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Article *in* Aquatic Geochemistry · January 2001

DOI: 10.1023/A:1017598400001

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3027

Aquatic Geochemistry **7:** 107–126, 2001.

Similar Adsorption Parameters for Trace Metals with Different Aquatic Particles

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(Received: 7 December 1999; accepted: 31 January 2001

Abstract. Conditional surface binding constants and complexation capacities for Zn, Pb, Cd, and Cu were determined from surface titration experiments of heterogeneous natural aquatic particulate matter of different origin and composition. Metals and particles were evaluated in naturally occurring concentration ranges in river water.

The adsorption of trace metals can be adequately described with a single conditional binding constant over a wide range of metal : particle ratios. Binding constants for aquatic particles at pH 8.0 are remarkably independent from particle composition and are specific for each metal: log $K_{\mathrm{Zn}}^{\mathrm{ads}}$ = 8.39, log $K_{\mathrm{Pb}}^{\mathrm{ads}}$ = 9.67, log $K_{\mathrm{Cd}}^{\mathrm{ads}}$ = 8.61, log $K_{\mathrm{Cu}}^{\mathrm{ads}}$ = 9.84. From competition experiments with Ca and Pb we extracted a sorption coefficient for Ca of log $K_{\mathrm{Ca}}^{\mathrm{ads}}$ = 2.5 (pH 8.0). Maximum surface binding capacities for all metal ions were found for particles containing high fractions of Mn-oxides which are associated with large specific surface areas. Generally, we found sorption capacities to decrease in the sequence Cu $\gg$ Pb, Zn > Cd.

The experiments suggest that the conditional surface binding constants and complexation capacities are applicable to model trace metal adsorption in the concentration ranges of natural waters under conditions similar to the experiments. Results also imply that the chemical nature of particle surface sites is rather uniform in the intermediate concentration range or that the array of binding sites averages out differences in sorption strength over the prevailing concentration range of metal ions, respectively.

Key words: adsorption, trace metals, natural particles, surface ligands, surface binding constants, complexation capacity, competitive sorption

1. Introduction

The sorption of trace metals to particulate surfaces influences metal speciation, concentration, bioavailability and residence time in natural waters. Substantial effort has been applied to investigate the sorption of metal to both well defined mineral particles (e.g., Dzombak and Morel, 1990), as well as environmental particulate matter (Lead et al., 1998; Hamilton-Taylor et al., 1997; Wang et al., 1997; Coston et al., 1995; Müller and Sigg, 1990; Gonçalves et al., 1987; Balistrieri and Murray, 1983, 1984; Mouvet and Bourg, 1983).

Natural aquatic particles are composed of assemblages of secondary minerals, surface precipitates or amorphous phases (Buffle, 1992), inorganic minerals are often coated with organic material, and weathering, diagenetic processes and bacterial growth alter surfaces continuously. Consequently, particles may be highly heterogeneous which makes a correspondence between model simulations and chemical 'reality' difficult (Gulmini et al., 1996; Honeyman and Santschi, 1988). Experimentally, it is not feasible to vary the pH in a wide range to measure adsorption isotherms since this may cause dissolution or precipitation of mineral phases (e.g., carbonate minerals), change in specific surface area and uncontrollable sorption/desorption reactions of organic conglomerates.

All sorption processes are described in the context of the surface complexation concept of Stumm and Schindler (e.g., Stumm, 1992) that treats the interaction of metal ions with particulate surfaces similar to complex formation in solution. Sorption is described in terms of chemical mass action equations, and surfaces are characterized with the maximum number of complexing sites. In addition, the effects of charges localized on the particle surface on sorption equilibria as well as ionic strength are considered by an electrostatic correction term. Two fundamentally different, however complementary approaches have been followed to understand and quantify metal adsorption to natural particulate matter: One approach is to regard the particles as being composed of a variety of distinct complexing sites each with its own concentration and binding energy. The result is a continuous distribution of binding energies. The sorption process is then described either by summing up all the individual sites or with a continuous distribution function (Buffle et al., 1990). The other approach determines 'conditional' or 'apparent' constants without claiming to describe the 'true' molecular situation of the adsorption process (Benjamin and Leckie, 1981; Balistrieri and Murray, 1983).

Davis et al. (1998) recently discussed two concepts dealing with complex mixtures of environmental particles. Their 'component additivity' approach predicts sorption by assembling adsorption data from pure mineral or organic phases, and their 'generalized composite' approach connects binding constants and sorption capacities to experimental data assuming one or several 'generic' complexing surface sites. The latter was capable to model sorption within a considerable range of pH values and Zn concentrations. This approach was found to be preferable for complex particles which could not easily be characterized.

In an earlier paper (Müller and Sigg, 1990) we applied a model similar to the 'generalized composite' of Davis et al. (1998) to determine conditional binding constants and sorption capacities for Pb and Zn on riverine suspended particles. Calculation of 'free' and 'sorbed' proportions using the parameters obtained agreed with field measurements from unfiltered and filtered water samples. The distribution of the binding constants for each of the metals did not vary significantly for sorption to particles of different organic carbon or Fe content. However, differences in particle composition were reflected in variations of particle-metal-binding capacities.

We are currently extending the database of conditional sorption parameters to a suite of transition metals and a broad range of environmental surfaces. Zn, Pb, Cd, and Cu in the concentration range of surface waters were used as sorbates. Eighteen particle types ranging from bacteria, sewage sludge, suspended particles, sediments, and natural Mn- and Fe-oxyhydroxides, to pure oxides of Al, Mn, and Fe were tested as adsorbing surfaces.

2. Materials and Methods

2.1. PARTICLE TYPE AND PARTICLE CHARACTERIZATION

The following types of particles were selected to provide a wide spectrum of surface types occurring among natural aquatic particles. Results of the physical and chemical characterization of the particle samples are given in Table 1. River Rhine sediment (No. 1) was a sample from a sediment core where the top 45 cm were sieved with a 63 μm Nylon net. The sample 'River Glatt s.m.' (No. 2) was suspended matter obtained from the River Glatt, a small river in the Swiss Plateau highly loaded with organic carbon from sewage treatment plants. Suspended particles were harvested on-site with a continuous flow centrifuge and freeze-dried a few hours later. Gotland s.m. (No. 3) are marine suspended particles from sediment traps from the Gotland Deep (deepest part of the Baltic Sea) which were centrifuged and freeze-dried. Suspended matter from Kirr Bay (No. 4), was centrifuged and freeze-dried. These brackish water lagoons are characteristic for the tideless part of the German Baltic Sea shore. Kirr Bay fl. (No. 5) was a freeze-dried fluffy layer of surficial sediment from the same location. Fresh sewage sludge (No. 6) was sampled from a sewage treatment plant. Two samples of the sulfide oxidizing bacteria *Beggiatoa* (Nos. 7 and 8) were harvested from bottom sediments of the eutrophic lake Sempach in Central Switzerland. The manganese nodule (No. 9) stems from the sediment of Mecklenburg Bay, a part of the Baltic Sea. The Na-rich birnessite (No. 10) was described by Silvester et al. (1997). γ-MnOOH (Manganite, No. 11), a Mn(III)-oxide, was synthesized and characterized by Friedl (1995). Goethite (No. 12) was a commercial product (Eisenoxidgelb 910, Bayer AG, Germany) and described in Müller and Sigg (1992). Rekingen (No. 13) and Lobith (No. 14) are two sites on the Rhine where suspended particles were centrifuged. E. coli (No. 15) were harvested from a culture, heat killed at 80 °C and freeze dried.δ-Al_2O_3 (No. 16) was obtained as 'Aluminiumoxid C' from Degussa AG. A second sample of γ-MnOOH (No. 17) and the amorphous Mn-oxide, δ-MnO_2 (No. 18) were not further characterized due to lack of material.

Specific surface areas were determined by N_2 adsorption (BET at 77 K). Particle size distributions were measured with a MasterSizer X (Malvern Instruments Ltd.). Chemical compositions of the particles were determined by acid digestion using 4 ml HNO_3 conc. and 1 ml H_2O_2 in a microwave oven. Ca, Mg, Fe, and Mn were measured with a Perkin Elmer AAS 2100. Total organic carbon (TOC) was analyzed with a CHNS-Analyzer (Vario EL, elementar Analysensysteme GmbH, Hahnau, Germany) with foregoing acidification to extrude carbonate-C.

Table I. Specific surface area (BET) in m^2/g, size distribution (weight percent <2 μm, between 2 μm and 15 μm, and larger than 15 μm), and chemical composition of the particulate matter used in sorption experiments. Analyses were performed if enough material was available (n.d.: not determined).

	BET $[m^2/g]$	<2 μm %	$2 < x < 15$ %	>15 μm %	Fe mol/kg	Mn mol/kg	Ca mol/kg	Mg mol/kg	TOC mg/g
1. River Rhine sed.	4.8	3.1	22.2	74.7	0.17	$9.25 \cdot 10^{-3}$	1.61	n.d.	20.3
2. River Glatt s.m.	n.d.	n.d.	n.d.	n.d.	0.70	$3.28 \cdot 10^{-2}$	2.50	n.d.	168
3. Gotland deep s.m.	50.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4. Kirr Bay s.m.	1.2	0.3	1.7	98	0.24	$1.83 \cdot 10^{-2}$	0.30	0.25	250
5. Kirr Bay fl.	10.9	0.8	7.2	92	0.23	$3.92 \cdot 10^{-3}$	0.14	0.18	71
6. Sewage sludge	11.9	n.d.	n.d.	n.d.	1.32	$5.15 \cdot 10^{-3}$	1.23	0.19	196
7. *Beggiatoa* A	n.d.	n.d.	n.d.	n.d.	0.47	$2.56 \cdot 10^{-2}$	3.21	0.18	150
8. *Beggiatoa* B	36.9	n.d.	n.d.	n.d.	0.43	$3.03 \cdot 10^{-2}$	3.27	0.18	144
9. Mn-nodule	118.7	n.d.	n.d.	n.d.	3.35	3.69	0.36	0.51	7.9
10. Na-Birnessite	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0
11. γ-MnOOH	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0
12. Goethite	15.6	44	21.6	34.4	n.d.	n.d.	n.d.	n.d.	0

2.2. VOLTAMMETRY

We used voltammetry as an analytical tool to determine the distribution of trace metals between particulate and dissolved phases in surface titration experiments. Polarography on the hanging mercury drop electrode discriminates metals sorbed to particles from free metal ions by the difference of their diffusion velocity through the diffuse boundary layer at the electrode surface (Gonçalves et al., 1985). By this means, we could avoid particle/water separation by centrifugation or filtration which can be a source of artefacts and contamination. The anodic stripping method allows detection limits in the sub-ppb range with good reproducibility. Continuous titrations can be performed under controlled conditions. Total concentrations of trace metals ($<10^{-7}$ M) and suspended matter corresponding to conditions similar to those occurring in the natural environment were used. Metal ion solution was titrated with increments of particle suspension. Free metal ion concentrations were determined by differential pulse anodic stripping voltammetry (DPASV) with a Metrohm 647VA polarograph combined with a 646VA processor (Metrohm Herisau, Switzerland). The analytical procedure applied here was presented in earlier papers (Müller and Sigg, 1990, 1992). The procedure was as follows: 19.4 ml doubly distilled water was transferred in a 50 ml polyethylene beaker, 200 μl of 1 M KNO_3 (Merck, suprapur) added and a blank measured after purging the solution oxygen free with a mixture of 0.05% CO_2 in N_2. 200 μl of a 10^{-5} M stock solution of either $ZnNO_3$, $CdNO_3$, $PbNO_3$, or $CuCl_2$ are added, and a '100%' value was recorded. 200 μl 0.1 M $NaHCO_3$ solution (Fluka, p.a.) was then added and the solution purged with N_2/0.05% CO_2. After the pH was adjusted to 8.0, the free metal concentration was measured again. The distribution between the metal adsorbed on vessel walls and dissolved metal in solution was accounted for in a distribution constant K_D. All measurements were repeated at least three times. Increments of particle suspensions (1 g/l) were then added. Zn, Cd, Pb, and Cu were detected by stirring and purging the suspensions for 10 min, accumulation at -1.2 V (-0.6 V for Cu) for 200 sec, pausing 30 sec, and scanning with 15 mV/sec applying pulses of 50 mV.

Desorption of metal ions from particulate matter was measured in a 0.01 M acetate buffer solution of pH 4 using the polarographic cell. This pH assured mild desorption by mere competition of H^+ for sorption sites without dissolution of Fe- or Mn-oxyhydroxides.

Reproducibility of titration experiments at constant pH (8.0) was calculated from three identical titrations of Pb with goethite suspension and parameters determined with the treatment described below: average values and standard deviation for Γ_{max} and log K_{ads} were $8.77.10^{-3} \pm 0.56.10^{-3}$ moles/kg, and 9.38 (SD 18.2%) respectively. We observed qualitatively a deterioration of the reproducibility with increasing C_{org} of the particle samples.

For the study of Pb adsorption to particulate matter in the presence of Ca and NTA we used 10 ppb ($4.83 \cdot 10^{-8}$ M) Pb and particles from the River Glatt. Ca concentrations were 10^{-4} to 10^{-3} M and NTA 10^{-8} to 10^{-6} M. The titration was modeled with the speciation calculation program ChemEQL (Müller 1995).

CALCULATION OF CONDITIONAL BINDING CONSTANTS AND SORPTION SITES

The sorption of trace metals to particulate surfaces in the context of the surface complexation models is generally written in the form of a simple chemical equilibrium:

$$L + Me^{2+} \Leftrightarrow L - Me. \qquad (1)$$

All surface binding sites are regarded as chemically equivalent which results in a Langmuir-type sorption isotherm. This model does not accurately describe the sorption stoichiometry or the exchange of protons at the surface.

Information on specific acid-base equilibria on the surfaces of natural particulate matter (Buffle, 1992) is hard to come by. Humic and fulvic acids do not give distinct protolysis steps, and minerals such as calcite and dolomite may dissolve due to pH-changes during titration. Since our experiments were performed with constant pH and ionic strength similar to natural surface water in a carbonaceous catchment (without bivalent cations), the protolysis equilibria of sorption sites merge with the 'apparent' or 'conditional' surface complexation constants. Hence, they do not show explicitly in the mass action law of Equation (1). The influence of ionic strength is included within the conditional binding constant. Ionic strength effects on sorption equilibria with strong binding cations are negligible (Dzombak and Morel, 1990). Pabalan et al. (1998) conclude from their sorption experiments with a variety of mineral surfaces that sorption of U(VI) was not sensitive to the various surface charge characteristics of such sorbents and that ionic strength effects were limited to situations where sorption was dominated by ion exchange.

Our experiments do not allow to consider coulombic effects. Thus, electrostatic interaction is included in the conditional binding constants and hence we have a non-electrostatic model. This approach very closely resembles the 'Generalized Composite Model' from Davis et al. (1998) proposed for heterogeneous mixed natural particles other than H$^+$-exchange was included there with a fixed stoichiometry.

The mass action equation is:

$$K_{\text{ads}} \quad \genfrac{}{}{0pt}{}{[L \quad Me]}{[L][Me^{2+}]} \quad [\text{L/mol}]. \qquad (2)$$

Sorption to vessel walls and electrode bodies is described with a distribution constant:

$$K_{\text{D}} \quad \frac{[Me_{\text{cell}}]}{[Me_{\text{sol}}]} \quad [\cdot\ ] \qquad (3)$$

The total concentration of the metal, Me_{tot}, consists of the concentration of Me in solution, the concentration sorbed to the vessel walls, and the concentration on particulate surfaces. Me_{sol} is the sum of all dissolved metal species (hydroxides, carbonates, nitrates), and the solution speciation is considered with the dimensionless ratio-factor α:

$$[Me_{\text{tot}}] = \alpha[Me^{2+}](K_{\text{D}} + 1 \quad + [L - Me] \quad [\text{mol/L}]$$

Values for α calculated from solution composition were $\alpha_{\text{Cu}} = 37.04$, $\alpha_{\text{Pb}} = 14.49$, $\alpha_{\text{Zn}} = 1.51$, $\alpha_{\text{Cd}} = 1.24$. Concentration of particulate sorption sites is

$$[L_{\text{tot}}] = \Gamma_{\max} A \quad [\text{mol/L}]$$

where $\Gamma_{\max}$ is the maximum adsorption capacity in moles/kg and A the concentration of particles in kg/l. The mass law Equation (2) of the sorption process is rearranged in the form of a linear equation. The parameters for surface complexation, K_{ads}, and adsorption capacity, $\Gamma_{\max}$, are extracted from intercept and slope:

$$\frac{A}{\frac{[Me_{\text{tot}}]}{[Me_{\text{sol}}]} - (K_{\text{D}} + 1)} = \frac{\alpha}{\Gamma_{\max} K_{\text{ads}}} + \frac{1}{\Gamma_{\max}}[Me_{\text{sol}}] \quad [\text{kg/L}].$$

Average binding constants were calculated from replicates of the same particles taking the arithmetic mean of K_{ads} and $\Gamma_{\max}$. Average binding constants for each metal ion were obtained as the arithmetic mean of the averaged constants from each particle type and then the log-value of K_{ads} taken. Standard deviations were calculated from the linear K_{ads}-values and given in percent values in brackets.

3. Results and Discussion

3.1. ADSORPTION EXPERIMENTS

Figures 1a–d show representative titration experiments for Pb, Zn, Cd, and Cu with a variety of particulate surfaces plotted according to Equation (6). The slope of the linearized plot is inversely proportional to the sorption capacity of the particles (= $\Gamma_{\max}^{-1}$), while the intercept with the y-axis is inversely proportional to the binding constant K_{ads} for a given α and $\Gamma_{\max}$. The titration points correspond to a linear relation, except for the region where the metal : surface ratio is especially high. The linearity indicates that adsorption of trace metals is consistently described with a single constant over a wide range of metal : surface ratios. The metal : surface ratio (as Γ in mol kg^{-1} particles) below, for which the titration function was linear, was between 1 and 10 for Pb, Zn, and Cd, and between 30 and 70 for Cu.

At the beginning of the titration the experimental points are not linear since the assumptions of the model were not fulfilled at very high metal : surface ratio.

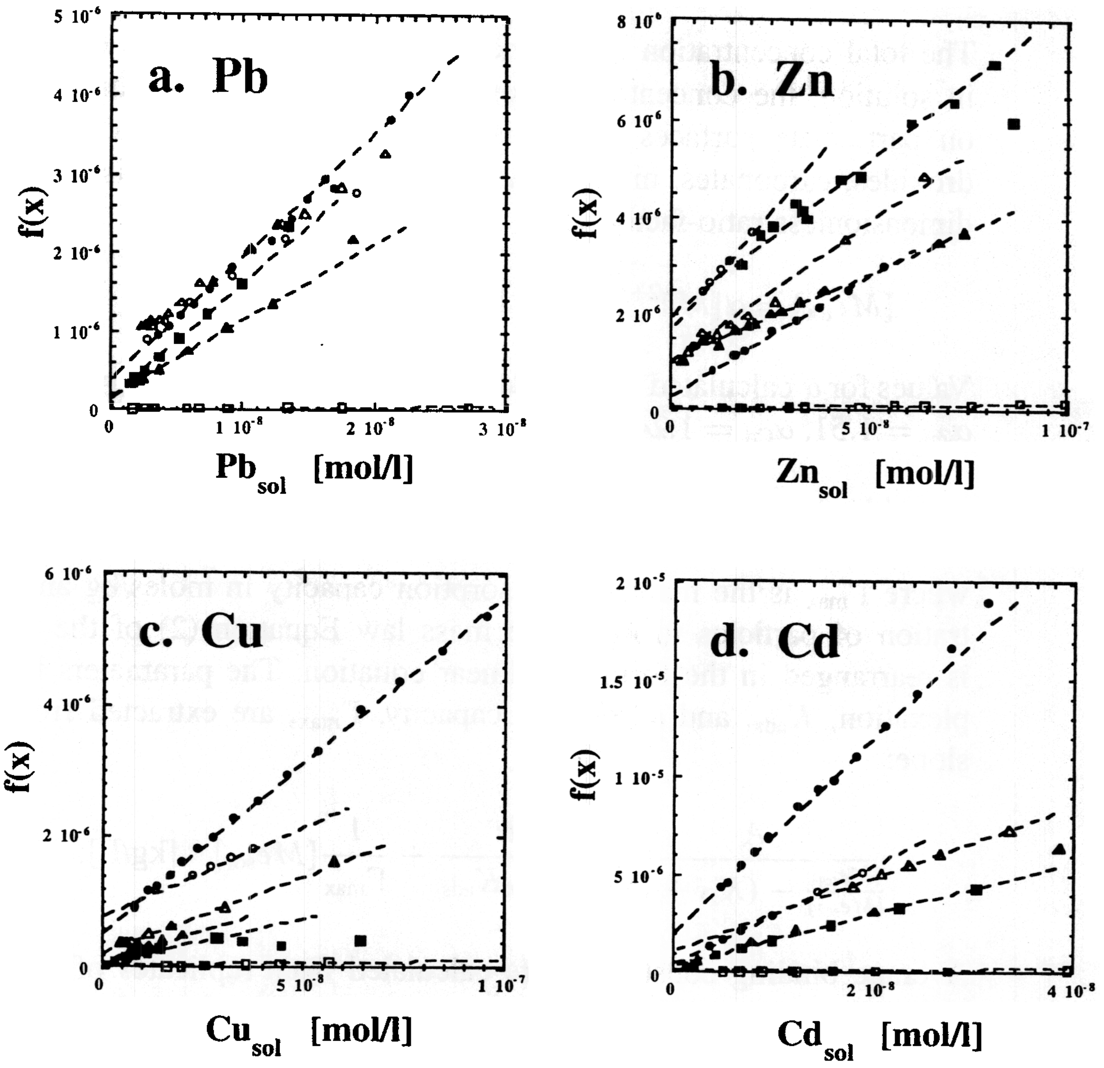

Figure 1. Representation of four titration experiments of (a) Pb, (b) Zn, (c) Cu, and (d) Cd with γ-MnOOH (□), goethite (△), river Glatt sediment (●), marine sediment trap material from the Gotland Deep (○), sewage from a municipal treatment plant (▲) and *Beggiatoa* A bacteria (■). The y-axis, $f(x)$, is the function calculated according to Equation (6). The first few titration points when adsorption densities are extremely high do not fall on a straight line. Later in the titration at lower metal : particle ratios the points fit the straight line indicating that the model assumption is fulfilled and that a single binding constant suffices to describe the sorption process in this range of metal : particles.

This may be due to electrostatic repulsion and the formation of a variety of surface complexes with different stoichiometry as there is a high density of sorbed metal ions on the particle surfaces. The sorption densities (Γ) calculated for these situations were in the same range or even higher than $\Gamma_{\max}$ extracted from the whole titration curve. Polarographic determinations showed that sorption equilibria were not attained within the time scale of the measurement of 0.5 hours. Additionally, the accuracy of the voltammetric determination of free trace metal and particle concentrations had a larger effect on the parameters of the linear function of Equation (6) than at lower metal : surface ratios. The majority of sorption sites cannot be treated as chemically equal at such high surface coverage. This is supported by the observation of Balistrieri and Murray (1983) that binding energies are dependent on adsorption density when sites are limited (very low particle concentration) and are independent of adsorption density when sites are available in excess.

The examples of particles chosen for Figure 1 included γ-MnOOH which showed an exceptionally high number of surface binding sites for all metals indicated by the low slope. The binding constants however, were similar to those of other particles. On the other hand, the set of sediment particles from the Glatt river gave rather low binding capacities for all trace metals, although binding constants were not different from those of other particles investigated.

The sorption constants determined were dependent on the composition of the suspensions. The spectrum of surface sites that interact with metal ions was not characterized in detail, e.g., by modeling a variety of individual chemically different sites, however a 'single' surface ligand was assumed to predominate over each concentration range investigated. Effects of electrostatic attraction or repulsion on the sorption process are incorporated in the conditional constants. Thus, the conditional constants merge site heterogeneity (various sites with a range of affinities) and electrostatic effects in the concentration range and condition (constant pH and ionic strength) of the experiment. Complexing sites with higher binding energies however, appear at significantly lower concentrations of free metal ion (when we apply NTA as a metal buffer as described later in this paper).

The most reactive surface ligands of the heterogeneous mixture of natural particulate matter consisted of amorphous hydrous oxide surfaces, carbonates, and organic functional groups such as –OH, –COOH, $-NH_2$, –SH etc. The composition of this mix differed widely within the set of particles we selected. The narrow range of binding constants for each metal with different particulate surfaces suggested that similar types of complexing functional groups were predominant in all particles (Stumm, 1992, p. 378). Differences in binding energies of these ligands may have been small hence no significant bends in the titration curves were caused. The affinity spectrum of surface binding sites (Buffle et al., 1990) consists of a small percentage of high affinity sites and increasing parts of surface sites with lower binding energies. Since our titration procedure started at high surface coverage with metal ions and proceeded to lower surface coverage, the functional surface groups with the largest number dominated in the titration. Less abundant sites with higher affinities would appear only at very small metal : particle ratios. The set-up of the titration however, undervalued this condition such that at our range of metal: particle ratios the sites prevalent dominated in the sorption process.

Table 2 presents experimental constants for adsorption ($\log K_{\mathrm{ads}}$) and maximum binding capacities ($\Gamma_{\max}$) for the trace metals Zn, Pb, Cd, and Cu. The data show considerable consistency among the conditional surface binding constants of each metal in spite of the variety of particles.

Conditional binding constants for Zn^{2+} ranged from 7.78 to 8.63 (mean $\log K_{\mathrm{Zn}}^{\mathrm{ads}} = 8.39$ (SD 62%, $n = 12$). The lowest $\log K_{\mathrm{ads}}$ were observed for γ-MnOOH with its very high surface area and for river Rhine sediments that had a small

Table II. Conditional surface complexation constants (log K_{ads}) and maximum adsorption capacities (Γ_{max}) for Zn^{2+}, Pb^{2+}, Cd^{2+}, and Cu^{2+}, from titration experiments with different natural aquatic particles. pH was 8.0 in solutions with 10^{-2} M KNO_3 and 10^{-3} M HCO_3^- in equilibrium with 0.05% CO_2 in N_2.

	Zn		Pb		Cd		Cu	
		Γ_{max} [mol/kg]		Γ_{max} [mol/kg]		Γ_{max} [mol/kg]		Γ_{max} [mol/kg]
1. River Rhine sed.	7.84	$1.4\ 10^{-2}$	9.38	$3.4\ 10^{-3}$	7.43	$7.0\ 10^{-4}$	9.57	$3.9\ 10^{-3}$
2. River Glatt s.m.	8.33	$1.7\ 10^{-2}$	9.83	$6.4\ 10^{-3}$	8.37	$1.9\ 10^{-3}$	9.54	$1.9\ 10^{-2}$
3. Gotland deep s.m.	7.91	$1.1\ 10^{-2}$	9.44	$8.5\ 10^{-3}$	8.97	$3.9\ 10^{-3}$	9.66	$4.7\ 10^{-2}$
4. Kirr Bay s.m.	8.44	$8.7\ 10^{-3}$	9.25	$1.7\ 10^{-2}$	8.29	$1.1\ 10^{-2}$	10.44	$5.7\ 10^{-2}$
5. Kirr Bay fl.	8.53	$1.6\ 10^{-3}$	9.40	$1.5\ 10^{-3}$	8.16	$2.2\ 10^{-3}$	9.93	$6.8\ 10^{-2}$
6. Sewage sludge	8.24	$4.0\ 10^{-2}$	9.90	$1.0\ 10^{-2}$	8.65	$6.8\ 10^{-3}$	9.60	$5.6\ 10^{-2}$
7. *Beggiatoa* A	8.44	$7.9\ 10^{-3}$	10.24	$6.7\ 10^{-3}$	8.69	$7.7\ 10^{-3}$	9.60	$8.7\ 10^{-2}$
8. *Beggiatoa* B	8.67	$6.5\ 10^{-3}$	9.77	$1.1\ 10^{-2}$	9.05	$6.0\ 10^{-3}$	9.51	$8.8\ 10^{-2}$
9. Mn-nodule	8.71	$1.3\ 10^{-2}$	9.46	$2.2\ 10^{-2}$	8.62	$8.8\ 10^{-3}$	9.71	$8.5\ 10^{-1}$
10. Na-Birnessite	8.58	$2.5\ 10^{-2}$	9.95	$3.8\ 10^{-2}$	8.84	$2.6\ 10^{-2}$	9.49	$7.6\ 10^{-2}$
11. γ-MnOOH	7.78	$7.0\ 10^{-1}$	9.77	$6.1\ 10^{-1}$	7.68	$3.9\ 10^{-1}$	9.58	$7.5\ 10^{-1}$
12. Goethite	8.11	$1.8\ 10^{-2}$	9.32	$8.8\ 10^{-3}$	8.25	$5.7\ 10^{-3}$	9.87	$5.0\ 10^{-2}$
13. Reckingen s.m.			9.31	$3.3\ 10^{-3}$				
14. Lobith s.m.			9.12	$1.4\ 10^{-2}$				
15. E. coli			8.87	$2.9\ 10^{-2}$				
16. δ-Al_2O_3			10.00	$9.6\ 10^{-3}$				
17. γ-MnOOH(2)			9.07	$4.7\ 10^{-2}$				
18. δ-MnO_2			9.22	$3.7\ 10^{-2}$				

surface area. Mn minerals produced the highest sorption capacities of all particles investigated.

Log K_{ads} for Pb^{2+} ranged from 8.82 to 10.24 (average log $K_{Pb}^{ads} = 9.67$ (SD 90%, $n = 18$). The lowest value was obtained from the purely organic surfaces of E. coli bacteria. As for Zn, we found the highest Γ_{max} for the Mn-oxides and the lowest Γ_{max} for the Kirr Bay fluffy material. No correlation between log K_{ads} and particle composition was found.

Binding constants for Cd^{2+} were between 7.43 and 9.05 (average log $K_{Cd}^{ads} =$ 8.61 (SD 85%, $n = 12$). As for Zn, low values were obtained for γ-MnOOH and river Rhine sediment. They did not correlate with particle compositions or surface areas otherwise. Sorption capacities were highest for the Mn-oxides and were very low for the Kirr Bay fluffy layer and river sediments as already observed for both Zn and Pb.

Conditional constants for Cu^{2+} were similar (between 9.49 and 9.93) with the exception of the Kirr Bay suspended matter (10.44), (average log $K_{Cu}^{ads} = 9.71$, SD 42%, $n = 11$). The Kirr Bay s.m. had an exceptionally small surface area (1.2 m^2/g) and the highest content of organic material. However, high content of organic carbon does not necessarily mean high surface complexation since other samples with high TOC values (e.g., sludge and *Beggiatoa*) have average binding constants. As for Cd, the lowest sorption capacities were measured for two river sediments, and the highest values obtained were again for the Mn-oxides. The values for all other particle samples were in a relatively narrow range of 0.05 to 0.09 mol/kg.

Considering the large spectrum of origin and composition of the particles, the scattering of the binding constants for all metals was remarkably small. We only found a few low complexation constants. These occurred with particulate matter of comparatively high adsorption capacities (Zn and Cd with γ-MnOOH, and Zn and Cd with river Rhine sediment). A few binding energies were above the average for particles of relatively low adsorption capacities (Pb with *Beggiatoa* A; Cd with *Beggiatoa* B). There was no apparent correlation between log K_{ads} and specific surface area or chemical particle composition. However, the highest sorption capacities for all trace metal ions were the Mn-oxides. Although we only had the specific surface for one Mn sample it is known that Mn oxides form small particles with high surface area (Stumm, 1992). Naturally and in agreement with the surface complexation models, the number of complexing sites per surface area is important and the sorption capacity is directly related to the surface area. The surface functional groups, however, are similar to hydroxyl groups of other metal oxides and thus variance in binding constants is low. This is consistent with what we observed for the Mn-oxides and typically for the γ-MnOOH (No. 11) where sorption capacities were extremely high for all metals, although binding constants were among the lowest of all samples.

Log K_{ads} was independent on specific surface areas. Even though surface areas from the Mn nodule and the Kirr Bay suspended matter (Table 2) differed by a factor of 100, binding constants of all metals were similar. The linear relationship between sorption constants and binding constants for solution complexes of OH^- or CO_3^{-2} as documented e.g., by Dzombak and Morel (1990) was not as pronounced as for the iron oxides, even though our sorption constants were similar to those presented by Dzombak and Morel (Table 3). This may be due to an increasing influence of 'soft bases', complexing surface sites such as amines, sulfides, organic acids, phenolic groups, etc., which competed with hydroxyl sites. Each metal interacts differently with these ligands, according to its tendency to form complexes with 'soft bases'. The small standard deviation of the conditional binding constants indicated that the surfaces of the aquatic particulate matter investigated may not vary too much. The sorption constants being more specific for the type of the sorbing metal ion than for the different particles suggested that the binding sites of the particle surfaces were of similar chemical constitution. The consistency of the binding constants in spite of the variety of particle samples suggested that only small variations in binding energies for various surface ligands occurred such that the differences in log K_{ads} were in the range of the standard deviation of all experiments.

Copper had the highest sorption capacity values of all metals ranging from $3.9 \cdot 10^{-3}$ to 0.75 mol/kg. The ratios for binding capacities were on an overall average for Pb : Zn : Cd : Cu = 1.9 : 2.2 : 1 : 10.6 (normalized to Cd with standard deviations around ±50% and omitting data from the river Rhine sediment). Zinc sorption capacities were 2–3 times higher than those for Pb and Cd when particles had increased Fe contents. Lead sorption capacities were 1.5–2 times higher than those for Zn and Cd when the particles composition was dominated by Mn. This contradicted observations of Coston et al. (1995) who found Pb adsorption to decrease with decreasing content of Fe minerals whilst Zn adsorption remained unaffected.

Table 3 is a collection of surface complexation constants of Zn, Pb, Cd, and Cu with environmental particles from other authors. Literature offers complexation constants for various models, e.g.

$$Me_{\mathrm{sol}} + \equiv L \rightleftarrows\ \equiv L\ \ Me \quad \text{(constant pH)} \tag{I}$$

$$Me^{2+} + \equiv L \rightleftarrows\ \equiv L\text{·}\ \text{·}Me \quad \text{(constant pH)}$$

$$Me^{2+} + \ \equiv LH \rightleftarrows\ \equiv L\text{·}\ Me^{+} + H^{+}$$

These may be converted as long as enough information on solution composition is given. Ionic strength is usually low (<0.1 M) and effects on binding constants are neglected. Speciation must be considered in surface complexation constants, otherwise they are not adaptable to other concentrations of anions or pH conditions of natural waters. The influence of the electrical double layer cannot be accounted for in the transposition of binding constants if $\mathrm{pH_{ZPC}}$ (zero proton condition) is not known for the particulate surfaces. Equation (III) is the most preferable form

Table III. Apparent surface complexation constants log K_{ads} for Zn^{2+}, Pb^{2+}, Cd^{2+}, and Cu^{2+} and various natural aquatic particles for the reaction : $Me^{2+} + \equiv L\text{-}H = \equiv L\text{-}Me^{+} + H^{+}$. The type of particles, model equation used by the authors, and analytical methods are given in subsequent columns.

Literature	Zn^{2+}	Pb^{2+}	Cd^{2+}	Cu^{2+}	Particles	Equation type	Method
This work	0.29	1.50	0.40	1.68	Average of 12 different	II ($x = 1$)	DPASV
Müller and Sigg (1990)	0.35	2.61			River susp. matter	II ($x = 1$)	DPASV
Müller (1989)			1.0	1.73	River sediment	II ($x = 1$)	DPASV
Dzombak and Morel (1990)	0.99	4.65	0.47	2.89	Fe-oxides		
Vorha and Davis (0000)		1.2			TiO_2	III	
Xue et al. (1988)			−0.6	1.3	Algae (lake)	II	DPASV
Palmqvist et al. (1997)	−2.0	0.17	−2.22	0.9	Goethite	III	DPASV
Gonçalves et al. (1985)		−2.0/1.25			Goethite/MnO_2	III	DPASV
Gonçalves et al. (1987)	−1.27, −0.13	−0.57, 0.57		0.24, 0.46	Bacteria	I (α calc.)	DPASV
Davis et al. (1998)	−2.20				Cape Cod sediment	III ($x = 1$)	filtr./ICP-AES
Fein et al. (1997)		−0.62	−1.42	−0.42	Bacteria: carboxyl sites	III	filtr./AAS
		−1.30	−1.50	−0.90	phosphate sites		
Balistrieri and Murray (1983)	−0.56				Ocean sediment	III ($x = 0.64$)	filtr./AAS
	−3.3		0.05	−1.35	Goethite in seawater	III	
Wen et al. (1998)			−1.960	−0.766	River sediment	III FITEQL	filtr./AAS
Bourg and Mouvet (1984)	−1.3	−0.85*	−1.5	−0.9	Estuary susp. matter	III	centrif./AAS
Mouvet and Bourg (1983)	−3.6	−1.7*	−3.7	−1.8	Freshwater particles	III	centrif./AAS
Wang et al. (1997)	−4.09	−2.74	−4.77	−2.99	River surface sed. ($n = 11$)	III FITEQL	DPASV
Hamilton-Taylor et al. (1997)		−4.94	−6.22	−5.57	Freshwater particles	III (no spec.)	filtr./AAS

*Estimated.

to express binding constants since it compensates for solution complexation of the metal ion and includes pH in the mass law equation. Equation (I) can be transferred to Equation (III) with the speciation coefficient α and pH, and Equation (II) by knowing the pH and proton exchange coefficient. Thus, in order to transpose reaction constants that were determined at a different pH (according to Equation (III)) the stoichiometric coefficient should be known. For conversion we assumed that one H^+ was exchanged at the adsorption of one metal ion ($x = 1$). In fact most authors working with natural particulate matter use this basic assumption. Hamilton-Taylor et al. (1997) and Mouvet and Bourg (1983) were able to fit their experiments on natural particulate matter with a stoichiometry of one proton released per metal ion sorbed in the narrow pH range of natural waters (5–9). Davis et al. (1998) modeled the pH dependent sorption of Zn using a marine sediment sample with a proton coefficient of either 1 or 2. Balistrieri and Murray (1983) found $x = 0.64$ for the sorption of Zn in ocean sediment, but $x = 1$ (Cu and Zn) and $x = 0.37$ (Cd) for the adsorption to goethite in seawater. Due to the large concentration range in their titration experiments, they demonstrated the decrease of the surface binding constants for Cu, Cd, and Zn when sorption densities exceed the limit of $\log \Gamma > -2.5$ [moles Me_{ads}/moles surface sites].

The literature data in Table 3 were transposed to the form of Equation (III) as mentioned in the caption. It should be noted that constants in Table 3 are conditional for the ionic medium because surface speciation, or competition with bulk ions, were not included in the constants. The effect of electrostatic interaction may be rather small for mineral particles since neutral surface species dominate in an almost neutral pH range and for a wide range of ionic strengths and metal ion sorption (Dzombak and Morel, 1990). With increasing content of organic carbon, however, surface charge becomes negative due to deprotonated organic functional surface groups. The range of binding constants is quite large, where the values of Hamilton-Taylor et al. (1997) and Wang et al. (1997) who used freshwater particles and river sediments, respectively, are the smallest. Hamilton-Taylor et al. (1997) did not consider metal speciation in their adsorption equation but estimated that the free Me^{2+} aquoions were generally predominant throughout the pH range used in their experiments (though this may not necessarily be the sorbing species). Our values are at the upper end of the range of binding energies and close to the numbers given by Dzombak and Morel (1990). The high values may be due to an underestimation of the proton exchange coefficient and pH-dependent sorption experiments must be performed to discuss this issue. It is remarkable that other experiments with high sorption constants also used DPASV as an experimental method. In spite of varying values the binding constants for Cu and Pb are similar and are 1 to 2 orders of magnitude higher than for Cd and Zn again being similar.

3.2. COMPETITION FROM Ca^{2+} AND NTA

Binding energy of sorption increases as site occupancy decreases (Honeyman and Santschi, 1988). This is explained by the abundance of high-energy sites in the affinity spectrum of the surface ligands. Indeed, at the end of several titration experiments (low metal: surface ratio) we observed a shift in the slope of the titration curve although the concentration range utilized for the method was too narrow to investigate the effect. Therefore, to investigate binding sites with higher sorption constants we performed

- Competition experiments with Pb(II) and Ca
- Competition experiments with Pb(II) and NTA.

For initial experiments Ca concentrations were increased from zero up to 1 mM in the presence of 10 ppb ($4.83 \cdot 10^{-8}$ M) Pb at a constant pH 8.0 (10^{-2} M KNO_3 and 10^{-3} M HCO_3^-) and titrated with suspended particles from river Glatt (No. 2). The sorption constant for Pb remained unaffected for all concentrations of Ca within the range of reproducibility. Also the binding capacity was not affected at low concentrations of Ca. It was only with the highest concentration of Ca (1 mM) that the sorption capacity for Pb decreased by about one third. From these data a conditional binding constant for the sorption of Ca

$$\equiv L + Ca \rightleftarrows \equiv L - Ca$$

of log $K_{Ca}^{ads} = 2.5$ was estimated (pH 8.0). The increase of binding constants is explained by the abandonment of sorption sites less favourable to Pb for the sorption of Ca^{2+}. At pH 8.0 most natural particulate matter carries a negative surface charge. The sorption of Ca suggests that the binding ligands are unspecific and electrostatic attraction or repulsion may be more effective than for the smaller B-type cations.

The second set of data in Table 4 shows sorption constants from similar titration experiments with Pb in the presence of various concentrations of NTA. The effect of NTA is that of a metal buffer and its effect on the adsorption process can be modeled as a competition with surface sites for the metal ions. pH-dependent sorption isotherms with NTA on Goethite showed the adsorption edge in the pH-range 5–7. At pH 8 NTA sorption was negligible. Vorha and Davis (1997) performed a study on sorption of Pb and NTA on TiO_2. Beneath individual sorption of Pb^{2+} and NTA to the surface they used a ternary anionic type ($\equiv$Ti-NTA-Pb^0) as well as a cationic type ($\equiv$Ti-OPb-NTA^{-2}) surface complex to model their adsorption isotherms in the pH range 2–9. The separate surface complexes $\equiv$Ti-OPb^+ and $\equiv$Ti-NTA^{-2} dominated the adsorption over the whole pH range. NTA showed anion-type sorption behavior, i.e., surface binding increased with decreasing pH. The surface complexation constant of NTA adsorption to TiO_2 was given as

$$\equiv \text{TiOH} + \text{NTA}^{-3} + \text{H}^+ \rightleftarrows \equiv \text{Ti-NTA}^{-2} + \text{H}_2\text{O} \quad \log K = 14.43$$

and showed negligible adsorption at pH 8.0.

Table IV. Maximum adsorption capacities and conditional surface complexation constants from titration experiments of 10 ppb Pb with river Glatt suspended particles. The solution consists of $4.83 \cdot 10^{-8}$ M Pb, 10^{-2} M KNO_3, 10^{-3} M HCO_3^-, and the various concentrations of $CaCl_2$ and Na_3NTA as indicated in the first two columns.

$[Ca^{2+}]$ [moles/l]	[NTA] [moles/l]	Γ_{max} [moles/kg]	$\log K_{ads}$
0	0	$6.83 \cdot 10^{-3}$	9.83
10^{-4}	0	$7.68 \cdot 10^{-3}$	9.82
$3 \cdot 10^{-4}$	0	$6.79 \cdot 10^{-3}$	9.79
10^{-3}	0	$4.52 \cdot 10^{-3}$	9.91
0	10^{-8}	$5.37 \cdot 10^{-3}$	9.65
0	$2 \cdot 10^{-8}$	$4.11 \cdot 10^{-3}$	9.72
0	$5 \cdot 10^{-8}$	$1.78 \cdot 10^{-3}$	10.78
0	10^{-7}	$1.67 \cdot 10^{-3}$	11.20
0	10^{-6}	$1.52 \cdot 10^{-3}$	11.73
10^{-3}	10^{-7}	$3.47 \cdot 10^{-3}$	10.00
10^{-3}	$5 \cdot 10^{-7}$	$2.40 \cdot 10^{-3}$	10.24
10^{-3}	10^{-6}	$1.52 \cdot 10^{-3}$	10.79

In our experiments, very small free concentrations of Pb were established in the presence of varying concentrations of NTA. As a result, binding constants increased significantly. The free concentration of Pb^{2+} (before addition of particle suspension) was almost 100 times smaller for the solution with 10^{-6} M NTA than for that without. The complexing capacities decreased with decreasing concentration of free Pb^{2+}. This is explained by the higher sensitivity of the analytical method to detect surface sites with higher sorption energy due to the much smaller range of Pb concentration covered by the titration. The concentration range of free Pb^{2+} during the titration without NTA was $1.7 \cdot 10^{-9}$ M to $2.4 \cdot 10^{-10}$ M. In the presence of 10^{-6} M NTA it was $5.2 \cdot 10^{-11}$ M to $5.3 \cdot 10^{-12}$ M Pb^{2+}. With this smaller concentration range the method revealed that metal ions prefer a range of high affinity sorption sites with higher binding energies which occur in small concentration on the surface (Buffle et al., 1990).

A crucial experiment with Pb, Ca, and NTA was performed to validate the constants extracted from the former experiments with a chemical speciation model. In the presence of 1 mM Ca and various concentrations of NTA (third set of data in Table 4) the largest part of Pb was complexed by NTA. Due to the small free concentration of Pb mainly high affinity sites were occupied indicated by the

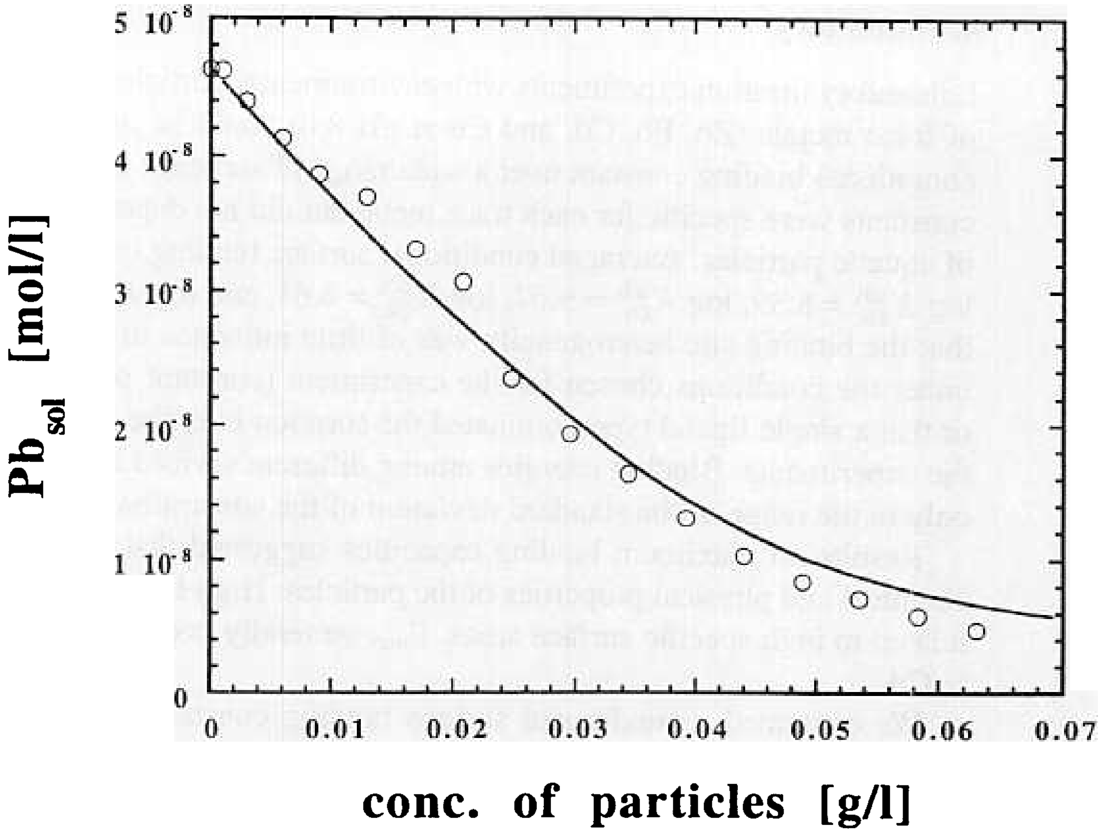

Figure 2. Experiment (dots) and model results (line) of the voltammetric titration experiment of 10 ppb ($4.83 \cdot 10^{-8}$ M) Pb with suspended river Glatt particulate matter in the presence of 10^{-2} M KNO_3, 10^{-3} M HCO_3, 10^{-3} M Ca, 10^{-6} M NTA in equilibrium with N_2/CO_2 (0.05%) at pH 8. Pb disappears from the solution due to increasing concentration of particulate matter. Ca surface complex is considered with the above estimated constant of $\log K_{Ca}^{ads} = 2.5$. No electrostatic interactions are considered. The particles contained $4.55 \cdot 10^{-4}$ moles/kg of desorbable Pb that was considered in the modelling.

high sorption constants. The presence of Ca allowed consideration of competition between the metal ions. Figure 2 illustrates the titration experiment of Pb with river Glatt particle suspension in the presence of 10^{-3} M Ca and 10^{-6} M NTA at pH 8.0. Good agreement was obtained when the titration curves were modeled using the experimental constants from Table 4.

These experiments at very low free metal concentrations showed that surface complexation depended on the metal : particles ratio. Sorption could be described with a single constant only for a limited range. When the concentration range of the sorbing metal fell below a certain limit a different (much smaller) spectrum of surface sites was occupied and detected by the experimental procedure. Surface sites with higher affinity towards the metal became more important and were reflected in the binding constant. The good fit of our titration experiments with only one surface complex of Pb at pH 8.0 is supported by the results of the study of Vorha and Davis (1997). The surface complexation constant for the adsorption reaction (Table 3) is close to the value extracted from our experiments with natural particulate matter.

4. Summary

Laboratory titration experiments with environmental particles showed that sorption of trace metals (Zn, Pb, Cd, and Cu at pH 8.0) could be described with a single conditional binding constant over a wide range of sorbent : surface ratios. Sorption constants were specific for each trace metal but did not depend on the composition of aquatic particles. Averaged conditional surface binding constants (pH 8.0) were $\log K_{\mathrm{Zn}}^{\mathrm{ads}} = 8.39$, $\log K_{\mathrm{Pb}}^{\mathrm{ads}} = 9.67$, $\log K_{\mathrm{Cd}}^{\mathrm{ads}} = 8.61$, and $\log K_{\mathrm{Cu}}^{\mathrm{ads}} = 9.84$. It appeared that the binding site heterogeneity was of little influence to the sorption constants under the conditions chosen for the experiment (constant pH and ionic strength), or that a single ligand type dominated the sorption over the concentration range of the experiments. Binding energies among different surface ligands seemed to vary only in the range of the standard deviation of the adsorption constants.

Results on maximum binding capacities suggested that they are a function of chemical and physical properties of the particles: High $\Gamma_{\max}$ for all metal ions were related to high specific surface areas. $\Gamma_{\max}$ generally decreased from Cu $\gg$ Pb, Zn $>$ Cd.

We estimated a conditional surface binding constant for Ca^{2+} of $\log K_{\mathrm{Ca}}^{\mathrm{ads}} = 2.5$ at pH 8.0 from competition experiments with Pb. Surface titration experiments with Pb in the presence of the metal buffer NTA produced increased conditional binding constants and a decrease in the concentration of corresponding surface sites ($\Gamma_{\max}$). This suggests that the heterogeneous mix of sites was composed of a spectrum of binding energies and hence complexation constants depended on the concentrations of metals and particles which were detectable only at very low metal : particle ratios.

Acknowledgement

We like to thank Daniel Kobler who generously performed the BET- and size distribution experiments, and Erwin Grieder and Toni Maresh who did the chemical analyses. Discussions with Werner Stumm and the suggestions of two reviewers helped to improve the manuscript. Support and encouragement by Michael Kersten is highly appreciated. Dave Howson took care of the English. Funding for A. Duffek was provided by the Deutsche Forschungsgemeinschaft (project “Graduiertenkolleg – Integrative Analyse gezeitenloser Küstenökosysteme” at Rostock University).

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