding type or habitat (USEPA, 1993).

* To whom all correspondence should be addressed.

☎ (0351) 93911; fax (0351) 93162; e-mail: vwepener@pan.uzulu.ac.za
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It is acknowledged that the EP method is simplistic since it does not make provision for the route of exposure or environmental factors

TABLE 1
COMPARISON OF DISSOLVED COPPER AND ZINC CONCENTRATIONS IN THE OLIFANTS RIVER AND SELATI RIVER WITH OTHER RIVERS. CONCENTRATIONS ARE PRESENTED AS $\mu\text{g}\cdot\text{t}^{-1}$

River	Copper	Zinc	References
Olifants River (Balule)	18.9	101.4	This study
Olifants River (Mamba weir)	16.4	74.2	This study
Selati River	16.3	35.8	This study
Huanghe River (China)	9.6-15.4	0.66-15.4	Zhang and Huang (1993)
Changjiang Estuary (China)	11.5-13.4	0.4-0.79	Edmond et al. (1985)
St Lawrence River	25.21	86.5	Yeats and Bewers (1982)
Mississippi River	14.72	1.98	Trefry et al. (1986)
Amazon River	15.42	0.2-2.5	Shiller and Boyle (1987) Boyle et al. (1982)
Orinoco River	12.16	1.32	Shiller and Boyle (1985)
Rhône River	14.5-32.9	12.1-69.3	Unpublished data reported by Zhang and Huang (1993)

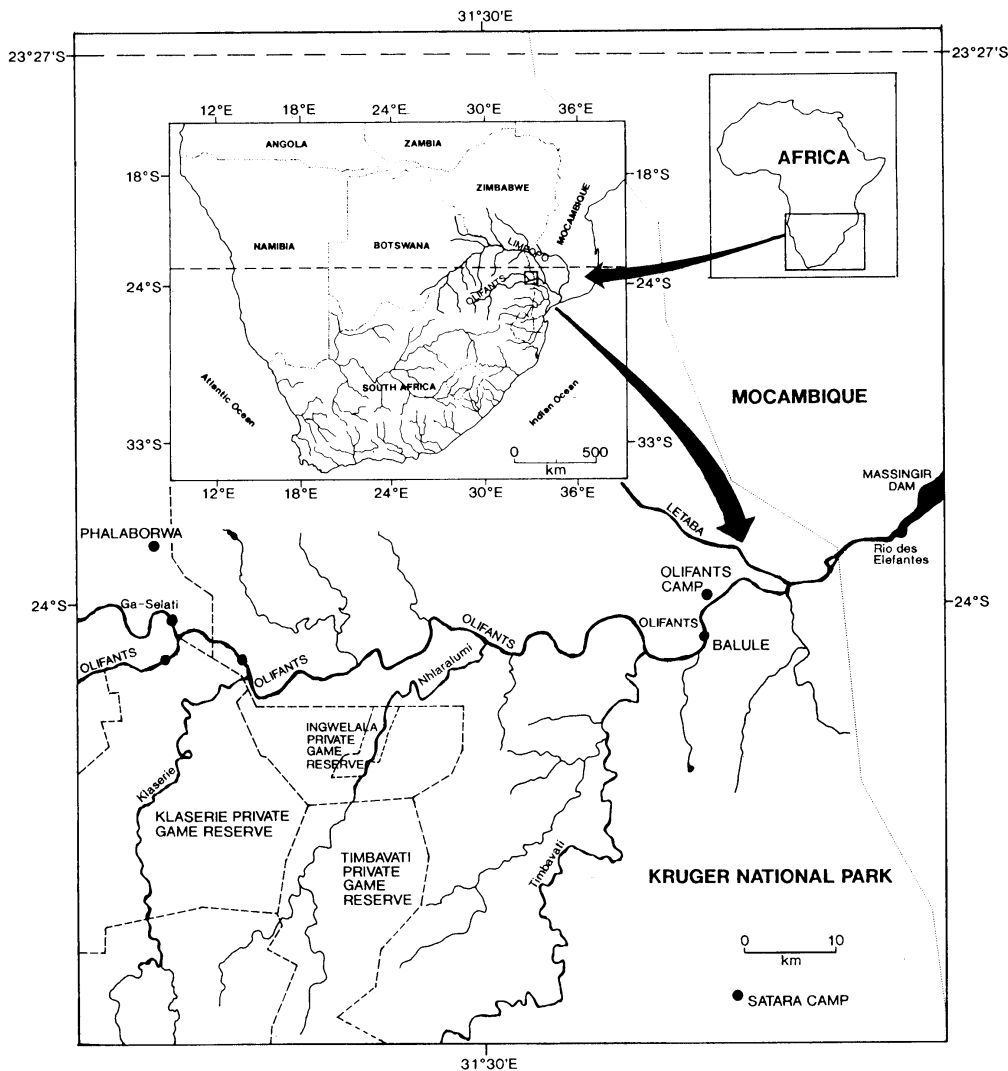


Figure 1

Map indicating sampling stations where water, sediment and axial muscle samples were collected. Sampling Site A is situated near Balule Rest Camp, Site B below Mamba Weir and Site C in the Selati River.

which affect the speciation of metals. However, the application of the technique has been proven to be realistic from a toxicological point of view (Connell et al. 1988; Jansen et al. 1997).

The concentrations of copper and zinc in the water of the Olifants and Selati Rivers were comparable to and in the same order of magnitude as concentrations in the Mississippi, St Lawrence and Rhône Rivers (Table 1). These are all large North-American and European rivers and the high dissolved trace metal concentrations are considered in close relation to anthropogenic contaminant input (Trefry et al., 1986). The water quality of the Olifants River, in the Kruger National Park, is influenced by siltation (due to injudicious agriculture practices) and mining effluent (Venter and Deacon, 1992). It is well documented that metals from mining effluents adsorb to sediments and suspended particles in the aquatic environment (Förstner and Wittman, 1979). Since extensive data on metal concentrations in water phases, sediment, and fish were available for the Olifants River (Wepener 1997) it provided the opportunity to apply the EP technique in deriving quality criteria for water and sediment.

This paper investigates the use of the EP method to derive quality criteria for two metals, i.e. copper and zinc using data obtained from the Olifants River. Criteria for the water (dissolved) phase, total concentration in the water (dissolved and particulate) and sediment were developed based on aquatic toxicity tests and product standards for the two metals. Emphasis was placed on the relationship between toxic effect data and physio-chemical data in the development of the quality criteria.

Materials and methods

The determination of quality criteria for copper and zinc was carried out by employing two forms of data sets i.e. toxic effect data and product standards.

Toxic effect data

The toxic effect data used for setting the quality criteria were based on the South African water quality guidelines for the protection of aquatic ecosystems (DWAF, 1996). The development of the guidelines was derived from the results of toxicity tests, which provided a degree of environmental realism and applicability (Roux et al., 1996). For the purpose of this assessment the chronic effect values (CEV) for copper and zinc were selected since they provide protection to most aquatic organisms even during chronic exposure.

Product standards

For many chemicals including copper and zinc, maximum allowable concentrations in foodstuffs for human consumption (e.g. in fish) are available (Verheul, 1992). These critical concentrations in organisms or tissues are translated into critical concentrations in water by means of a bioconcentration factor (BCF). The rationale behind using product standard concentrations is based on the assumption that concentrations, which are deemed acceptable for human consumptive purposes, will also provide protection to other aquatic organisms.

Axial muscle samples were collected bimonthly from February 1990 to February 1992 from different fish species at two sampling stations in the Olifants River (Fig. 1, Stations A and B) and one station in the Selati River (Fig. 1, Station C). Tissue samples were collected from *Oreochromis mossambicus* (Mozambique tilapia),

Labeo rosae (red-nosed mudfish), *Barbus marequensis* (large-scale yellowfish), *Clarias gariepinus* (African sharp-tooth catfish) and *Hydrocynus vittatus* (tigerfish - only at Station A). The large numbers of fish species sampled provided samples which are representative of different trophic positions in the ecosystem. The rationale behind the frequent sampling protocol over a two-year period was to provide bioaccumulation data during the different environmental conditions experienced during different seasons and flow conditions in the Olifants and Selati Rivers.

The tissue samples were prepared and analysed with a Varian AA Spectre-10 atomic absorption spectrometer. Du Preez and Steyn (1992) present a detailed description of the methods and techniques used in the preparation of tissue samples. Total copper and zinc concentrations in the axial muscle tissue were determined by standardised atomic absorption spectrophotometrical (AAS) techniques.

Water samples were also collected from these sampling stations and copper and zinc concentrations were measured. The BCF was calculated as the ratio of the chemical concentration in the muscle tissue to the total concentration in the surrounding water column (Hawker and Connell, 1991).

$$BCF = C_{org}/C_w \quad (1)$$

where:

$$\begin{aligned} BCF &= \text{bioconcentration factor } (\ell \cdot \text{kg}^{-1}) \\ C_{org} &= \text{content of chemical in organism } (\mu\text{g} \cdot \text{kg}^{-1}) \\ C_w &= \text{concentration of chemical in the water } (\mu\text{g} \cdot \ell^{-1}) \end{aligned}$$

Solids-water partition coefficient

The BCF's and toxic effect data were translated into critical concentrations in solids by using a solids-water partition coefficient. Solids-water coefficients (K_{sw}) were derived from field measurements of copper and zinc concentrations in water before and after filtration (Van der Kooij et al., 1991). Duplicate water samples and sediment samples were collected from the aforementioned sampling stations. A known volume (200 mL) of the first set of water samples was filtered through 0.45 µm filter paper (Singh et al., 1988). The filtrate was retained and 50 mL was transferred to an Erlenmeyer flask and acidified with 5 mL HNO₃ (analytical grade). The second set of unfiltered water samples were transferred to a 100 mL Erlenmeyer flask and acidified in the same manner as the filtered samples. The water samples were evaporated on a hotplate, reducing it to 2 mL. The samples were transferred to a 50 mL volumetric flask and carefully made up with doubly-distilled water. Sediment samples were collected from the same stations as water and tissue samples. Total metal extraction of 1 g (dry mass) sediment was performed with 55% HNO₃ and 70% HClO₄, and copper and zinc concentrations were determined by AAS.

According to Aiking and Bruggeman (1987) the concentrations of micropollutants in sediments differ systematically from concentrations in suspended solids in the water column above the sediments. The ratio of concentrations in the suspended matter to sediment (r) was obtained by calculating the concentration ratios of metal concentrations in the suspended phase (the difference between the total metal concentrations and the dissolved metal concentrations) and sediments from the Olifants and Selati Rivers as presented in Table 2. The dimensionless ratio (r) was substituted in Eqs. (5) and (8).

The K_{sw} values were calculated with the following equation:

$$K_{sw} = (C_{total} - C_{water}) / (SM \times C_{water}) \quad (2)$$

TABLE 2
MEAN CONCENTRATIONS OF COPPER AND ZINC MEASURED IN WATER AND SEDIMENT SAMPLES AND
THE CALCULATED SOLIDS-WATER PARTITIONING COEFFICIENT FROM SELECTED SITES IN THE OLIFANTS
AND SELATI RIVERS FROM FEBRUARY 1990 TO FEBRUARY 1992 (DATA AFTER SEYMORE ET AL.,
1994 AND WEPENER, 1997)

	Copper			Zinc		
	Balule	Mamba weir	Selati River	Balule	Mamba weir	Selati River
Total concentration in water ($\mu\text{g}\cdot\text{L}^{-1}$)	58.1	34.8	72.9	483.9	338.2	578.8
Dissolved concentration in water ($\mu\text{g}\cdot\text{L}^{-1}$)	18.9	16.4	16.3	101.4	74.2	35.8
Total concentration in sediments ($\text{mg}\cdot\text{kg}^{-1}$)	25.3	24.7	138.8	48.6	33.7	33.7
K_{sw} ($\text{L}\cdot\text{g}^{-1}$)	74.07	47.91	124.01	134.72	127.07	541.70

where:

- C_{total} = total concentration in the water before filtration ($\mu\text{g}\cdot\text{L}^{-1}$)
 C_{water} = concentration in the water phase after filtration ($\mu\text{g}\cdot\text{L}^{-1}$)
 SM = concentration of suspended matter ($\text{g}\cdot\text{L}^{-1}$)

The suspended matter concentration used in Eq. (2) was taken as the median value recorded for suspended matter concentrations measured monthly at Mamba Weir in the Olifants River during 1992 (Bauermann et al., 1995).

The following equations for determining quality criteria were taken from the equations proposed by Van der Kooij et al. (1991):

Toxic effect data

The South African water quality guideline value (CEV) was used as quality criterion for the chemical in the dissolved phase (Cr_{w}^1):

$$\text{Cr}_{\text{w}}^1 = \text{CEV} \quad (3)$$

The CEV-related criterion for total metal concentration (Cr_{tot}^1) in water was calculated as:

$$\text{Cr}_{\text{tot}}^1 = \text{Cr}_{\text{w}}^1 \times (1 + K_{\text{sw}} \times \text{SM}) \quad (4)$$

Finally the CEV-related criterion for metals in the sediment (Cr_{sed}^1) was calculated as:

$$\text{Cr}_{\text{sed}}^1 = (K_{\text{sw}} \times \text{Cr}_{\text{w}}^1) / r \quad (5)$$

The r-value was taken as the concentration ratio of suspended matter to sediment and is presented as a dimensionless value.

Product standard data

Starting from a product standard the criterion for dissolved metals (Cr_{w}^2) can be calculated by using the equation:

$$\text{Cr}_{\text{w}}^2 = C_{\text{org}} / \text{BCF} \quad (6)$$

The product-related criterion for total metals in water (Cr_{tot}^2) was calculated as:

$$\text{Cr}_{\text{tot}}^2 = C_{\text{org}} \times (1 + K_{\text{sw}} \times \text{SM}) / \text{BCF} \quad (7)$$

The product-related criterion (Cr_{sed}^2) for metals in the sediment was obtained by using:

$$\text{Cr}_{\text{sed}}^2 = (K_{\text{sw}} \times C_{\text{org}}) / r \times \text{BCF} \quad (8)$$

With both the CEV and product standards, quality criteria can be calculated. This procedure yields two sets of criteria for each chemical.

Results and discussion with sample calculations

Toxic effect and product standard values

The water quality guidelines (CEV values) for copper and zinc are 0.8 and $2 \mu\text{g}\cdot\text{L}^{-1}$ respectively (DWAF, 1996). The product standard for maximum allowable concentrations of metals in fish tissue for consumption in South Africa is

reported as $30 \mu\text{g}\cdot\text{kg}^{-1}$ and $40 \mu\text{g}\cdot\text{kg}^{-1}$ for copper and zinc respectively (Verheul, 1992).

The copper and zinc BCFs for fish species at the different sampling stations are presented in Table 3. It was noticeable that the copper BCFs in substrate feeding fish (i.e. *L. rosae* and *O. mossambicus*) and to a lesser extent *C. gariepinus*, were much higher (>200) than the BCFs in *B. marequensis* and *H. vittatus*. The zinc BCFs in *C. gariepinus* and *B. marequensis* were higher than those reported for the other species. A comparison with other results from systems in South Africa revealed that zinc BCFs were similar to those reported in fish tissue from the upper Olifants River catchment, Crocodile Rivers and the Elsburg and Natalspruit wetland systems. However, the BCFs from the Southern African systems were far less than BCFs reported for fish (*C. commersoni*) from metal-polluted lakes in Canada. Copper BCFs from the Olifants River system (including Loskop Dam) were higher than values recorded in fish from the industrial and sewage polluted Elsburg and Natalspruit wetland. They were, however, similar to BCFs recorded in fish tissue from metal-contaminated lakes in Canada (Miller et al., 1992).

The BCFs for biota reported in the literature for copper and zinc display a wide range from <100 to 50 000 (USEPA, 1979; USEPA, 1980; Mance and Yates, 1984). The majority of the BCF values for fish is in the lower range of <100 to 1 000. According to Taylor (1983) the bioaccumulation potential of chemicals in fish varies from insignificant (<100) to highly significant (>1 000).

The results from this study supported the findings by Taylor (1983) that BCFs for copper and zinc decrease with increasing trophic level (i.e. high BCFs in *L. rosae* - a substrate feeder and low BCFs in *H. vittatus* - a piscivorous feeder). In order to obtain an integrated BCF value for all trophic levels the geometric mean for all the species was taken for each BCF. This is in accordance with the methodologies adopted by Van der Kooij et al. (1991) for cadmium BCFs.

Solids-water partition coefficient

The solids-water partition coefficients, water and sediment concentrations for copper and zinc are presented in Table 2. The bi-monthly metal concentrations on which the concentrations used for the calculations in this study were based, as well as the physico-chemical conditions during each sampling survey are presented elsewhere (Seymore et al., 1994). The K_{sw} values for both copper

Species and reference	Sampling site	Copper	Zinc
<i>Oreochromis mossambicus</i> (Wepener, 1997)	Balule	102	38
	Mamba Weir	155	44
	Selati River	949	35
<i>Labeo rosae</i> (Wepener, 1997)	Balule	250	69
	Mamba Weir	403	63
	Selati River	207	50
<i>Barbus marequensis</i> (Van Vuren et al., 1994)	Balule	103	142
	Mamba Weir	158	164
	Selati River	85	120
<i>Clarias gariepinus</i> (Maartens, 1994) (Du Preez et al., 1997)	Balule	61	117
	Mamba Weir	75	189
	Selati River	52	182
<i>Hydrocynus vittatus</i> (Du Preez and Steyn, 1992)	Balule	36	14
<i>Oreochromis mossambicus</i> (Grobler et al., 1994)	Phalaborwa Barrage		43
<i>Schilbe intermedius</i> (Grobler et al., 1994)	Phalaborwa Barrage		82
	Loskop Dam		50
Freshwater fish (Roux et al., 1994)	Crocodile River		70
<i>Oreochromis mossambicus</i> (Kotze et al., 1999)	Loskop Dam	430	43
<i>Barbus aeneus</i>	Natalspruit wetland	22	67
<i>Labeo umbratus</i>		35	53
<i>Clarias gariepinus</i> (Van Eeden, 1990)		20	76
<i>Catostomus commersoni</i> (Miller et al., 1992)	Metal-contaminated lakes in Canada	172	410

	Copper	Zinc
K_{sw} ($\ell \cdot g^{-1}$)	74.04	130.9
BCF ($\ell \cdot kg^{-1}$)	103	69
C_{org} ($\mu g \cdot kg^{-1}$)	30	40
SM ($mg \cdot \ell^{-1}$)	0.028	0.028
CEV ($\mu g \cdot \ell^{-1}$)	0.8	2
r	1.5	1.5 ¹
K_{sw}	Solids-water partition coefficient	
BCF	Bioconcentration factor	
C_{org}	Product standard concentration value	
SM	Concentration in suspended matter	
CEV	SA water quality guideline-related toxic effect concentration	
r:	Suspended matter to sediment concentration ratio.	
¹	See discussion text for reason why calculated value was not used.	

product standards were used for the calculations. Since very limited field data were available, the lowest concentration ratio suspended matter: sediment (r) was selected for calculating the criterion values. This was done to limit the influence of site-specific conditions on the data (i.e. the extremely high r-value of 7.9 found in the Olifants River system). A single r-value for inorganic chemicals can only be refined once more data on suspended matter and sediment concentrations are available for South African systems. For the purposes of calculating criterion values the r-value for copper, i.e. 1.5 was used. This was in accordance with r-values reported for inorganic chemicals in the Netherlands (Van der Kooij et al., 1991).

In order to illustrate the above-mentioned approaches an example for copper at Balule is presented. The calculated criterion values for copper and zinc are summarised in Table 5.

and zinc were highest for the Selati River and the Balule station in the Olifants River. Furthermore, K_{sw} values for zinc were greater than those for copper at all the stations sampled. The great variation in K_{sw} values are a product of the different physico-chemical factors, e.g. pH, dissolved oxygen, salinity, etc. experienced at the three sampling sites used in this study. The solids-water partition coefficients were a similar order of magnitude to those reported for copper and zinc in Dutch rivers (Van der Kooij et al., 1991). For the purposes of calculating the criterion values, a single K_{sw} value was used for copper and zinc. In accordance with the methodologies used by Van der Kooij et al. (1991) the K_{sw} values for the individual metals were obtained by calculating the median of the available K_{sw} values for surface waters (Table 4). It must be borne in mind that the K_{sw} values are based only on the results from two rivers and would change as water quality from more systems are added.

The field data obtained during this study were substituted into the equations and both types of effects i.e. the toxic effect and

Example: Copper

Starting with the direct toxic effect data

As quality criterion in the dissolved phase the water quality guideline value (CEV) is used:

$$\begin{aligned} Cr_w^l &= CEV \\ &= 0.8 \mu g \cdot \ell^{-1} \end{aligned}$$

By using Eq. (4) the CEV-related criterion for total copper concentration in water is calculated as follows:

$$\begin{aligned} Cr_{tot}^l &= Cr_w^l \times (1 + K_{sw} \times SM) \\ &= 0.8 \mu g \cdot \ell^{-1} \times (1 + 74.04 \ell \cdot g^{-1} \times 0.028 g \cdot \ell^{-1}) \\ &= 2.46 \mu g \cdot \ell^{-1} \end{aligned}$$

The CEV-related criterion for total copper in sediment was calculated using Eq. (5).

TABLE 5 COPPER AND ZINC QUALITY CRITERIA FOR TOTAL, DISSOLVED AND SEDIMENT CONCENTRATIONS USING THE PHYSICO-CHEMICAL AND BIOLOGICAL DATA FROM THE OLIFANTS AND SELATI RIVERS AS AN EXAMPLE				
	Copper		Zinc	
	Cr ¹	Cr ²	Cr ¹	Cr ²
Cr _w (µg·l ⁻¹)	0.8	0.29	2	0.58
Cr _{tot} (µg·l ⁻¹)	2.46	0.9	9.33	2.7
Cr _{sed} (µg·g ⁻¹)	39.49	14.38	174.53	50.59
Cr _w	Concentration in dissolved phase			
Cr ¹	Toxic effect-derived quality data			
Cr _{tot}	Total concentration			
Cr ²	Product standard-derived quality data			
Cr _{sed}	Concentration in sediment			

$$\begin{aligned} Cr_{sed}^1 &= (K_{sw} \times Cr_w^1) / r \\ &= (74.04 \text{ } \ell \cdot \text{g}^{-1} \times 0.8 \text{ } \mu\text{g} \cdot \text{l}^{-1}) / 1.5 \\ &= 39.5 \text{ } \mu\text{g} \cdot \text{g}^{-1} \end{aligned}$$

Starting with the product standard

Starting from the product standard for copper the criterion for dissolved copper can be calculated using Eq. (6):

$$\begin{aligned} Cr_w^2 &= C_{org} / BCF \\ &= 30 \text{ } \mu\text{g} \cdot \text{g}^{-1} / 103.9 \text{ } \ell \cdot \text{g}^{-1} \\ &= 0.29 \text{ } \mu\text{g} \cdot \text{l}^{-1} \end{aligned}$$

The product standard related criterion for total concentration of copper in water has been calculated using Eq. (7):

$$\begin{aligned} Cr_{tot}^2 &= C_{org} \times (1 + K_{sw} \times SM) / BCF \\ &= 30 \text{ } \mu\text{g} \cdot \text{g}^{-1} \times (1 + 74.04 \text{ } \ell \cdot \text{g}^{-1} \times 0.028 \text{ } \text{g} \cdot \text{l}^{-1}) / 103.9 \text{ } \ell \cdot \text{g}^{-1} \\ &= 0.9 \text{ } \mu\text{g} \cdot \text{l}^{-1} \end{aligned}$$

Finally the product-related criterion for copper in sediment has been obtained using Eq. (8):

$$\begin{aligned} Cr_{sed}^2 &= (K_{sw} \times C_{org}) / r \times BCF \\ &= 74.04 \text{ } \ell \cdot \text{g}^{-1} \times 30 \text{ } \mu\text{g} \cdot \text{g}^{-1} / 1.5 \times 103.9 \text{ } \ell \cdot \text{g}^{-1} \\ &= 14.38 \text{ } \mu\text{g} \cdot \text{g}^{-1} \end{aligned}$$

Although two types of effects were used to derive criteria, only one criterion per substance can be used. According to Van der Kooij et al. (1991) the definite criterion is obtained by choosing the lowest value. The results from this study indicated that the product standard-based criteria produced the lowest values. However, for the purposes of this demonstration in criteria development the product standard-based criteria were discounted. The reason for this being that the South African product standard concentration for copper and zinc for fish consumption is deemed unrealistically low. This is seen against the background of the Netherlands cadmium product standard for fish consumption (Van der Kooij et al., 1991), which is higher than the South African standards for copper and zinc (*viz.* 50 µg·kg⁻¹ against 30 µg·kg⁻¹ and 40 µg·kg⁻¹ respectively). This does not mean that product standard-derived criteria are unsuitable for future use. A revision of the South African metal product standards for fish consumption to more realistic values in

line with international standards could make this method applicable. By way of example, if the product standards for copper and zinc were to increase to more realistic concentrations of 80 µg·kg⁻¹ and 120 µg·kg⁻¹ the criterion values for sediment would change to 38.3 µg·g⁻¹ and 151.8 µg·g⁻¹ respectively. These criterion values are in close agreement with the toxic effect-based criteria. Similarly the dissolved- and total water concentration criteria would approximate the toxic effect-based criteria. For the purposes of the rest of this discussion the toxic effect-based criteria are used.

The toxic effect-based quality criteria derived for copper and zinc in the dissolved phase are in line with criteria from other countries (Table 6). The copper and zinc criteria values obtained for total metal concentrations (dissolved and in the particulate phase) were less stringent than the water quality criteria for dissolved concentrations but still remained within the same range as criteria for other countries (Table 6). Due to the lack of toxicological data, environmental quality criteria for sediment and suspended matter are derived from water quality standards (Van Den Hoop, 1993). This is achieved by multiplying the water quality standard with an EP coefficient. The toxic effect-derived sediment quality criteria for copper (39.5 µg·g⁻¹) and zinc (174.5 µg·g⁻¹), obtained in this study, were very similar to the Netherlands sediment quality standards (Cu - 36 and Zn - 140 µg·g⁻¹ respectively). The sediment quality criteria are also similar to USA sediment quality criteria, i.e. 34 µg·g⁻¹ Cu and 150 µg·g⁻¹ Zn (OSWER, 1996). The USA sediment criteria were also derived using the EP approach.

The EP method discussed in this paper demonstrated how it is possible to make use of two types of criteria to successfully derive quality criteria for water and sediment. However, it is essential that the disadvantages of using this methodology be borne in mind. Significant complexities are associated with inorganic chemicals when using the EP approach. Uptake (and therefore effects) of sediment-associated contaminants is largely a function of bioavailability. Bioavailability is strongly influenced by a complex suite of physical, chemical and biological factors in the sediments. Trace metals can be adsorbed at particle surfaces, bound to carbonates, occluded in iron and/or manganese oxyhydroxides, bound to organic matter, bound to sulphide, bound to a matrix, or dissolved in the interstitial water. The complexity of trace metal bioavailability associated with these phases hinders the prediction of effects (Campbell and Tessier, 1991).

Conclusions

The use of the EP method for setting quality criteria was implemented with success in the Netherlands (Van der Kooij et al., 1991) and the results obtained from this study indicated that this method has merit for deriving quality criteria in South Africa. However, at this stage the database for metal concentrations in the different water phases is very limited. Although the methodology presented in this paper is aimed at setting generic quality criteria, the data used were limited almost exclusively from the Olifants River during 1990 to 1992 as this was the only suitable available data. By including the analysis of metals in the different water phases in future water quality monitoring programmes and obtaining data on a more frequent basis, quality criteria could be refined to greater degree.

It was not possible to evaluate the product standard-based criteria objectively due to the low standard concentrations for copper and zinc. It is therefore essential that the current South African product standard concentrations for metals in fish for human consumption be reassessed.

<p style="text-align: center;">TABLE 6 QUALITY CRITERIA FOR DISSOLVED WATER AND TOTAL SEDIMENT QUALITY CRITERIA FOR COPPER AND ZINC CONCENTRATIONS AS OBTAINED IN THIS STUDY COMPARED WITH OTHER CRITERIA VALUES. DISSOLVED CONCENTRATIONS IN WATER AND TOTAL SEDIMENT CONCENTRATIONS ARE PRESENTED IN $\mu\text{g}\cdot\text{L}^{-1}$ AND $\text{mg}\cdot\text{kg}^{-1}$ RESPECTIVELY.</p>			
Criteria	Copper	Zinc	References
<i>Dissolved concentration in water</i>			
This study (dissolved; total)	0.8; 2.5	2; 9.3	This study
South Africa	0.8	2	DWAF, 1996
Australia	10	100	Hart, 1974
Canada	4	30	Environment Canada, 1987
Netherlands	3	4.9	Cappon, 1991 & Janus, 1993
United Kingdom	1-28	8-125	Gardiner and Zabel, 1989
<i>Total concentration in sediment</i>			
This study	39.5	174.5	This study
South Africa	100	185	Department of National Health and Population Development, 1991
Australia/New Zealand	60	200	Australian and New Zealand Guidelines for the Assessment and Management of Contaminated Sites, 1992
Germany	60	200	Töpfer, 1992
Netherlands	36	140	Slooff et al., 1989 & Janus, 1993
United Kingdom	135	300	Omex Environmental Ltd., 1990
United States of America	34	150	OSWER, 1996
Switzerland	50	200	Webster et al., 1994

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