Biogeochemistry **23**: 21–34, 1994.

Suspended particulate oxides and organic matter interactions in trace metal sorption reactions in a small urban river

LESLEY A. WARREN & ANN P. ZIMMERMAN
Department of Zoology, University of Toronto, Toronto, Ontario, M5S 1A1, Canada

Received 19 January 1993; accepted 19 November 1993

Key words: metal complexation, organic matter, oxides, suspended sediments

Abstract. The relative scavenging abilities of suspended particulate oxides (SPOX), and organic matter (SPOM) for Cd, Zn and Cu were evaluated in a small, anthropogenically influenced river. In addition, the factor most important in influencing the sorption density (A_d: metal concentration associated with a given phase divided by the concentration of that geochemical phase in the suspended particulate pool) of each metal to SPOX and SPOM were identified through multiple linear regression analyses from the suite of: pH, temperature, dissolved metal concentration, and the concentration of the other particulate fraction. Results indicate that SPOX-SPOM interactions do occur in trace metal complexation reactions; and interactions are both phase and cation specific. Fe oxides are able to outcompete discrete organic binding sites for Cu and Zn as a relative decrease in the amount of these two cations sorbed to organic matter was observed with increasing particulate Fe oxides. SPOM concentration was identified as being most important in influencing Cu sorption densities associated with the SPOX fraction. Organic matter – oxide complexes are postulated to occur that enhance oxide sorption of Cu such that relatively more Cu is sorbed to particulate oxides with increasing particulate organic matter concentrations. Dissolved concentrations of Cd and Zn were found to be most important in influencing the sorption densities for these two metals associated with the oxides fraction. The sorption behaviour appears to follow Freundlich isotherm behaviour where the amount sorbed is a function of the dissolved concentration.

Introduction

Trace metal complexation by particulates in aquatic systems has received a great deal of attention in the last two decades due to ever increasing contamination problems (e.g., Erel & Morgan 1991; Chen et al. 1989; Clegg & Sarmiento 1989; Probst 1986). While a trace metal sorption paradigm has yet to be completely described, some pieces of this complex puzzle have emerged: It is generally held that sorption processes at the solid surface are the principal mechanism governing trace metal particulate interactions (Stumm & Morgan 1981); thus pH is the master variable in trace metal complexation due to its controlling influence on these reactions (Johnson 1990; Benjamin & Leckie 1981).

Sediment geochemistry plays a key role in determining trace metal complexation, transport and ultimate fate as not all geochemical phases are equally adept at scavenging, or exposed at the particulate surface to participate in trace metal sorption reactions. While clays can effectively scavenge trace metals due to their associated high surface areas, their role is thought to be predominantly as carrier particles for oxide and/or organic matter coatings (Helios-Rybicka & Forstner 1986; Jenne 1968). It is thought that most particles are coated by a surface film of oxides and/or organic matter which are the active binding sites for trace metals in aquatic systems (Tipping 1986; Davis 1984; Tipping & Heaton 1983; Davis & Gloor 1981; Vuceta & Morgan 1978; Whitney 1975). The role of oxides of Fe and Mn, and particulate organic matter as efficient scavengers of trace metals has been widely demonstrated (Bendell-Young & Harvey 1992; Lovgren & Sjoberg 1989; Balikungeri & Haerdi 1988; Tessier et al. 1985; Vuceta & Morgan 1978; Gardiner 1974). Thus particulate trace metal complexation can be viewed as a process principally controlled by surficial sorption reactions involving the adsorbed layer(s) of oxides and organic matter on particulate surfaces. Even though these layers may represent minute percentages of the solid mass.

Some pieces of the puzzle remain somewhat of a mystery. At constant pH the extent of metal binding is dependent on the concentration of available surface groups, and thus on the geochemical composition of the particles (Muller & Sigg 1990). However the processes involved remain unclear, and the effects are poorly understood (Honeyman & Santschi 1988; Clegg & Sarmiento 1989). Thus the exact nature of possible oxides – organic matter interactions in trace metal sorption reactions remains to be determined. Thermodynamic calculations demonstrate particle binding sites to be in excess in most systems, and thus, the possibility of competition between the two geochemical phases for trace metals is plausible, especially in oxic, high pH systems where sorption is favoured. Alternatively, organic matter may itself be sorbed to oxide surfaces. Its presence may create new sorption sites or stabilize previously nonfunctioning sites on the oxide. In either case, the sorptive capacity of the oxide is enhanced. Evidence for both scenarios exist in the literature (Turner et al. 1986; Laxen 1985; Buffle et al. 1984; Davis 1984; Frimmel et al. 1984; Lion et al. 1982).

Few studies evaluating either the relative scavenging abilities of suspended particulate organic matter (SPOM) and suspended particulate oxides (SPOX); or factors important in influencing metal adsorption densities associated with these phases in natural environments exist. The objectives of this study were: 1. to determine the relative affinities of SPOM and SPOX for Cd, Cu and Zn; and 2. to identify any interaction between the two sedimentary phases in sorption reactions in an urban impacted system (Don River, Toronto, Ontario, Canada). While pH in this system is relatively high (> 7.6 during sampling period), it also remains relatively static, playing no significant role in explaining variance in trace metal concentrations associated with particulate phases (Warren & Zimmerman 1993). Trace metal complexation in this system is thought to be primarily a function of available particulate binding sites.

Methods

As a detailed description of the methodology and study site have been given elsewhere (Warren & Zimmerman 1993, 1994), only a brief summary will be provided here. Suspended particulate matter (SPM) samples were isolated from Don River water by continuous flow centrifugation on ten occasions between October 1990 and February 1991. Samples were collected from the point of maximum flow at one site on the river by pumping river water into acid washed polypropylene carboys. Water samples for SPM analyses were separated by continuous flow centrifugation maintained at *in situ* temperatures, within 24 hours of collection. Samples for dissolved analyses were collected by filtering the centrifuge eluent (< 1 μm in size) through 0.45 μm filters.

For all analyses, all glassware, centrifuge tubes, and vials were acid washed in 10% HNO_3 and rinsed in ultrapure deionized water 5 times prior to use. Isolated SPM samples were divided into 4 aliqouts, each of which was subsequently analysed in 3 subsamples. The subsamples were used to extract one of 4 operationally defined geochemical phases using a simultaneous extraction scheme (Bendell-Young et al. 1992; Tessier et al. 1979). Fe and Mn oxides (SPOX) associated trace metals were estimated by the reducible extraction step, and the oxidizable extraction step was used to estimate trace metals associated with the organic matter fraction (SPOM).

Filtered water samples for dissolved metals were divided into 3 subsamples of 500 mls, digested with hot HNO_3 and brought up to volume in 0.1 M HNO_3. Deionized water blanks were also filtered, digested and brought up to volume to account for any contamination of dissolved samples. Cd, Zn and Cu concentrations associated with the SPOX and SPOM fractions and with the dissolved pool, were determined by analyzing the supernatants with flame atomic absorption. The particulate Fe and Mn oxide content (SPOX) was determined as the sum of the Fe and Mn concentrations in the reducible fraction of the extraction scheme. The particulate organic content (SPOM) was determined by loss on ignition analyses at 550 °C for 1 hour. The complete dataset for metal and SPM concentrations, and other system parameters such as temperature, pH, and NaCl concentration, are provided in Warren & Zimmerman (1994).

NBS river sediment samples (NBS 2704 Buffalo River Sediment), were run through the extraction scheme as well, and the total phase 4 concentrations were compared to the certified total values for the sediment. NBS river sediment standards were within the certified ranges for all metals measured. Blanks run with every set of particulate associated samples indicated negligable contamination of glassware or reagents.

Statistical analyses were performed on untransformed data. A general linear model procedure (GLM; SAS 1987) was used to compare particulate concentrations of SPOM and SPOX ($mg \cdot g^{-1}$); and the SPOX (Me^{2+}_{ox}) and SPOM (Me^{2+}_{om}) associated concentrations (μmoles/g^{-1}) for each cation. Adsorption densities (A_d; μmoles/g^{-1}) were determined as $[Me^{2+}_{ox}]/[SPOX]$ for the oxide fraction (A_{dox}), and $[Me^{2+}_{om}]/[SPOM]$ for the particulate organic fraction (A_{dom}).

Multiple linear regression (MLR) analyses were used to identify which variables were most important in influencing A_ds from the following suite: pH, temperature, dissolved metal concentration for each cation ($mg \cdot l^{-1}$), and the concentration of the other particulate phase of interest ($mg \cdot g^{-1}$), e.g., in the analysis for A_{dox} Cd, SPOM concentration was entered, while in the analysis for A_{dom} Cd, Fe oxides and Mn oxides concentrations were entered.

This suite of variables were chosen for the following reasons. pH and temperature have been shown to be important variables influencing trace metal sorption reactions. Generally as pH and temperature increase, there is an increase in metal sorption to the solid phase (Barrow 1992; Brummer 1986). The dissolved metal concentration may be important if binding sites are in excess, and thus sorption reactions follow Freundlich isotherm behaviour (Tipping 1981). And, finally, if interactions between the two phases occurs in trace metal sorption reactions then the concentration of the other phase may be important in influencing adsorption densities. The first variable identified by the MLR analyses was subsequently input into a linear regression analysis (LR) with the A_d.

Results

SPOM concentrations ranging from 0 to 255 $mg \cdot g^{-1}$ were significantly higher than those of SPOX which ranged from 13·5 $mg \cdot g^{-1}$ to 119.6 $mg \cdot g^{-1}$ ($p < 0.01$; Table 1; Figs. 1a and 2a). SPOX associated Cd and Zn concentrations were significantly higher than their SPOM associated concentrations (Table 1; Figs. 1b,c and 2b,c). In contrast, SPOM associated Cu concen-

Table 1. Summary statistics from GLM analyses comparing concentrations of SPOM and SPOX ($mg \cdot g^{-1}$) within the SPM pool; and comparing concentrations of Cd, Zn and Cu associated with each geochemical fraction (μmoles$\cdot g^{-1}$).

	(x ± S.E.)		(x ± S.E.)	F	d.f.	$p =$	r^2
	SPOM		SPOX				
	151.5 ± 38.7	>	42.7 ± 9.8	7.42	19	0.01	0.29
	Me_{om}		Me_{ox}				
Cd	0.0002 ± 0.001	<	0.011 ± 0.003	5.83	19	0.02	0.24
Zn	0.49 ± 0.2	<	3.97 ± 1.2	8.71	19	0.008	0.33
Cu	0.93 ± 0.3	>	0.32 ± 0.1	4.64	19	0.04	0.20

trations were significantly higher than SPOX associated concentrations (Table 1; Figs. 1d and 2d). A_{dox} values for Cd and Zn are higher than A_{dom} values, while A_{dom} Cu values are higher than A_{dox} Cu values (Table 2). Metal concentrations associated with the SPOM and SPOX fractions do not increase linearly with increasing particulate concentrations of these fractions (Figs. 1 and 2); suggesting that other variables than the mass of particulate oxide or organic matter available for sorption, influence the concentration of cations associated with these phases.

Results from the MLR analyses for A_{dox} values revealed that dissolved concentrations were most important in influencing A_{dox} Cd and A_{dox} Zn

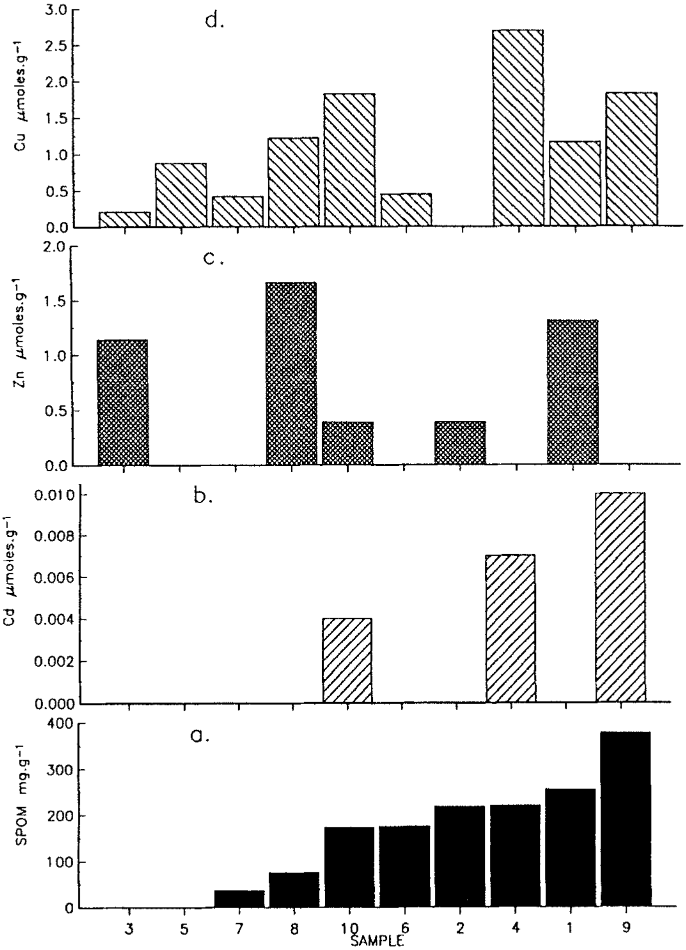

Fig. 1. Concentrations of SPOM (mg·g^{-1} (a)) and SPOM associated cations (μmoles.g^{-1}) across 10 samples: Cd (b), Zn (c) and Cu (d). Note that samples are ordered by increasing SPOM concentrations on the x axis. Also note scale differences on y axis for b, c and d.

Table 2. Sample and mean adsorption densities (A_d; μmoles·g^{-1}) for each metal associated with each geochemical phase.

Sample	A_{dox} Cd	A_{dox} Zn	A_{dox} Cu
1	0.032	3.05	0.65
2	0.04	3.23	0.39
3	0.02	0	0.14
4	0.01	8.36	0.59
5	0.01	4.82	0.26
6	0.02	4.30	1.29
7	0	0	0
8	0.12	19.59	0.28
9	0	3.51	0.56
10	0.26	47.83	0.25
$\bar{x}$ ± S.E.	0.05 ± 0.03	9.47 ± 4.6	0.44 ± 0.1
Sample	A_{dom} Cd	A_{dom} Zn	A_{dom} Cu
1	0	0.34	0.29
2	0	0.2	0
3	0	0	0
4	< 0.01	0	0.84
5	0	0	0
6	0	0	0.17
7	0	0	0.77
8	0	1.44	1.06
9	< 0.01	0	0.08
10	< 0.01	0.15	0.69
$\bar{x}$ ± S.E.	0.001 ± 0.0006	0.26 ± 0.2	0.49 ± 0.1

(Figs. 3 and 4). Both of the subsequent LR analyses (A_{dox} Cd versus dissolved Cd and A_{dox} Zn versus dissolved Zn) were positive, indicating a relative increase in the density of metal sorbed to the SPOX fraction with increasing dissolved metal concentrations. In both cases, most of the variance in A_{dox} values was explained by the dissolved metal concentration; $r^2 = 0.80$ for Cd, and $r^2 = 0.92$ for Zn. SPOM concentration was identified as the most important variable influencing A_{dox} Cu values by MLR analysis (Fig. 5). The subsequent LR analysis between A_{dox} Cu and SPOM was positive, indicating a relative increase in the density of Cu sorbed per unit oxide with increasing particulate organic matter concentration. However the relationship is weak, being statistically significant at the $p < 0.12$ level.

MLR analyses identified Fe oxides concentration specifically, as the most important variable influencing variance in both A_{dom} Zn and A_{dom} Cu. Both of the subsequent LR relationships were negative, indicating a relative decrease in the concentration of Zn or Cu sorbed to the SPOM fraction with increasing particulate Fe oxides concentration (Fig. 6). Concentrations of SPOM associated Cd above the detection limit were only observed in 3 out

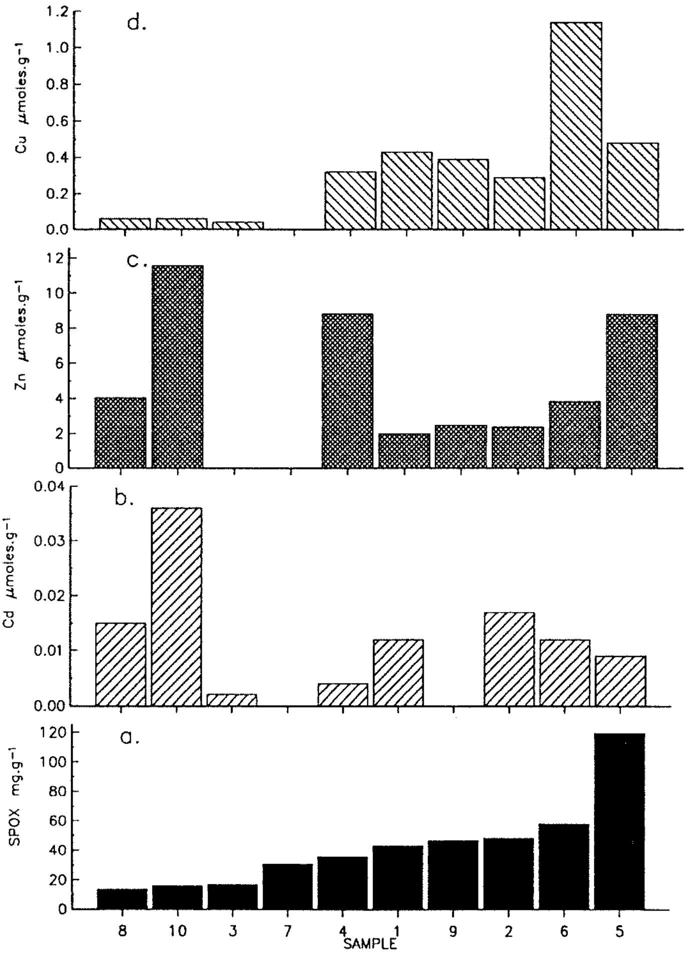

Fig. 2. Concentrations of SPOX (mg·g^{-1} (a)) and SPOX associated cations (μmoles·g^{-1}) across 10 samples: Cd (b), Zn (c) and Cu (d). Samples are ordered on the x axis by increasing SPOX concentrations, thus the order of samples differs from that in Figure 1. Note scale differences on y axis for b, c and d.

of the 10 samples (Fig. 1b). Thus the low degrees of freedom associated with any statistical analysis involving this variable excluded it from the analyses.

Discussion

The results of this study indicate that organic matter – oxides interactions do occur in trace metal sorption reactions, and play an important role in determining the amount of metal sorbed to particulate phases. These reactions appear to be both phase and cation specific. Enhanced oxide sorption of Cu was observed with increasing particulate organic matter concentration

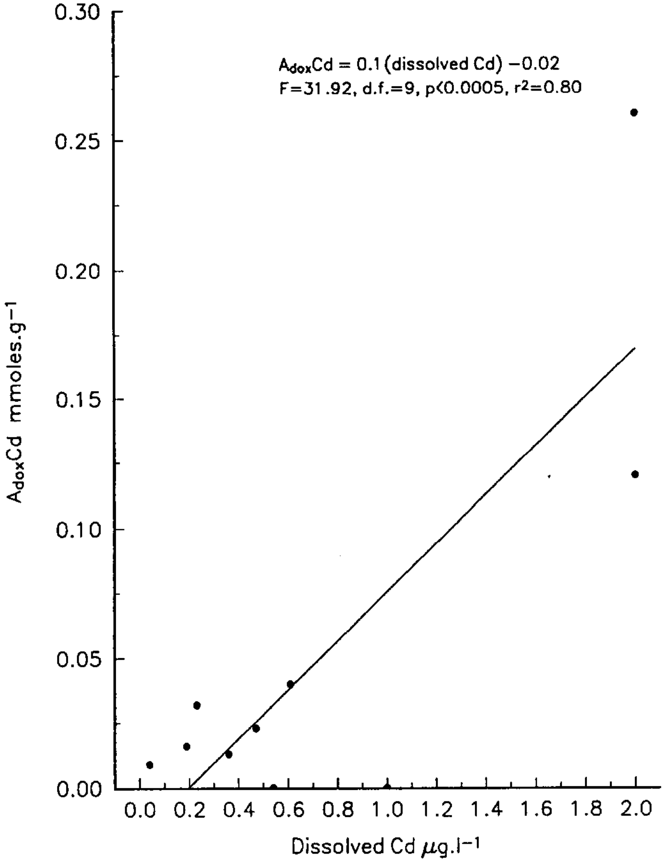

Fig. 3. $A_{dox}Cd$ versus dissolved Cd. Dissolved Cd was identified as the most important variable explaining variance in $A_{dox}Cd$ by MLR analysis. Subsequent LR summary statistics and the regression equation are shown on the figure.

(Fig. 5), but no organic matter influence on oxide sorption of Cd or Zn was found. Enhanced oxide sorption specifically of Cu in the presence of organic matter has been noted by other authors (e.g., Tipping 1986; Davis 1984; Bourg 1983; Inskeep & Baham 1983). Proposed mechanisms by which this may occur include a change from repulsive to attractive electrostatic interaction by the sorbed organic matter and the formation of oxide – Cu – organic matter bridges.

In contrast to the results for Cu, variance in both A_{dox} Cd and A_{dox} Zn is best explained by their respective dissolved concentrations (Figs. 3 and 4). As the dissolved concentrations of Cd and Zn increase in the Don, the relative concentration of these cations associated with the SPOX fraction also increases in an approximately linear fashion. These results are not surprising as the pH in the Don River is high and the SPM fraction is oxidized. Thus, sorption to oxides should be favoured, and as binding sites are in excess, sorption follows

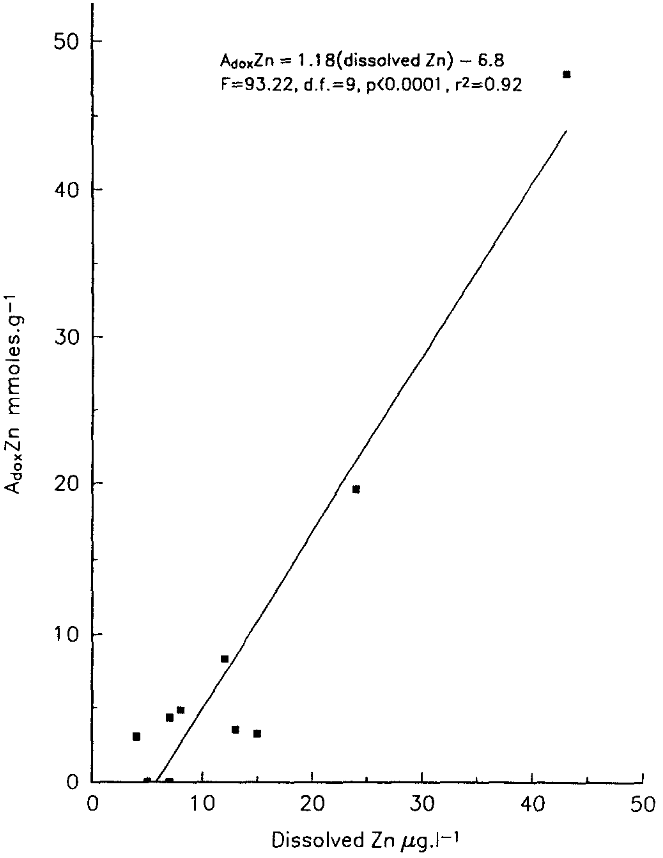

Fig. 4. $A_{dox}Zn$ versus dissolved Zn. Dissolved Zn was identified as the most important variable explaining variance in $A_{dox}Zn$ by MLR analysis. Subsequent LR summary statistics and the regression equation are shown on the figure.

Freundlich isotherm behaviour where the oxide associated concentration is a function of the dissolved ion concentration. The dissolved concentrations of Cd in the Don (in the order of 10^{-8}M; Fig. 3) fall within the range termed low to moderate by Dzombak & Morel (1986) for which they observed Cd sorption to Fe oxides to follow Freundlich isotherm behaviour in a laboratory study. Also as found in our study, Davis (1984) noted no significant effects on Cd sorption to oxides by organic matter.

Increasing Fe oxides concentrations associated with the suspended particulate pool decreased the relative concentration of both Cu and Zn sorbed to particulate organic matter (Fig. 6). The results for Cu indicate that the concentration of the other particulate fraction was the most important in explaining variance in the A_d values observed for each geochemical phase (Figs. 5 and 6b). Cu sorption to Fe oxides was enhanced by increasing concentrations of particulate organic matter (Fig. 5); while organic matter sorption

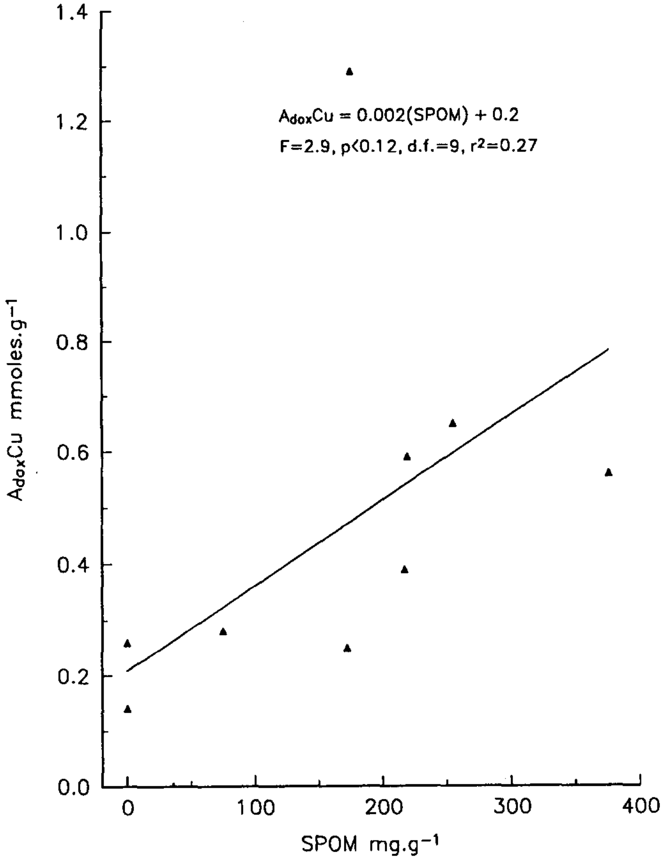

Fig. 5. $A_{dox}Cu$ versus SPOM. In contrast to the other A_{dox} analyses (see Figs. 3 and 4), variance in $A_{dox}Cu$ is best explained by SPOM concentration. LR summary statistics and the regression equation are shown on the figure.

of Cu was decreased by increasing concentrations of particulate Fe oxides (Fig. 6b). The results suggest that there are two mechanisms occuring in the sorption of Cu to oxides and organic binding sites: 1. competition between distinct oxides and organic matter binding sites with Fe oxides sites more effectively scavenging Cu; and 2. some oxides – organic matter complex formation which increases the sorptive capacity of the oxide for Cu. The results from this study on the Don, highlight the observations made by other authors that the binding intensity for the same solid depends on the cation involved e.g., strong binding sites for one metal are not necessarily preferred binding sites for other metal ions; and that different binding energy sequences are expected for the same cations with respect to different geochemical fractions (Hansen et al. 1990; Inskeep & Baham 1983; Benjamin & Leckie 1981; Vuceta & Morgan 1978).

Don River SPOX scavenges greater quantities of Cd and Zn than SPOM material, despite significantly lower SPOX concentrations (Table 1). The

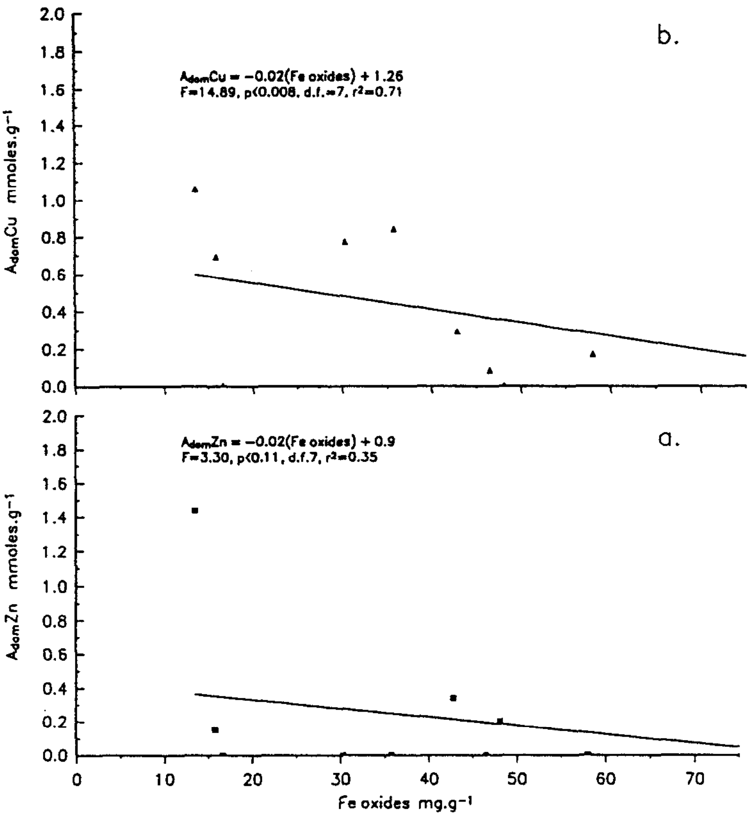

Fig. 6. $A_{dom}Zn$ (a) and $A_{dom}Cu$ (b) versus Fe oxides concentration which was identified as the best predictor variable for both MLR analyses. LR summary statistics and the regression equations are shown on the figure.

ability of oxides to scavenge trace metals despite being a small fraction of the overall mass of the solid pool is well documented (Tessier et al. 1989; Farley et al. 1985; Forstner & Wittmann 1981). Don River SPOM is probably more labile in nature due to treated sewage effluent entering the system, than nonanthropogenically influenced systems where refractory organic matter e.g., humic substances (HS) can be significant scavengers of trace metals (Tipping & Hurley 1992; Weber 1988; Fish et al. 1986; Perdue & Lytle 1983). However, significantly greater concentrations of Cu are associated with the SPOM fraction in comparison to the SPOX fraction (Table 1; Figs. 1d and 2d). These results provide further evidence for the cation specificity involved in trace metal sorption reactions. Previous results (Warren & Zimmerman 1994) have shown that distribution coefficient estimates for SPOM associated Cu (Cu_{SPOM}/dissolved Cu) are highest for the three cations examined, suggesting that Cu has a higher affinity for organic binding sites than the other two cations. This result is predicted by stability sequences for metal organic ligands which predict Cu will be bound preferentially over the other 2 metals (Smith

& Martell 1976; Stevenson 1976). In addition, other studies have demonstrated the strong affinity of organic matter for Cu (Pardo et al. 1990; Tessier et al. 1980).

Conclusions

Interactions between suspended particulate oxides and organic matter were demonstrated to occur in trace metal complexation reactions. These reactions are both phase and cation specific, and play an important role in determining the amount of metal sorbed to particulate oxides and organic matter in the Don River. Results from A_d analyses indicate that Fe oxides are able to out-compete discrete organic binding sites for Cu and Zn as a relative decrease in the amount of these two cations sorbed per unit organic matter was observed with increasing Fe oxides concentration. In contrast, organic matter oxide complexes are postulated to occur that specifically enhance oxide sorption of Cu such that relatively more Cu is sorbed per unit oxide with increasing particulate organic matter concentrations. Dissolved concentrations of Cd and Zn were found to be most important in influencing the sorption densities for these two metals associated with the oxides fraction. The sorption behaviour appears to follow Freundlich isotherm behaviour where the amount sorbed is a function of the dissolved concentration.

Acknowledgements

This work has been funded through an RAC grant to Ann P. Zimmerman from the Ontario Ministry of the Environment. Additional support was provided by an NSERC Operating Grant to APZ.

References

Balikungeri A & Haerdi W (1988) Complexing abilities of hydrous manganese oxide surfaces and their role in the speciation of heavy metals. Intern. J. Environ. Anal. Chem. 34: 215–225

Barrow NJ (1992) A brief discussion on the effect of temperature on the reaction of inorganic ions with soil. J. Soil Sci. 43: 37–45

Bendell-Young LI & Harvey HH (1992) The relative importance of manganese and iron oxides and organic matter in the sorption of trace metals by surficial lake sediments. Geochim. Cosmochim. Acta 56: 1175–1186

Bendell-Young LI, Dutton M & Dick F (1992) Contrasting two methods for determining trace metal partitioning in oxidized lake sediments. Biogeochemistry 17: 205–219

Benjamin MM & Leckie JO (1981) Conceptual model for metal-ligand-surface interactions during adsorption. Environ. Sci. Technol. 15: 1050–1057

Bourg ACM (1983) Role of fresh water/sea water mixing on trace metal adsorption phenomena. In: Wong CS, Boyle E, Burton JD & Goldberg ED (Eds) Trace Metals in Sea Water (pp 195–208). Plenum, New York

Brummer GW (1986) Heavy metal species, mobility and availability in soils. In: Bernhard M, Brinckman FE & Sadler PJ (Eds) The Importance of Chemical "Speciation" in Environmental Processes (pp 169–192). Springer-Verlag, Berlin

Buffle J, Tessier A & Haerdi W (1984) Interpretation of trace metal complexation by aquatic organic matter. In: Kramer CJM & Duinker JC (Eds) Complexation of Trace Metals in Natural Waters (pp 301–316). Junk Publ., The Hague

Chen J, Dong L & Deng B (1989) A study on heavy metal partitioning in sediments from Poyang Lake in China. Hydrobiol. 176/177: 159–170

Clegg SL & Sarmiento JL (1989) The hydrolytic scavenging of metal ions by marine particulate matter. Prog. Oceanog. 23: 1–21

Davis JA (1984) Complexation of trace metals by adsorbed natural organic matter. Geochim. Cosmochim. Acta 48: 679–691

Davis JA & Gloor R (1981) Adsorption of dissolved organics in lake water by aluminum oxide. Effect of molecular weight. Environ. Sci. Technol. 15: 1223–1229

Dzombak DA & Morel FMM (1986) Sorption of cadmium on hydrous ferric oxide at high sorbate/sorbent ratios: equilibrium, kinetics and modeling. J. Colloid Interf. Sci. 112: 588–598

Erel Y & Morgan JJ (1991) The effect of surface reactions on the relative abundances of trace metals in deep-ocean water. Geochim. Cosmochim. Acta 55: 1807–1813

Farley KJ, Dzombak DA & Morel FMM (1985) A surface precipitation model for the sorption of cations on metal oxides. J. Colloid Interface Sci. 106: 226–242

Fish W, Dzombak DA & Morel FMM (1986) Metal-humate interactions. 2. Aplication and comparison of models. Environ. Sci. Technol. 20: 676–683

Forstner U & Wittmann GTW (1981) Metal Pollution in the Aquatic Environment, 2nd Ed. Springer-Verlag, Berlin

Frimmel FH, Immerz A & Niedermann H (1984) Complexation capacities of humic substances isolated from freshwater with respect to copper (II), mercury (II) and iron (II,III). In: Kramer CJM & Duinker JC (Eds) Complexation of Trace Metals in Natural Waters (pp 329–344). Junk Publ., The Hague

Gardiner J (1974) The chemistry of cadmium in natural water – II. The adsorption of cadmium on river muds and naturally occurring solids. Wat. Res. 8: 157–164

Hansen AM, Leckie JO, Mandelli EF & Altmann RS (1990) Study of copper (II) association with dissolved organic matter in surface waters of three mexican coastal lagoons. Environ. Sci. Technol. 24: 683–688

Helios-Rybicka E & Forstner U (1986) Effect of oxyhydrate coatings on the binding energy of metals by clay minerals. In: Sly PG (Ed) Sediments and Water Interactions (pp 381–385). Springer-Verlag, Berlin

Honeyman BD & Santschi PH (1988) Metals in aquatic systems: predicting their scavenging residence times from laboratory data remains a challenge. Environ. Sci. Technol. 22: 862–871

Inskeep WP & Baham W (1983) Competitive complexation of Cd(II) and Cu(II) by water-soluble organic ligands and Na-montmorillonite. Soil Sci. Soc. Am. J. 47: 1109–1115

Jenne EA (1968) Controls on Mn, Fe, Co, Ni, Cu and Zn concentrations in soils and water: the significant role of hydrous Mn and Fe oxides. In: Baker RA (Ed) Trace Inorganics in Water (pp 337–387). ACS Publication #73, Washington

Johnson BB (1990) Effect of pH, temperature, and concentration on the adsorption of cadmium on goethite. Environ. Sci. Technol. 24: 112–118

Laxen DPH (1985) Trace metal adsorption/coprecipitation on hydrous ferric oxide under realistic conditions. Wat. Res. 19: 1229–1236

Lion LW, Altmann RS & Leckie JO (1982) Trace metal adsorption characteristics of estuarine particulate matter: evaluation of contributions of Fe/Mn oxide and organic surface coatings. Environ. Sci. Technol. 16: 660–666

Lovgren L & Sjoberg S (1989) Equilibrium approaches to natural water systems – 7. Complexation reactions of copper(II), cadmium(II) and mercury(II) with dissolved organic matter in a concentrated bog-water. Wat. Res. 23: 327–332

Muller B & Sigg L (1990) Interaction of trace metals with natural particle surfaces: Comparison between adsorption experiments and field measurements. Aquat. Sci. 52: 75–91

Pardo R, Barrado E, Perez L & Vega M (1990) Determination and speciation of heavy metals in sediments of the Pisuerga River. Wat. Res. 24: 373–379

Perdue EM & Lytle CR (1983) Distribution model for binding of protons and metal ions by humic substances. Environ. Sci. Technol. 17: 654–660

Probst JL (1986) Dissolved and suspended matter transported by the Girou River (France): mechanical and chemical erosion rates in a calcareous molasse basin. Hydrol. Sci. J. 31: 61–79

Smith RM & Martell AE (1976) Critical Stability Constants. Plenum Press, New York

Stevenson FJ (1976) Stability constants of Cu^{2+}, Pb^{2+} and Cd^{2+} complexes with humic acids. Soil Sci. Soc. Am. J. 40: 665–672

Stumm W & Morgan JJ (1981) Aquatic Chemistry, 2nd Ed. Wiley and Sons, New York

Tessier A, Carignan R, Dubreuil B & Rapin F (1989) Partitioning of zinc between the water column and the oxic sediments in lakes. Geochim. Cosmochim. Acta 53: 1511–1522

Tessier A, Rapin F & Carignan R (1985) Trace metals in oxic lake sediments: possible adsorption onto iron oxyhydroxides. Geochim. Cosmochim. Acta 49: 183–194

Tessier A, Campbell PGC & Bisson M (1980) Trace metal speciation in the Yamamaska and St. Francois Rivers (Quebec). Can. J. Earth Sci. 17: 90–105

Tessier A, Campbell PGC & Bisson M (1979) Sequential extraction procedure for the speciation of particulate trace metals. Anal. Chem. 51: 844–851

Tipping E & Hurley MA (1992) A unifying model of cation binding by humic substances. Geochim. Cosmochim. Acta 56: 3627–3641

Tipping E (1986) Some aspects of the interactions between particulate oxides and aquatic humic substances. Mar. Chem. 18: 161–169

Tipping E & Heaton MJ (1983) The adsorption of aquatic humic substances by two oxides of manganese. Geochim. Cosmochim. Acta 47: 1393–1397

Tipping E (1981) The adsorption of aquatic humic substances by iron oxides. Geochim. Cosmochim. Acta 45: 191–199

Turner DR, Varney MS, Whitfield M, Mantoura RFC & Riley JP (1986) Electrochemical studies of copper and lead complexation by fulvic acid. I. Potentiometric measurements and a critical comparison of metal binding models. Geochim. Cosmochim. Acta 50: 289–297

Vuceta J & Morgan JJ (1978) Chemical Modeling of trace metals in fresh waters: role of complexation and adsorption. Environ. Sci. Technol. 12: 1303–1315

Warren LA & Zimmerman AP (1994) The influence of temperature and NaCl on cadmium, copper and zinc partitioning among suspended particulate and dissolved phases in an urban river. Wat. Res. (accepted)

Warren LA & Zimmerman AP (1993) Trace metal/SPM associations in a fluvial system: physical and chemical influences. In: Rao S (Ed) Particulate Matter and Aquatic Contaminants (pp 127–155). CRC Press, Lewis Publ., Boca Raton.

Weber JH (1988) Binding and transport of metals by humic materials. In: Frimmel FH & Christman RF (Eds) Humic Substances and their Role in the Environment (pp 165–178). Wiley and Sons, New York

Whitney PR (1975) Relationship of manganese-iron oxides and associated heavy metals to grain size in stream sediments. J. Geochem. Explor. 4: 251–263