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## The chemical behaviour of heavy metals and their bioavailability and toxicity to organisms: implications for environmental quality criteria

P.J. Pretorius<sup>a\*</sup>, P.W. Linder<sup>b</sup>, J.L. Slabbert<sup>c</sup> and P.W. Wade<sup>c</sup>

Observed mortalities of *Daphnia pulex* exposed to a single concentration of zinc in different test waters are explained in terms of the chemical behaviour of zinc in solution, as predicted by chemical speciation modelling. Multivariate correlation analysis indicates that the hydrated zinc species,  $Zn^{2+}$ , was primarily responsible for the observed *Daphnia* mortality. Although this method provides useful results in a well-defined laboratory setting, its application to field conditions proves to be less certain because of our incomplete understanding of processes affecting metal speciation in complex natural systems. These results indicate that metal bioavailability should be accounted for in the management of metal discharges into the natural environment.

### Introduction

Environmental quality criteria or standards are the primary benchmarks against which environmental pollution is measured.<sup>1</sup> Currently, it is common practice to express these criteria in terms of total metal concentration.<sup>17</sup> It has been observed that in certain instances, however, metal concentrations in the environment exceed the value prescribed by these criteria without any adverse effects on ecosystems,<sup>2</sup> suggesting that total metal concentration in an environmental compart-

ment such as water, soil or sediments is not a good predictor of its potential biological effects.<sup>3</sup>

The bioavailability and toxicity of metals are related to their chemical behaviour, or *chemical speciation*, in aquatic systems.<sup>4–8</sup> Thus, only certain chemical forms of a metal may be available for uptake by an organism. Because of this, much effort is concerned with the incorporation of data on metal bioavailability in environmental quality criteria.<sup>9,10,12</sup> For these efforts to succeed, information on the identities of bioavailable/toxic metal species, and the toxic response of organisms in terms of these metals, are required. Furthermore, methods that allow the concentration of toxic species to be reliably predicted in the natural environment should be available to both regulators and industry. Several techniques are available for the description of metal speciation in aqueous solutions.<sup>11</sup> Of these, only the mathematical modelling of chemical speciation lends itself for predictive purposes. This technique is based on fundamental thermodynamic principles and the only site-specific data required are pH and concentrations of cations (which include metals) and anions, or ligands. For soils and sediments, potential sorption phases, such as hydrous ferric oxide (HFO), manganese dioxide ( $MnO_2$ ) and natural organic matter (NOM) have to be identified and quantified.

This paper illustrates the dependence of zinc toxicity on metal speciation in aqueous solutions by combining results from bioassays and chemical speciation calculations. Problems associated with the prediction of metal speciation in natural systems are illustrated using soil data collected in The Netherlands.

### Method

**Toxicity tests.** Bioassays were carried out, using *Daphnia pulex* mortality as endpoint, in very soft, soft and hard waters.<sup>16</sup> Test organisms were exposed to a total zinc concentration of  $0.5 \text{ mg dm}^{-3}$  in solutions buffered with N-2-hydroxyethyl-piperazine-N'-2-ethansulphonic acid (HEPES). Zinc was added as zinc chloride (Saarchem). Tests were carried out in triplicate for each water type using five individuals of *Daphnia* per test vessel. Control tests were also carried out for each water type. Mortality was recorded after 48 h and expressed as percentage mortality. Solution pH was monitored at the start of each test and at 24-h intervals after that. pH measurements were taken with a Beckman pH meter and electrode. The electrode was calibrated against standard buffer solutions.

**Chemical speciation.** Zinc speciation in each of the test solutions was calculated using the MINTQA2 speciation package.<sup>20</sup> In simulating the buffered solutions, pH was set at the negative logarithm of the average hydrogen ion concentration observed

<sup>a</sup>Division of Water, Environment and Forestry Technology, CSIR, P.O. Box 320, Stellenbosch, 7599 South Africa.

<sup>b</sup>Department of Chemistry, University of Cape Town, Private Bag, Rondebosch, 7701 South Africa.

<sup>c</sup>Division of Water, Environment and Forestry Technology, CSIR, P.O. Box 395, Pretoria, 0001.

\*Author for correspondence. Present address: Water and Environmental Technology, Sasol Technology, P.O. Box 1, Sasolburg, 1947 South Africa.  
E-mail: julius.pretorius@sasol.com

throughout the bioassays (very soft, 6.67; soft, 6.83; hard, 7.40). Component concentrations in the simulations were taken as nominal concentrations instead of analytically determined values.

**Identification of toxic zinc species.** Percentage mortality observed in the various tests was related to the corresponding zinc speciation by multivariate correlation and linear regression analysis, using STATGRAPHICS version 6.1 (Statistical Graphics Corporation).

Test results from the three experiments were pooled and the correlation coefficients were determined.

**Metal partitioning in soils.** The partitioning of Ni, Cu, Zn, Cd and Pb in Dutch soils, as determined by van den Hoop<sup>14</sup> and Janssen *et al.*,<sup>15</sup> was simulated using MINTEQA2.<sup>20</sup> Detailed sampling and analysis procedures are described in Janssen *et al.*<sup>15</sup> The soil solid phase was characterized in terms of amorphous hydrous ferric oxide and aluminium hydroxides using an ammonium oxalate-oxalic acid extraction. Total metal concentrations in the soil solid phase was determined from concentrated nitric acid digestions. Pore water was collected by centrifugation.

Processes accounted for in the equilibrium model were adsorption, precipitation, and metal complexation by both inorganic ligands and natural organic matter. Adsorption phases included in the simulations were hydrous ferric oxide and manganese dioxide ( $\delta$ -MnO<sub>2</sub>). Manganese dioxide concentration was estimated as 2% of the HFO concentration.<sup>21</sup> Adsorption was described according to the surface complexation approach in conjunction with the diffuse double-layer model of the solid/solution interface.<sup>27</sup> Adsorption constants for HFO were obtained from Dzombak and Morel<sup>22</sup> and those for  $\delta$ -MnO<sub>2</sub> from Pretorius and Linder.<sup>13</sup> Metal complexation properties of dissolved organic matter (DOM) were simulated using the RANDOM model.<sup>23-25</sup> Redox processes were excluded from the model because no estimates of redox potential were available.

## Results and discussion

Observed mortalities are shown in Table 1. The effect of the different water types on zinc toxicity is clearly illustrated by the decrease in mortality observed with increasing water hardness. A coefficient of variability of less than 20% was found for all tests. The results indicate that, for the same quantity of zinc (0.5 mg dm<sup>-3</sup>), very different toxicity responses were obtained. An approximately five-fold difference was observed for mortalities in the very soft and hard waters.

The concentrations and identities of zinc species in the various

**Table 1.** *Daphnia* mortality (%) observed after 48 h exposure to 0.5 mg/l zinc in water of different hardness.

Test number	Very soft	Soft	Hard
TB1	85	65	15
TB2	100	85	20
TB3	95	90	25
Average	93 ± 6	80 ± 10	20 ± 4

**Table 3.** Correlation coefficients obtained for zinc species and mortality in solutions buffered with HEPPES, using 0.5 mg/l total zinc. Test data were combined (n = 9).

Species	Correlation coefficients [significance level] All tests (n = 9)
Zn <sup>2+</sup>	0.97 [0.0000]
ZnCl <sup>+</sup>	-0.94 [0.0002]
ZnCl <sub>2</sub>	-0.97 [0.0000]
ZnCl <sub>3</sub> <sup>-</sup>	-0.97 [0.0000]
ZnCl <sub>4</sub> <sup>2-</sup>	-0.96 [0.0000]
ZnOH <sup>+</sup>	-0.97 [0.0000]
Zn(OH) <sub>2</sub>	-0.97 [0.0000]
Zn(OH) <sub>3</sub> <sup>-</sup>	-0.96 [0.0000]
Zn(OH) <sub>4</sub> <sup>2-</sup>	-0.96 [0.0000]
ZnOHCl	-0.96 [0.0000]
ZnSO <sub>4</sub>	-0.97 [0.0108]
Zn(SO <sub>4</sub> ) <sub>2</sub> <sup>2-</sup>	-0.93 [0.0003]
ZnCO <sub>3</sub>	-0.96 [0.0000]
ZnHCO <sub>3</sub> <sup>+</sup>	-0.97 [0.0000]
Zn(CO <sub>3</sub> ) <sub>2</sub> <sup>2-</sup>	-0.96 [0.0000]

solutions are listed in Table 2. Also listed are the equilibrium constants used in the calculations. The following trends were observed: hydrated zinc concentration, [Zn<sup>2+</sup>], decreased from the very soft water to the hard water. At the same time, concentrations of all other zinc species increased from the very soft water to the hard water. This observed trend for Zn<sup>2+</sup> concentration corresponds qualitatively with that observed for organism mortality.

The correlation coefficients and corresponding significance levels for the correlation analysis are shown in Table 3. All correlations are significant at the 95% confidence level. Results indicate that the hydrated (or free) zinc species, Zn<sup>2+</sup>, was responsible for the observed mortality. This was the only zinc species positively correlated with observed mortality data. All

**Table 2.** Zinc speciation in the test solutions, as calculated using MINTEQA2, together with the equilibrium constants employed in the calculations.

Species	Log β I = 0; T = 25°C	Species concentration (mol dm <sup>-3</sup> )		
		Very soft	Soft	Hard
Zn <sup>2+</sup>	-	7.360 × 10 <sup>-6</sup>	6.753 × 10 <sup>-6</sup>	3.102 × 10 <sup>-6</sup>
ZnCl <sup>+</sup>	0.43	3.911 × 10 <sup>-10</sup>	6.223 × 10 <sup>-10</sup>	9.293 × 10 <sup>-10</sup>
ZnCl <sub>2</sub>	0.45	8.536 × 10 <sup>-15</sup>	2.473 × 10 <sup>-14</sup>	1.083 × 10 <sup>-13</sup>
ZnCl <sub>3</sub> <sup>-</sup>	0.50	2.108 × 10 <sup>-19</sup>	1.168 × 10 <sup>-18</sup>	1.353 × 10 <sup>-17</sup>
ZnCl <sub>4</sub> <sup>2-</sup>	0.20	2.450 × 10 <sup>-24</sup>	2.726 × 10 <sup>-23</sup>	7.532 × 10 <sup>-22</sup>
ZnOH <sup>+</sup>	-8.96	3.479 × 10 <sup>-8</sup>	4.288 × 10 <sup>-8</sup>	8.541 × 10 <sup>-8</sup>
Zn(OH) <sub>2</sub>	-16.89	1.822 × 10 <sup>-9</sup>	3.167 × 10 <sup>-9</sup>	2.469 × 10 <sup>-8</sup>
Zn(OH) <sub>3</sub> <sup>-</sup>	-28.39	2.770 × 10 <sup>-14</sup>	7.132 × 10 <sup>-14</sup>	1.961 × 10 <sup>-12</sup>
Zn(OH) <sub>4</sub> <sup>2-</sup>	-41.20	2.228 × 10 <sup>-20</sup>	8.922 × 10 <sup>-20</sup>	7.804 × 10 <sup>-18</sup>
ZnOHCl	-7.48	2.190 × 10 <sup>-11</sup>	4.913 × 10 <sup>-11</sup>	2.871 × 10 <sup>-10</sup>
ZnSO <sub>4</sub>	2.37	1.446 × 10 <sup>-7</sup>	4.214 × 10 <sup>-7</sup>	7.386 × 10 <sup>-7</sup>
Zn(SO <sub>4</sub> ) <sub>2</sub> <sup>2-</sup>	3.28	1.224 × 10 <sup>-10</sup>	1.379 × 10 <sup>-9</sup>	6.099 × 10 <sup>-9</sup>
ZnHCO <sub>3</sub> <sup>+</sup>	12.40	7.555 × 10 <sup>-8</sup>	2.793 × 10 <sup>-7</sup>	6.906 × 10 <sup>-7</sup>
ZnCO <sub>3</sub>	5.30	2.731 × 10 <sup>-8</sup>	1.424 × 10 <sup>-7</sup>	1.378 × 10 <sup>-6</sup>
Zn(CO <sub>3</sub> ) <sub>2</sub> <sup>2-</sup>	9.63	1.350 × 10 <sup>-11</sup>	4.866 × 10 <sup>-10</sup>	6.559 × 10 <sup>-8</sup>

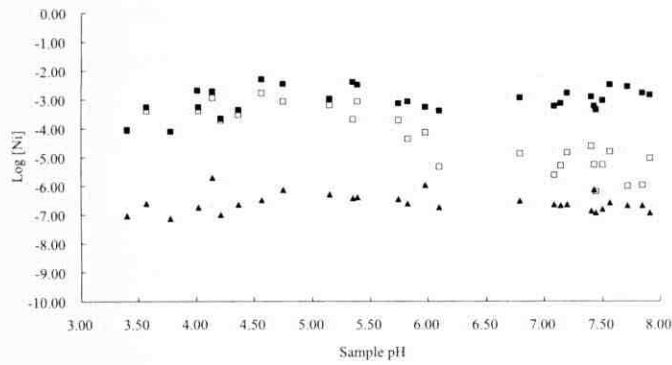


Fig. 1. Comparison between observed (▲) and calculated (□) pore water concentrations for nickel. Also shown is total nickel concentration observed in the soil (■).

other zinc species were strongly negatively correlated with observed mortality, which suggest that they were not responsible for the observed toxicity.

These observations may be explained by viewing metal uptake as a chemical reaction occurring at an active site on the organism's surface.<sup>4,19</sup> The site responsible for uptake may be treated as a ligand, S, competing for available metal with other ligands in the system. The concentration of the ligands  $\text{CO}_3^{2-}$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  increases from the very soft to the hard water. At the same time, [S] remains constant. This diminishes the role of S as a ligand due to competition for available metal. The nett result is lower levels of metal being assimilated by the organism.

The fact that solution conditions, in this case pH and inorganic ligand concentration, were able to modify zinc toxicity greatly, argues against using one single value for the protection of all waters. The toxicity tests were carried out in solutions containing far fewer modifiers of the aqueous chemistry of zinc than commonly found in natural waters. Natural waters contain varying amounts of dissolved organic matter, inorganic ligands such as  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{3-}$  and suspended matter consisting of the oxyhydroxides of Fe, Al and Mn, as well as clay minerals. Ligands such as DOM, which consist mainly of humic and fulvic compounds, are strong metal complexing agents in natural systems.<sup>18</sup> Suspended particles also adsorb metals strongly.<sup>27</sup> Both DOM and suspended particles are therefore important modifiers of metal bioavailability and toxicity in natural systems. These factors should be taken into account in any water quality management plan aimed at regulating the discharge of metals containing effluents.

How well can we predict the amount of bioavailable metal species in the environment? Results presented above suggest that equilibrium modelling provides a useful means for predict-

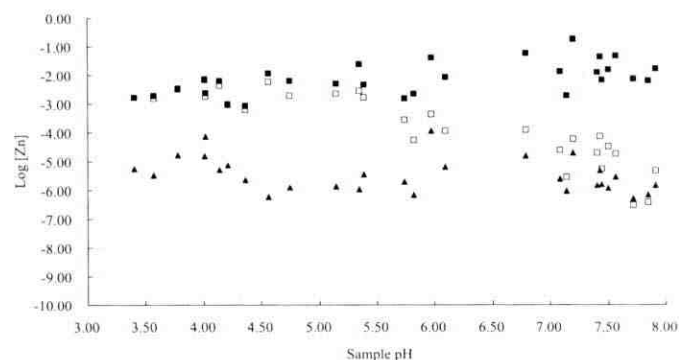


Fig. 3. Comparison of observed (▲) and calculated (□) pore water concentrations for zinc. Also shown is total zinc concentration observed in the soil (■).

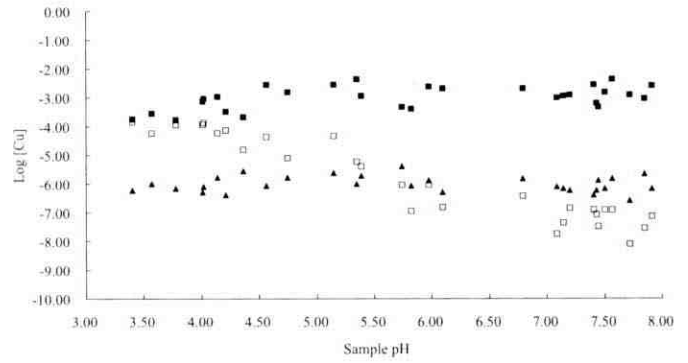


Fig. 2. Comparison of observed (▲) and calculated (□) pore water concentrations for copper. Also shown is total copper observed in the soil (■).

ing the concentration of bioavailable metal species in aqueous systems. It should, however, be kept in mind that these results were obtained using well-defined laboratory conditions. Predicting metal speciation in the natural environment is complicated by the presence of DOM and particulate phases. The results obtainable using current knowledge may be illustrated by considering the conceptually simple problem of metal partitioning at the solid/solution interface in soils.

Predicted metal partitioning in the soils sampled is compared with observed partitioning in Figs 1–5, which show the logarithm of metal concentration in both the pore water and soil solid phase as a function of pore water pH observed for the various soil samples. Of importance to this discussion is the agreement of measured and predicted pore water concentrations. It is evident that the model predicts metal partitioning in the different samples with a variable degree of success. In general, partitioning is best predicted for (a) lead (Fig. 5) and copper (Fig. 2) in all samples and (b) samples with pH greater than 6 for all metals.

A number of reasons may be advanced for the observed discrepancy between observed and calculated pore water concentrations. These pertain to both the model and experimental data employed. The most obvious weakness in the model is the number of adsorption phases considered — only HFO and  $\delta\text{-MnO}_2$  were included. Humic material associated with the soil solid phase was not considered. These compounds are known to adsorb strongly onto mineral surfaces, such as HFO, at low pH.<sup>28–30</sup> Because of this, the surface properties and hence adsorption properties of the minerals are modified.<sup>26</sup> Spark *et al.*<sup>26</sup> found that metal adsorption in oxide–humic systems are enhanced compared to those consisting of only the oxide as sorbent. The soils modelled here had significant levels of organic material

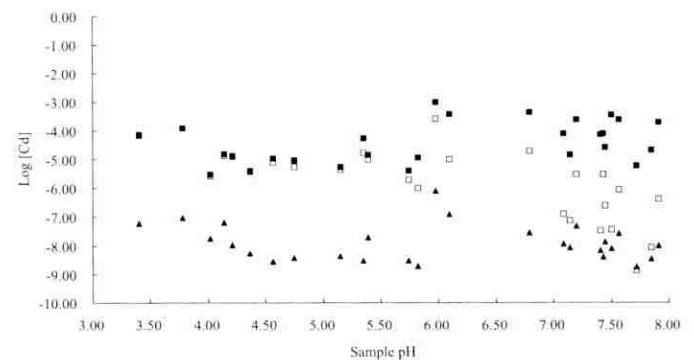


Fig. 4. Comparison of observed (▲) and calculated (□) pore water concentrations for cadmium. Also shown is total cadmium concentration observed in the soil (■).

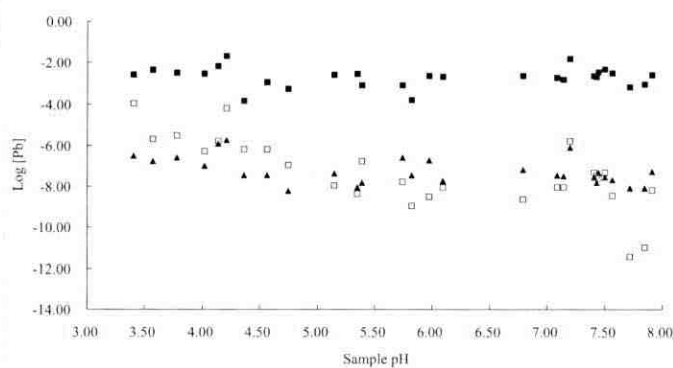


Fig. 5. Comparison of observed (▲) and calculated (□) pore water concentrations for lead. Also shown is total lead concentration observed in the soil (■).

associated with the solid phase (3–22% on a dry weight basis). It is thus postulated that the discrepancy between model and experimental observations in the low pH region is due mainly to an incomplete model.

Incorporation of metal sorption by adsorbed humic compounds into an equilibrium model in a general manner presents a number of problems. These are related to the lack of thermodynamic data describing the adsorption of humic compounds by particulate matter. This implies that, although promising results have been obtained using an *a priori* approach for the prediction of metal speciation in aqueous systems, work is still needed to solve a number of fundamental problems. This, however, does not preclude the application of the principles of bioavailability to metal quality criteria, or any effort aimed at regulating metal discharges into the environment. Recent advances<sup>31,32</sup> in the application of semi-empirical approaches have been made and encouraging results obtained. These methods can be used while research continues into the fundamental processes affecting metal bioavailability and toxicity.

## Conclusion

Results from toxicity tests indicate that the biological effect of metals on organisms in aquatic systems is modified by metal speciation, which, in turn, is influenced by solution conditions, such as the nature and concentration of both organic and inorganic ligands and pH. These observations argue against the use of a single, universally applicable criterion expressed in terms of total metal concentration. Rather, metal quality criteria should be based on the bioavailable metal fraction. This, however, requires methods for predicting bioavailable concentrations in natural systems. Chemical equilibrium modelling may be used for this purpose. However, while it is possible to predict the chemical speciation of metals in well-defined laboratory systems, there are factors that complicate the use of this technique under field conditions. These factors are related mainly to a lack of data describing certain key processes, which underscores our limited knowledge and understanding of crucial processes influencing the bioavailability and toxicity of metals in natural systems.

In cases where discharges violate proposed environmental criteria for metals, affected parties should therefore insist on the implementation of site-specific criteria which take into account the modifying influence of environmental conditions on metal toxicity and bioavailability. Furthermore, the relationship between metal toxicity and chemical speciation should be accounted for in any water quality management plan aimed at regulating the discharge of metal-containing effluents.

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