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Prediction of *In Situ* Trace Metal Distribution Coefficients for Suspended Solids in Natural Waters

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Metal distribution coefficients (K_D) are used in fate models and environmental impact assessment. Typically they are entered as constants, whereas variations in environmental conditions affect their magnitude. Therefore, a model that expresses K_D for suspended solids as a function of aqueous and solid phase characteristics was developed. The model estimates K_D values from easy-to-measure water quality variables and accounts for (a) surface complexation of metal species to the major phases comprising suspended solids, (b) metal complexation by dissolved ligands, (c) competition by major cations, and (d) electrostatic effects. Most of the model parameters were derived from the literature and fixed. A few parameters for which K_D was most sensitive were calibrated on field K_D values for stagnant waters in The Netherlands. The estimated parameters were well within the literature ranges. The model was capable of explaining 75% (Zn) and 95% (Cu) of the observed variability of K_D . We conclude that laboratory constants for surface and aqueous phase complexation are useful for predicting Zn and Cu sorption to suspended solids in natural waters.

Introduction

Distribution coefficients (K_D) are important parameters in fate models or risk assessment procedures as they describe the speciation over adsorbed and dissolved states. In the current practice of metal fate modeling in the aquatic environment, several problems may be identified. First, K_D values are entered as metal-specific constants or are estimated empirically using a limited set of solid and solution characteristics (e.g., pH, salinity, CEC, total dissolved solids, etc.) (1–6). Empirical descriptors like CEC or salinity represent many interactions that are not individually taken into account. Therefore, the parameters in empirical models are conditional and model dependent (1, 7–11). This limits their applicability in natural waters where other conditions prevail. The problem may be solved by coupling speciation models with surface complexation models (SCM) (10, 12). These models represent the state-of-the-art in the modeling of metal adsorption. However, sorption studies employing the SCM usually focus on a simple electrolyte solution or on a single solid phase, usually an oxide (13, 14) or treat the natural sediment as a single phase (11, 15). Only a few of them treat the adsorption on natural particles as a process of partitioning among a number of discrete phases (1, 7–9).

In the majority of studies, the data are obtained from laboratory sorption tests that limit the translatability to the natural environment. To our knowledge, no earlier studies applied the concepts of competitive surface complexation to predict *in situ* K_D values for suspended solids.

In this study a conceptual K_D model (SWAMP, Sediment Water Algorithm for Metal Partitioning) has been developed. The model expresses K_D as a function of aqueous and solid phase characteristics. The model uses the concept of additivity of discrete-site binding of free and complexed metal to solid phases, accounts for electrostatic effects and competitive adsorption, and includes aqueous phase complexation. Following Tessier *et al.* (10), our main objective is to reduce the gap between the detailed concepts of chemical speciation and the practice of metal fate modeling in natural systems. Therefore, the input variables were restricted to those usually available from routine water quality monitoring programs. The model was tested and calibrated on *in situ* trace metal K_D values for suspended solids in several surface waters in the Netherlands.

Model Description

The distribution of trace metals between particles and solution in aquatic environments is quantified by a distribution coefficient, K_D (L kg⁻¹):

$$K_D = \frac{C_s}{C_w} \quad (1)$$

where C_s (mol kg⁻¹) is the concentration of metal adsorbed to the solids and C_w (mol L⁻¹) is the total metal concentration in the aqueous phase. Equation 1 can be rewritten using chemical species concentrations (2, 12):

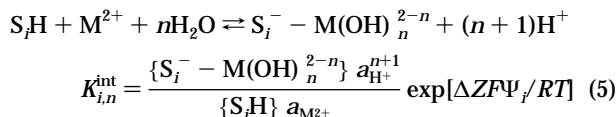
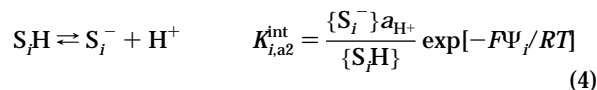
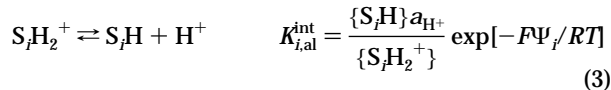
$$K_D = \frac{\sum \{S_i^- - M(OH)_n^{2-n}\}}{[M^{2+}] + \sum [ML_j^{-kz+2}]} \quad (2)$$

in which $S_i^- - M(OH)_n^{2-n}$ is the surface complex of the n order of hydrolysis species of metal M with solid phase i , and ML_j^{-kz+2} is the complex of the metal ion M^{2+} with the j th ligand for k th order association (mol dm⁻³). The numerator accounts for the concentrations of metal species sorbed on all sorbing phases of particulate matter (e.g., manganese oxyhydroxides, iron oxyhydroxides, organic matter, etc.) while the denominator represents the sum of free and complexed metal ion concentrations in the aqueous phase (e.g., MOH^+ , MCl^+ , etc.). Application of eq 2 requires that metals held in the crystal lattice of clay minerals or held in metal precipitates are not extracted or have negligible concentrations with respect to the sorbed concentrations. Calculations of background concentrations and ion activity products showed the validity of these assumptions. Equation 2 further uses the "adsorptive additivity" concept introduced by Oakley *et al.* (7) and confirmed by others (1, 8, 12). This concept assumes that the total amount of sorbed metal can be calculated from the amounts sorbed to the distinct sorbing phases by simple addition. Tessier (10) concluded that the additivity depends on pH but may be expected at circum-neutral pH values as in the current study (Table 2). The approach is further justified by the fact that, in contrast to sediments, suspended solids are "loosely packed" materials with a much better accessibility of metal binding sites. For aqueous phase complexation reactions and surface complexation reactions to pure inorganic phases, kinetics is sufficiently fast (less than 1 h) to allow the assumption of

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sorption equilibrium (16). However, for porous solids such as natural suspended particles, kinetics may be slower. Still it seems reasonable to assume equilibrium as a first approximation, especially for waters with long residence times (17).

Description of the Numerator in Equation 2. The intrinsic equilibrium constants of the surface reactions are defined in eqs 3–5 (18):



where S_i represents the heterogeneous i th surface phase, K^{int} is the intrinsic stability constant, F is the Faraday constant ($C \text{ mol}^{-1}$), n is the order of metal hydrolysis, ΔZ is the change in the charge of the surfaces species due to the sorption reaction, R is the ideal gas constant ($J \text{ mol}^{-1} K^{-1}$), T is the absolute temperature (K), and Ψ_i is the electrostatic potential (V). In the case of organic surfaces, the proton transfer at the solid/solution interface is expressed by eq (4) only.

For *inorganic surfaces*, Ψ_i is related to the electrostatic charge, σ ($C \text{ m}^{-2}$), by the Gouy–Chapman model for a planar impenetrable surface (18):

$$\Psi_i = \frac{2RT}{zF} \sinh^{-1} \left(\sigma_i \sqrt{\frac{\pi F^2 10^{-3}}{2\epsilon RTI}} \right) \quad (6)$$

where I is the ionic strength (M), z is the average of the valence of the ions in the surface water, and ϵ is the dielectric constant of water ($7.2 \times 10^{-10} C \text{ V}^{-1} \text{ m}^{-1}$ at 25°C).

For *organic surfaces*, assuming impenetrable point charges with spherical boundaries, the expression of the potential–charge relationship is given by (19)

$$\psi_i = 2wZ_i(RT/F) \quad (7)$$

where Z_i is the charge number of polyelectrolyte ($C \text{ mol}^{-1}$) and w is the electrostatic interaction function. w can be estimated using an empirical relationship for aquatic humic substances (20, 21):

$$w = P \log I \quad (8)$$

in which P is a constant.

The total site concentration, $\{S_iH\}_T$, can be related to the concentration of the i th geochemical phase in the suspended solids by the following equation:

$$\{S_iH\}_T = N_i c_{i,el} x_i s_i G_i \quad (9)$$

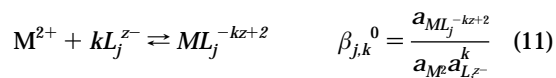
where N_i is the number of moles of sites per mol of i th phase in the suspended solids; $c_{i,el}$ is the concentration of the element selected for the quantification of the i th phase, e.g., Fe for $\text{Fe}(\text{OH})_3$ (mol kg^{-1}); x_i is the fraction of the main element present as i th phase, s_i is the stoichiometric factor (molar ratio of element in i th phase); and G_i is an accessibility factor (dimensionless) that quantifies the accessible fraction of the surface of the i th phase. With the assumption that trace

metal sorption occupies a negligible fraction of the total site concentration and combining eqs 3–9, the general expression for the nominator in eq 2 becomes

$$\{M\}_T^{\text{bound}} = a_{M^{2+}} \sum_{i=1}^N \sum_{n=0}^S K_{i,n}^{int} e^{-\Delta ZF\Psi_i/RT} a_{H^+}^{-(n+1)} N_i c_{i,el} x_i s_i G_i \left(\frac{a_{H^+}}{K_{i,al}^{int} e^{F\Psi_i/RT}} + 1 + \frac{K_{i,a2}^{int} e^{F\Psi_i/RT}}{a_{H^+}} + \sum_{x=0}^L \sum_{p=1}^Q \frac{K_{i,x,p}^{int} e^{-\Delta ZF\Psi_i/RT} a_{M_p^{2+}}}{a_{H^+}^{x+1}} \right)^{-1} \quad (10)$$

The assumption is valid as long as the free sorption sites are in excess with respect to sites occupied by sorbed trace metals. In lake Volkerak/Zoom and the inlet waters, median trace metal concentrations are in the range of 10^{-11} – 10^{-7} M (Table 1) while only 1–50 % of these total concentrations is available for surface complexation. In contrast, reported site concentrations are 10^{-6} M (lakes) and 10^{-4} M (rivers) (22), which justifies the assumption. Equation 10 includes the summations over N binding phases, S metal species, Q competing major cations, and L competing major cation species. The binding phases considered were iron oxyhydroxide (-OH sites), manganese oxyhydroxides (-OH sites), and organic matter (type A, -COOH sites and type B, -OH sites) ($N = 4$). The adsorption of free metal ion (M^{2+}) as well as hydroxo complexes (MOH^+ and $\text{M}(\text{OH})_2$) were considered ($S = 3$). It was assumed that the main competing species are free calcium and calcium hydroxo complexes ($Q = 1$ and $L = 3$) (10).

Description of the Denominator in Equation 2. The aqueous phase complexation to inorganic ligands and organic ligands (humic and fulvic acids, exudates of aquatic organisms) is represented by the equilibrium expression:



where $\beta_{j,k}^0$ is the thermodynamic stability constant of j th association and k th order, $a_{M^{2+}}$ is the activity of the metal ion (mol dm^{-3}), $a_{L_j^{z-}}^k$ is the activity of j th ligand for k th order association (mol dm^{-3}), and ML_j^{-kz+2} is the activity of the complex. Individual activity coefficients are calculated with the Davies equation (23). The ionic strength is estimated from electric conductivity using the empirical relationship (23)

$$I = 1.6 \times 10^{-5} \times \text{EC} \quad (12)$$

in which EC is the electric conductivity ($\mu\text{S cm}^{-1}$). The mass action equation used in calculating the trace metal speciation in the aqueous phase is

$$[M]_T = [M^{2+}] + \sum_{j=1}^M \sum_{k=1}^P \beta_{j,k}^0 [M^{2+}] [L_j^{z-}]^k \frac{\gamma_{M^{2+}} \gamma_{L_j^{z-}}^k}{\gamma_{ML_j^{-kz+2}}} \quad (13)$$

Complexes with Cl^- , SO_4^{2-} , CO_3^{2-} , HCO_3^- , OH^- , and dissolved organic matter (DOM) were considered ($M = 6$). Second-order associations were limited to the Cl^- and OH^- complexes ($P = 1-2$). Higher order associations and mixed ligand complexes were neglected (23). It was assumed that the molecular weight of DOM is 1500 g mol^{-1} and that carbon makes up 50% of DOM on a weight basis (20, 21). It was assumed that complexation with DOM was monodentate with R-COOH or Ar-OH type sites.

TABLE 1. Median Aqueous Trace Metal Concentrations (C_w , mol/L), Median Suspended Solid Trace Metal Concentrations (C_{ss} , mol/kg), and Median K_0 Values (10^3 L kg $^{-1}$)

| location ^a | Cd ^b | | | Cu ^c | | | Ni ^d | | | Pb ^e | | | Zn ^f | | |
|-----------------------|-----------------------|----------------------|-------|----------------------|----------------------|-------|----------------------|----------------------|-------|-----------------------|----------------------|-------|-----------------------|-----------------------|-------|
| | C_w | C_{ss} | K_0 | C_w | C_{ss} | K_0 | C_w | C_{ss} | K_0 | C_w | C_{ss} | K_0 | C_w | C_{ss} | K_0 |
| DM | 4.4×10^{-11} | 2.5×10^{-5} | 451 | 6.7×10^{-8} | 1.1×10^{-3} | 14.7 | 1.3×10^{-7} | 1.1×10^{-3} | 8.14 | 2.9×10^{-10} | 3.5×10^{-4} | 1413 | 1.6×10^{-10} | 9.7×10^{-3} | 78.5 |
| HD | 1.4×10^{-10} | 3.7×10^{-5} | 288 | 5.2×10^{-8} | 1.3×10^{-3} | 25.2 | 5.8×10^{-8} | 7.5×10^{-4} | 15.7 | 4.7×10^{-10} | 6.3×10^{-4} | 1294 | 1.6×10^{-10} | 10.9×10^{-4} | 78.8 |
| VZ3 | 7.8×10^{-11} | 8.0×10^{-6} | 134 | 5.8×10^{-8} | 4.3×10^{-4} | 7.45 | 9.3×10^{-8} | 7.3×10^{-4} | 9.57 | 3.9×10^{-10} | 2.4×10^{-4} | 645 | 1.2×10^{-10} | 4.8×10^{-3} | 46.4 |
| VZ7 | 6.3×10^{-11} | 4.0×10^{-6} | 108 | 5.6×10^{-8} | 4.4×10^{-4} | 7.11 | 8.8×10^{-8} | 6.3×10^{-4} | 8.64 | 2.4×10^{-10} | 1.8×10^{-4} | 665 | 1.2×10^{-10} | 2.9×10^{-3} | 26.6 |

^a DM, river Dintel; HD, Lake Hollandsch Diep; VZ3, Lake Volkerak; VZ7, Lake Zoom. ^b Number of records: DM, 20; HD, 29; VZ3, 23; VZ7, 24. ^c Number of records: DM, 21; HD, 29; VZ3, 23; VZ7, 24. ^d Number of records: DM, 21; HD, 29; VZ3, 23; VZ7, 24. ^e Number of records: DM, 21; HD, 29; VZ3, 23; VZ7, 24. ^f Number of records: DM, 21; HD, 29; VZ3, 23; VZ7, 24.

Expression for K_D . Substitution of eqs 10 and 13 into equation 2 yields

$$K_D = \frac{\sum_{i=1}^N \sum_{n=0}^S K_{i,n}^{\text{int}} e^{-\Delta Z F \Psi_i / RT} a_{H^+}^{-(n+1)} c_{i,\text{el}} N_i x_i s_i G_i}{\gamma_{M^{2+}}^{-1} + \sum_{j=1}^M \sum_{k=1}^P \beta_{j,k}^0 [L_j^{Z-}]^k \frac{\gamma_{L_j^{Z-}}^k}{\gamma_{ML_j^{Z-k+2}}}} \left(\frac{a_{H^+}}{K_{i,\text{al}}^{\text{int}} e^{F \Psi_i / RT}} + 1 + \frac{K_{i,\text{a2}}^{\text{int}} e^{F \Psi_i / RT}}{a_{H^+}} + \sum_{x=0}^L \sum_{p=1}^Q \frac{K_{i,x,p}^{\text{int}} e^{-\Delta Z F \Psi_i / RT} a_{M_p^{2+}}}{a_H^{x+1}} \right)^{-1} \quad (14)$$

The symbols, variables, and parameters in eq 14 are defined throughout the text. An overview is given in the Supporting Information. The free aqueous ligand concentrations ($[L_j^{Z-}]$) were approximated by measured total species concentrations, except OH^- which follows from pH. As the activity coefficients, γ , can be calculated from EC, equation 14 therefore expresses K_D as a function of chemical equilibrium constants and measurable suspended solid and water quality variables, that is, organic carbon (OC), Fe, and Mn content (solid phase) and pH, EC, Cl^- , SO_4^{2-} , alkalinity, DOC, and Ca^{2+} (aqueous phase).

Selection of Parameter Values. Stability constants for inorganic aqueous complexation reactions were obtained from the literature (24, 25). For a full overview of stability constants for aqueous phase organic complexation, intrinsic surface complexation constants, and surface properties of binding phases, we refer to the Supporting Information and to ref 26. Effects of temperature on equilibrium constants were not taken into account because of (a) the rather low effect in the 10–20 °C range (27) and (b) a lack of enthalpy data for surface- and DOM complexation constants. For amorphous iron oxyhydroxides (a-FeOX), we assumed the stoichiometry $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ($M = 177.7$ g mol $^{-1}$). The surface ionization constants for this phase, $\text{p}K_{1,\text{a1}}^{\text{int}}$ and $\text{p}K_{1,\text{a2}}^{\text{int}}$, were set at the values 5.0 and 10.9, respectively (28). The ranges for σ_1 were obtained from ref 29. For amorphous manganese oxyhydroxide (a-MnOX), the stoichiometry, $\text{MnO}_2 \cdot \text{H}_2\text{O}$ ($M = 104.9$ g mol $^{-1}$), and surface properties $\text{p}K_{2,\text{a1}}^{\text{int}} = -1.6$; $\text{p}K_{2,\text{a2}}^{\text{int}} = 6.2$, and $\sigma_2 = -4.116 \times 10^{-6}$ C m $^{-2}$ were assigned (30). Because of the low sorption density, it was assumed that the surface charge (σ_2) is determined by the proton exchange reactions only (29). Intrinsic surface complexation constants for a-FeOH ($i = 1$) and a-MnOH ($i = 2$) were taken from Smith and Jenne (28) or estimated using their predictive equation $\text{p}K_{\text{a2}}^{\text{int}} = \text{p}K_{\text{a2}}^{\text{int}} - \log K^{\text{SC}} - \log \beta_1$ (28). Values of surface complexation (K^{SC}) and first hydrolysis (β_1) constants were taken from Smith and Jenne (28) and Smith and Martell (24), respectively. Mathematically, the parameters N_i , x_i , s_i , G_i , and $K_{i,n}^{\text{int}}$ in eq 14 cannot be estimated separately. Therefore, they were fitted as one lumped parameter for each binding phase. Following Tipping (20) and Tipping and Hurley (21), particulate organic matter (OM) was modeled as fulvic substances (FS), assuming that the OM/OC conversion factor is 2 and that the molecular weight of FS is 1500. Adsorptive characteristics of OM were described by $\text{p}K_{3,\text{a2}}^{\text{int}} = 3.3$, $N_3 = 4.7$ mmol g $^{-1}$, and $\text{p}K_{4,\text{a2}}^{\text{int}} = 9.53$, $N_4 = 2.35$ mmol g $^{-1}$ for A- and B-type sites, respectively; $P = -103$; $Z = -5 \times 10^{-3}$ C mol $^{-1}$; $x_i = 1$ ($i = 3, 4$); $s_i = 0.0165$ ($i = 3, 4$) (20, 21). Intrinsic surface complexation constants were taken from Tipping (20) and Tipping and Hurley (21) or were estimated using the same predictive equation as for the mineral surfaces with the assumption: $K_{M^{2+}}^{\text{SC}} = K_{\text{MOH}^+}^{\text{SC}} = K_{\text{M(OH)}_2}^{\text{SC}}$.

Materials and Methods

Study Area. Water and suspended solid samples were sampled monthly (May 1992–December 1994) from the river

TABLE 2. Variable Ranges of the Calibration Data Set (1992–1994)

| variable | location | | | |
|--|-------------|-------------|------------|-------------|
| | DM | HD | VZ3 | VZ7 |
| OC (mol kg ⁻¹) | 8.8–17 | 4.3–15 | 8.9–27 | 4.2–22 |
| Fe (mol kg ⁻¹) | 0.58–2.3 | 0.33–0.88 | 0.11–0.98 | 0.22–0.87 |
| Mn (mol kg ⁻¹) | 0.009–0.12 | 0.018–0.092 | 0.035–0.17 | 0.034–0.14 |
| pH | 7.3–8.5 | 6.5–8.6 | 8.1–9.2 | 8.1–9.3 |
| EC (μS cm ⁻¹) | 260–948 | 472–930 | 950–1450 | 950–1710 |
| Cl ⁻ (mmol L ⁻¹) | 0.99–5.2 | 0.93–5.8 | 6.1–10 | 8.9–15 |
| SO ₄ ²⁻ (mmol L ⁻¹) | 0.58–1.1 | 0.40–0.93 | 0.55–1.2 | 0.89–2.1 |
| HCO ₃ ⁻ (mmol L ⁻¹) | 1.6–3.8 | 2.2–4.7 | 2.1–3.1 | 1.70–3.2 |
| CO ₃ ²⁻ ^a (mmol L ⁻¹) | 0.016–0.036 | 0.022–0.045 | 0.021–0.03 | 0.017–0.031 |
| DOM ^b (μmol L ⁻¹) | 9.2–24 | 0.9–13 | 3.2–14 | 6.8–13 |
| Ca ²⁺ (mmol L ⁻¹) | 1.2–2.1 | 0.95–2.3 | 1.5–2.0 | 1.5–2.2 |
| T (K) | 274–296 | 278–298 | 275–297 | 276–297 |
| SS (mg L ⁻¹) | 6–15 | 4–22 | 1–11 | 1–15 |

^a Calculated from [HCO₃⁻] and pH. ^b Assumptions: M = 1500 g mol⁻¹ and C makes up 50% of DOM on a weight basis.

Dintel (DM), Lake Hollandsch Diep (HD), Lake Volkerak (VZ3), and Lake Zoom (VZ7), The Netherlands. The sampling locations were selected to represent a gradient of salinity and other chemical characteristics. For the morphology and exact locations of the sampling sites, we refer to earlier reports (1, 31).

Sample Collection and Storage. Sampling was performed by the Dutch Institute for Fresh Water Management and Waste Water Treatment. Suspended solids were collected using continuous flow centrifuges (Pennwalt, AS 16). The water was centrifuged at a speed of 1000 L h⁻¹ and 15000 rpm (13200g). Teflon sheets were attached to the inner surface of the centrifuge in order to prevent contamination with metals from the walls. The solids were immediately frozen, freeze-dried, and stored at -18 °C. Water samples for trace metal analysis were taken in triplicate using a peristaltic pump with Teflon tubing, a Teflon filter unit, and 0.45-μm cellulose nitrate membrane filters. All filter and filter unit manipulations were done with gloves and polyethylene pincettes. The Teflon inlet tube was flushed with water for 5 min prior to the sampling and was held as close as possible to the inlet of the continuous-flow centrifuge used for suspended solids sampling. After rejection of the first 0.5 L of filtrated water, 1-L samples were collected in acid-cleaned polyethylene bottles using positive (N₂) pressure. Samples were acidified (1 mL of HNO₃/L, Merck p.a.) and stored in the dark at 4 °C before analysis.

Suspended Solid Analysis. Total organic carbon (OC) was measured using the method described by Begheijn (32). The aqua regia-soluble metals Cd, Cu, Pb, Ni, Zn, Fe, and Mn were extracted from the samples using HNO₃/HCl digestion at 100 °C for 3 h. Detection was by graphite furnace AAS (Cd) and flame AAS (Cu, Pb, Ni, Zn, Fe, Mn) (Varian Spectra-300 with background correction).

Water Analysis. Trace metals were preconcentrated according to Nojiri *et al.* (33). In the final residue, Cd and Pb were measured using graphite furnace AAS, and Ni, Cu, and Zn were measured using flame AAS. Sulfate was measured by ionchromatography (Krators Pump Type 400, Spectraphysics autosampler Type 8810, water conductivity detector Type 431, and Vydac 300IC column). Determination of temperature, pH, conductivity, chlorinity, alkalinity, and calcium and dissolved organic carbon concentrations was performed by the Dutch Institute for Fresh Water Management and Waste Water Treatment.

Data Treatment. Table 2 presents an overview of the 1992–1994 water quality variables of the complete data set (all locations pooled). Triplicate *in situ* K_D values were

calculated as the ratio of measured solid and aqueous phase metal concentrations. Records containing missing K_D values were excluded from the analysis. Missing variable values (less than 10% of the data set) were estimated from other variables (for example, multiple regression of Cl⁻ with EC and SO₄²⁻, R² = 0.905, P < 0.0001). The SWAMP model equations were programmed in FORTRAN to allow communication with the software packages for sensitivity analysis and parameter estimation that are discussed below. A spreadsheet version of SWAMP is available from the corresponding author on request.

Sensitivity Analysis. The sensitivity analysis was performed to select the parameters in eq 14 for which K_D was most sensitive. The analysis was performed using Monte Carlo simulations as available in the software package UNC SAM (34). The basic concept of these simulations is sampling from a priori distributions of the input variables and parameters and successive simulation for all sampled inputs. An estimate of the sensitivity with respect to individual parameters can be obtained from linear regression between the model output and inputs. The sensitivity with respect to a parameter is quantified by the standardized regression coefficient (SRC). The simulations were carried out using the Latin Hypercube Sampling technique within the ranges for the parameter and variable values. Variable ranges were set to span the solid/solution macro chemistry of the lake (Table 2). Boundaries in the parameter values were set according to the ranges in literature values. It appeared that five parameters significantly (p < 0.05, t-test) affected the K_D.

Parameter Estimation. The five parameters selected by the sensitivity analysis were estimated using nonlinear weighted relative least squares regression. The weighing factors (w_i) were inversely proportional to the variances of the measured K_D values. The parameters were estimated using a gradient-free global optimization method, using the software package GLOBOPT (35), followed by the Downhill Simplex local search algorithm (36). The parameters were estimated within the ranges of literature values after log transformation. All other parameters were fixed at their best (median) literature value.

Results and Discussion

Measured K_D Values. An overview of median trace metal aqueous and suspended solid concentrations and K_D values for all locations is presented in Table 1. Errors in K_D values (not shown) were calculated from the propagated errors in C_W and C_S. The resultant relative errors in K_D were smallest

for Ni and Cu (typically 15%), followed by Zn and Pb (typically 20%) and finally Cd (40%). Among the metals, the order in the error in K_D follows the order of the aqueous concentration (Table 1). So, the larger errors for Cd may be explained from the low Cd concentrations. Among locations, the error decreases in the order DM, HD, VZ3, and VZ7. We have no conclusive explanation for the observed order. A possible reason for higher errors at DM and HD locations might be the interference of suspended silica and other colloidal and suspended particles with the aqueous phase measurements (33). Generally, K_D values are lower for the more saline waters (VZ3 and VZ7). The slight differences in the order of magnitude of K_D , when compared with literature values, are caused by the different complexation characteristics of the surface waters. At each location, the trend in the K_D values among the metals is relatively constant, i.e. $Pb > Cd > Zn > Cu, Ni$. Comparison of the observed sequence in K_D with the sequence of metal hydrolysis constants [i.e., $Pb > Cu > Zn > Cd > Ni$ (24)] indicates that Cu is less reactive towards particles than is expected from hydrolysis constants, while the reverse is true for Cd. Considering the fact that Cu interacts strongly with the dissolved ligands (e.g., DOM) such a trend may be expected. Furthermore, the heterogeneous character of the natural suspended particles may account for the differences in trend. The variation in the K_D values is mainly due to the variation of suspended solid and water composition (Table 2) and partly due to the uncertainty/errors in K_D measurements.

Model Fits and Parameter Estimates. SWAMP was capable of predicting the correct order of magnitude of the K_D for all five metals, within physically realistic parameter ranges. The best fits, which also adequately described the time course of K_D were obtained for Cu and Zn. Because of space economy, the discussion below focuses on the results for Cu and Zn. For a complete discussion of the results for Pb, Ni, and Cd, the reader is referred to our earlier report (26). The model predictions are compared with *in situ* K_D values for Cu and Zn in Figures 1 and 2, respectively. The figures show results for the pooled data from locations with long water residence time (Figures 1a and 2a) and for the single best location (Figures 1b and 2b). Note that for the judgment of weighted regression results, the K_D values must be plotted as weighted values ($w_i^{0.5} \times K_{D,i}$) (37). The coefficients of determination, R^2 , are summarized in Table 3. The results for copper are slightly better than for Zn. The quality of fit appears to improve in the sequence DM; HD; VZ3; VZ7 < HD; VZ3; VZ7 < VZ7, for both metals. Among the stagnant waters, the best fit was obtained for location VZ7, although a slight overprediction of the modeled K_D can be observed (Figures 1b and 2b). Better fits for the waters with long residence times (HD; VZ3; VZ7: 60–130 days) can be attributed to the relatively long contact times between particles and water of more or less constant composition. The frequent wind-induced cycling of particles in the semi-stagnant water column allows sorption equilibria to be approached. In contrast, contact times in the river Dintel are short for two reasons. First, resuspension of particles in the river Dintel is caused by less frequent discharge fluctuations. Further, also particle and water composition depend on the flow regime and are more variable in time. As a result, the K_D values measured for the Dintel do not necessarily reflect an equilibrium state.

Figures 1 and 2 show that no significant systematical differences between the predictions of the conceptual model and the observed K_D values are found. We conclude that the factor 10 variation in Cu and Zn K_D is adequately described by the model. The residual lack of fit may be explained from trivial causes, such as the measurement error in literature values and measurements or from processes not accounted for in the model. Such processes may be the shielding of

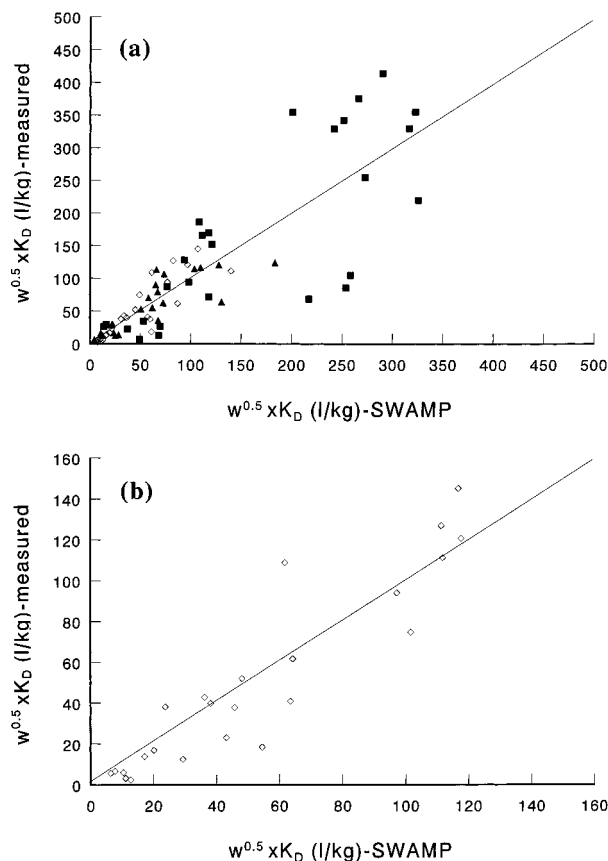


FIGURE 1. Comparison between $w^{0.5} \times K_{D,i}$ (predicted by SWAMP) and $w_i^{0.5} \times K_{D,i}$ (measured) for Cu and (a) stagnant waters (■, HD; ▲, VZ3; ◇, VZ7), and (b) VZ7. The 1:1 line is shown for guidance.

phases, differences in the type of DOM (e.g., during primary production), or adsorption of other than hydrolyzed metal complexes (e.g., MCl_2 , MSO_4 , etc.).

Sensitivity Analysis and Parameter Estimates. The relative importance of the parameters as well as the parameter estimates themselves are presented in Table 4. The relative importance of parameters is indicated by ranking their respective SRC values. Here, the SRC rank of a parameter can be interpreted as the relative importance of the adsorption or complexation process governed by that parameter. Under the prevailing geochemical conditions, the most dominant binding phases for copper and zinc are iron and manganese oxyhydroxides, which is in good agreement with literature reports (1, 2, 7, 8). The most significant process in the solid phase is the sorption of second-order hydrolysis species to iron oxyhydroxide, followed by the free metal sorption to manganese oxyhydroxides with competition by Ca^{2+} . This is consistent with the fact that mono- and divalent cations (e.g., Cu, Zn, Ni) primarily associate with manganese oxides (1, 38). The adsorption on organic matter also contributed to the K_D , but to a much lesser degree. As an example, the solid phase speciation was calculated at the median values for suspended solid and water composition. The relative contributions of the binding phases for Zn were 69.6% (Fe), 27.1% (Mn), and 3.3% (OC) and for Cu 99.2 (Fe), 0.7% (Mn), and 0.1% (OC). An important observation is that for our dataset multiple solid phases appear to be relevant in the modeling of metal uptake. This justifies the multiphase approach as opposed to the single phase approach (3) or the use of one intrinsic surface complexation constant for the heterogeneous solid phase (11, 12, 15). In the aqueous phase, the copper and zinc complexes with dissolved organic matter are the most important, which is in agreement with other Cu and Zn speciation studies (39–41).

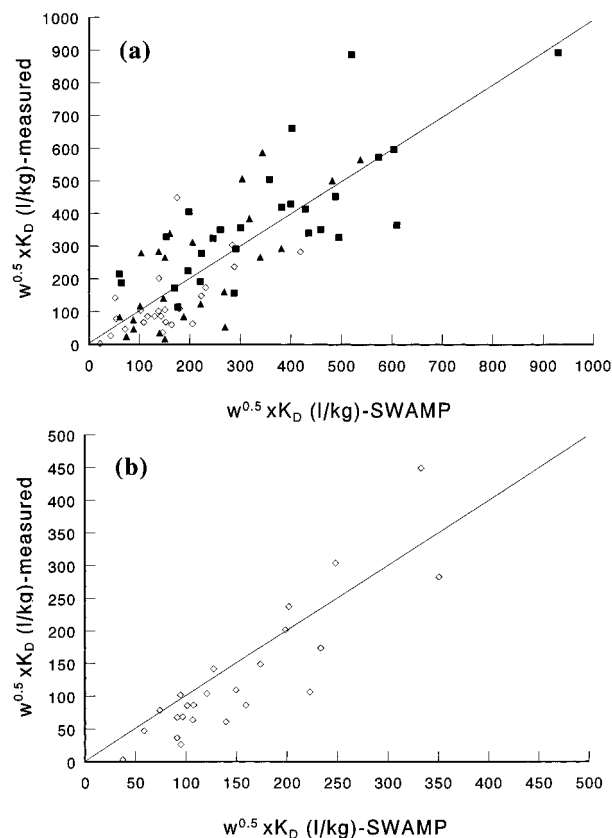


FIGURE 2. Comparison between $w_i^{0.5} \times K_{D,i}$ (predicted by SWAMP) and $w_i^{0.5} \times K_{D,i}$ (measured) for Zn and (a) stagnant waters (■, HD; ▲, VZ3; ◇, VZ7), and (b) VZ7. The 1:1 line is shown for guidance.

TABLE 3. Overview of R^2 for Linear Regression of Field vs Predicted K_D values^a

| data set | Cu | | Zn | |
|-------------------------------------|-------|-------|-------|-------|
| | R^2 | N^b | R^2 | N^b |
| complete data set: DM; HD; VZ3; VZ7 | 0.640 | 97 | 0.551 | 95 |
| stagnant waters: HD; VZ3; VZ7 | 0.728 | 73 | 0.650 | 76 |
| best single location: VZ7 | 0.853 | 24 | 0.786 | 24 |

^a All regressions significant at $P < 0.0001$. ^b Number of records.

In all cases, parameter estimates (Table 4) were close to or well within the parameter value ranges reported in the literature. This confirms the validity of the model and the assumptions made. Differences between literature and estimated parameter values may have several causes. First, the naturally occurring solid binding phases and DOM are

poorly defined and characterized. In SWAMP, these phases are assumed equal to model compounds with well-defined surface characteristics. When this assumption on the phase identity does not hold for a group of particles, the intrinsic surface complexation constants will differ. Second, the difference may be due to the uncertainty carried by the literature ranges themselves. The ranges for the literature values in Table 4 are taken from one source and do not relate to the full range of values that can be found in the literature. For example, the range of stability constants for the complexation of Zn to DOM (Table 4, $\beta_{6,1}^\circ$) seems rather narrow in respect to the intrinsic heterogeneity of DOM. In some literature studies on Zn speciation in fresh and marine waters, the reported ranges in stability constants are $\log \beta_{6,1}^\circ > 7$ (39, 42). Furthermore, it should be noted that the reported literature range for the surface charge of the manganese- and iron (oxy)hydroxide phases correspond to the primary surface charge (i.e., charge that is solely developed by the proton exchange reactions). Finally, the factors explaining the lack of fit in the Figures 1 and 2, which were already discussed above, may also contribute to the differences.

To summarize, this study shows that surface and solution complexation equilibria explain the major part of the variation of *in situ* Cu and Zn K_D values for suspended solids in (semi-) stagnant waters. Additionally, the results of this study show that (literature) laboratory-derived parameter values for distinct chemical phases and ligands may be useful for predicting metal adsorption in the field. As the data requirements are limited, SWAMP may be used to predict water and sediment quality, to evaluate emission reduction scenarios, or to assess ecotoxicological risks of trace metal pollution.

Acknowledgments

Financial support from the Institute of Fresh Water Management and Waste Water Treatment (RIZA), The Netherlands, is acknowledged (Grants RI-1261 and RI-1566). The authors thank R. Jovin for his programming work; F. Gillissen for his technical assistance, and M. Grum, L. Lijklema, and R. H. Alderink for helpful discussions and comments on the manuscript.

Supporting Information Available

Five tables giving an explanation of symbols, variables, and parameter in SWAMP and a summary of thermodynamic data (10 pp) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the Supporting Information from this paper or microfiche (105 × 148 mm, 24× reduction, negatives) may be obtained from Microforms Office, American Chemical Society, 1155 16th St. NW, Washington, DC 20036. Full bibliographic citation (journal, title of article, names of authors, inclusive pagina-

TABLE 4. Overview of Estimated Parameters for Copper and Zinc and Stagnant Waters

| parameter | Cu | | | | Zn | | | |
|---|------------|------------------|-----|-----------------------|------------|------------------|-----|-----------------------|
| | HD;VZ3;VZ7 | literature range | ref | SRC rank ^g | HD;VZ3;VZ7 | literature range | ref | SRC rank ^g |
| $\sigma_1 \times 10^7 \text{ (cm}^{-2}\text{)}^a$ | 19.8 | −5–10 | 29 | 1 | 1.05 | −5–10 | 29 | 1 |
| $\beta_{6,1}^\circ \text{ (log)}^b$ | 10.4 | 8.42–10.9 | 43 | 2 | 6.13 | 5.05–5.31 | 43 | 4 |
| $N_1x_1s_1G_1K_{1,2}^{\text{int}} \text{ (pK)}^c$ | 14.7 | 11.3–18.1 | 28 | 6(3) ^h | 18.3 | 14.4–21.2 | 28 | 6(5) ^h |
| $K_{2,0}^{\text{int}} \text{ (pK)}^d$ | 3.85 | −1.4–1.6 | 28 | 4 | fixed | | | |
| $K_{2,0,1}^{\text{int}} \text{ (pK)}^e$ | 7.37 | 3.8–6.8 | 28 | 5 | 6.78 | 3.8–6.8 | 28 | 3 |
| $N_2x_2s_2G_2K_{2,0}^{\text{int}} \text{ (pK)}^f$ | fixed | | | | 3.04 | −0.544–8.00 | 28 | 7(2) |

^a Net total surface charge of Fe solid phase. ^b Thermodynamic stability constant of first order DOM association. ^c Lump parameter ($N_1x_1s_1G_1$ surface properties of Fe solid phase; $K_{1,2}^{\text{int}}$ intrinsic surface complexation constant of M(OH)_2 and Fe solid phase). ^d Intrinsic surface complexation constant of M^{2+} and Mn solid phase. ^e Intrinsic surface complexation constant of Ca^{2+} and Mn solid phase. ^f Lump parameter ($N_2x_2s_2G_2$ surface properties of Mn solid phase; $K_{2,0}^{\text{int}}$ intrinsic surface complexation constant of M^{2+} and Mn solid phase). ^g Sensitivity estimator (Standardized Regression Coefficient). ^h Value in parentheses refers to the rank of surface complexation constant.

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Received for review May 30, 1997. Revised manuscript received December 30, 1997. Accepted January 5, 1998.

ES970481V