**ABIOTIC FACTORS INVOLVED IN
PREDICTING TRACE METAL LEVELS IN
FRESHWATER BIVALVES.**

Final report - R.A.C. Project 469G

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PREDICTING TRACE METAL LEVELS
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1. INTRODUCTION.

Industrialization has led to increasing fluxes of trace metals from terrestrial and atmospheric sources towards the aquatic environment. Mining operations and metal refining and processing industries are important point sources of trace metals. In certain parts of the world (Eastern Canada), atmospheric deposition also represents an important direct contribution of trace metals to surface waters; the concomitant acidic deposition may also lead to increased mobilization of trace metals from terrestrial sources to the aquatic system. As a result of complex physical, chemical and biological processes, most of the trace metals introduced into the aquatic environment are found associated with the bottom sediments, where they constitute a potential danger for benthic organisms.

Management of in-place contaminants is one of the major problems confronted by governmental agencies responsible for the protection of the environment. In principle, remedial actions such as reduction in waste disposal, chemical treatment of in-place contaminants, capping or dredging can be undertaken; these actions are however costly. It is clear that the development of rational, effective and economical strategies to solve the problem posed by sediment-bound toxic metals will depend greatly on our ability to predict how remedial actions will improve water quality and how these changed conditions will affect aquatic organisms. Important progress in this direction will be made only by understanding the biogeochemical processes governing metal accumulation by benthic organisms under field situations.

Abstract

We have developed and tested in the field a deterministic model to predict metal accumulation in benthic organisms. In the formulation of the model, we used concepts derived from the free-ion activity model of metal-organism interactions and from surface complexation theory, to relate metal concentrations in the organisms to those in the water or in the surficial oxic sediments.

The model was successfully tested in the field for cadmium accumulation in the freshwater bivalve *Anodonta grandis*. Linear regression analysis indicated that Cd concentrations in the soft tissues of the bivalve, [Cd(org)], are related to the free cadmium concentrations, $[Cd^{2+}]$, estimated from the total dissolved Cd and inorganic ligands concentrations: $[Cd(org)] = 44\ [Cd^{2+}] + 10$ ($r^2 = 0.81$). In a further step, partitioning of cadmium between water and surficial oxic sediments was interpreted, using surface complexation concepts, in terms of sorption of this metal on two sediment components: organic matter and iron oxyhydroxides. This partitioning model relates the free Cd^{2+} concentrations to sedimentary variables (e.g., total sedimentary Cd, iron oxyhydroxides and organic carbon concentrations) and water pH; sedimentary variables can then be used to predict cadmium concentrations in the tissues of *A. grandis*.

The general objective of the present project was to develop and test in the field a deterministic model, based on well accepted theories, to predict metal accumulation in benthic organisms. The idea behind this development was that such a model, because of its mechanistic basis, should be of general applicability (i.e. it should apply to sites others than those used in the model calibration). The specific objectives were: i) to derive predictive equations for trace metal concentrations in bivalves that are valid for any aquatic environment where these organisms can be found; ii) to evaluate the utility of the bivalves as bioindicators for trace metals. By coupling concepts from the free-ion model of trace metal organisms interactions with the surface complexation theory, we have made substantial progress towards this general objective, using Cd as our test metal.

2. MATERIAL AND METHODS.

2.1. Study area.

The sediments, associated porewater samples and bivalve specimens were collected at littoral stations in lakes located in the Muskoka area, Ontario (Table 1; Figure 1). They lie on the Precambrian Shield. The closest areas of industrial activities are Sudbury ($\approx$ 200 km northwest) and Toronto ($\approx$ 250 km south).

2.2. Sampling.

The interstitial and overlying water samples were obtained with *in situ* samplers (porewater peepers; 1 cm vertical resolution; 3 per lake) similar to those described by Hesslein (1976) and Carignan *et al.* (1985). The peepers were filled with demineralized water and bubbled with nitrogen for at least 24 h in plexiglass cylinders filled with demineralized water before being inserted vertically in the lake sediments by a diver. After a two week equilibration period, the peepers were retrieved from the sediments by a diver; samples were collected immediately from five compartments above and five below the water-sediment interface, and pH was measured in each sample (Carignan, 1984). Samples for dissolved sulfate and chloride analysis were removed from the peepers with a syringe and injected into prewashed polypropylene tubes; those for inorganic carbon determinations were obtained with a syringe and injected through a septum into pre-evacuated and pre-washed glass tubes. The samples for the
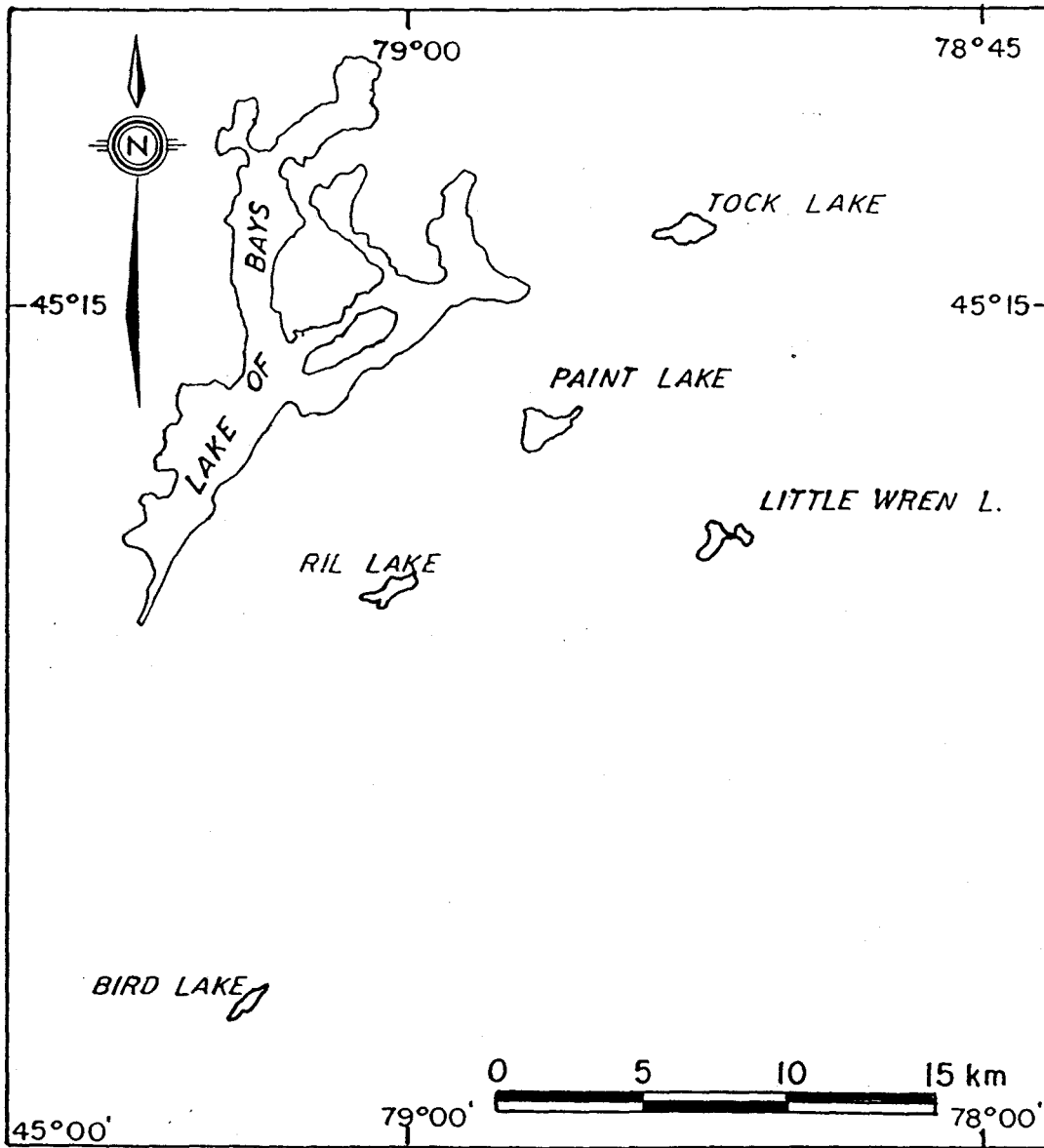
Figure 1. Location of sampling stations in the Muskoka area.

Table 1. Sample identification and location of sampling stations in the Muskoka area.

Site I. D.	Lake	Location
BI-01	Bird	45°02'N 79°04'W
PA-01	Paint	45°13'N 78°57'W
RI-01	Ril	45°10'N 79°00'W
TO-01	Tock	45°16'N 78°53'W
WR-01	Little Wren	45°11'N 78°51'W

analysis of trace metals were collected by piercing the membrane (Gelman HT-200, 0.2 μm nominal pore size) with a Gilson pipette fitted with acid cleaned tips: these samples were injected into pre-washed and pre-acidified (30 uL of 1N Ultrex HNO_3, final pH $<$ 2.5) Teflon[R] vials. Additional water was collected from the compartments 6 and 7 cm above the sediment-water interface of each peeper (combined content 5 mL) for analysis, if necessary, by multiple injection in flameless atomic absorption spectrophotometry (see below). On several occasions during the summer, water samples were also collected by divers at many of the sites with a clean polyethylene bottle close to the sediment-water interface for pH measurement. The purpose of this measurement was to calculate time-averaged pH values (-log ($\Sigma[H^+]/n$)) for the summer period.

Sediment cores (4-5 per site) were collected by a diver, close to the peepers, with plexiglass tubes (9 cm diameter). The tubes were tightly closed to minimize perturbations of the sediments during their transport to the shore. The sediment cores were extruded on the shore, and only the uppermost half centimeter, containing oxidized sediments, was retained. These samples were placed in 500 mL centrifugation bottles half filled with lake water, and kept at $\approx$4°C during transport to the laboratory where they were kept frozen until analysis.

Specimens of *Elliptio complanata* (10 per site) were obtained by a diver at each site, within a radius of $\approx$ 50 m from the sediment and porewater collection site. The bivalves were placed in plastic bags with lakewater and maintained at $\approx$ 4 °C during transport to the laboratory where they were left to depurate for at least 24 h in aerated lake water. They were then dissected into gills, mantle, hepatopancreas and remaining tissues, hereafter referred to as "remains". For each sampling site, individual tissue types from the ten animals collected were pooled and frozen at -20 °C until needed for analysis.

2.3 Analyses.

The water samples were analyzed for Cd, Cu, Ni, Pb, Zn, Fe, Mn, SO_4, Cl, major cations and organic and inorganic carbon. The metal concentrations were obtained by flame atomic absorption spectrophotometry (AA) when possible (Fe, Mn, Ca, Mg, Na, K; Varian Techtron, Model 575ABQ or Model Spectra AA-20) or, otherwise, by flameless AA (Fe, Mn, Cd, Cu, Ni, Pb, Zn; Varian Techtron, Model 1275 or Spectra AA-30; GTA-95 or GTA-96). When initially

measured levels of cadmium in the overlying waters did not exceed a concentration threshold of five times the analytical detection limit (0.13 nmol L^{-1}), its concentration was determined by a multiple injection technique. The necessary number of aliquots were injected successively and subjected to the preliminary drying steps; the combined sample was then atomized. The detection limits for Ni and Pb were not improved with this technique. The National Research Council of Canada (NRC) Riverine Water Reference Material (SLRS-2) was analysed for Cd, Cu and Zn; we obtained 0.024 ± 0.003 μg Cd L^{-1} (N=4; certified value 0.028 ± 0.004 μg Cd L^{-1}), 2.96 ± 0.13 μg Cu L^{-1} (N=6; certified value 2.76 ± 0.17 μg L^{-1}) and 3.38 ± 0.07 μg Zn L^{-1} (N=7; certified value 3.33 ± 0.15 μg L^{-1}). The National Bureau of Standards Reference Material 1643b (Trace Elements in Water) was analyzed after 10X to 40X dilutions for Pb; we obtained: 25.7 ± 2.4 μg Pb L^{-1} (N=4; certified value 24.1 ± 0.7 μg Pb L^{-1}). Sulfate and chloride concentrations were determined by ion chromatography (Dionex AutoIon, System 12); dissolved inorganic carbon was measured by gas chromatography (Carignan 1984) and dissolved organic carbon by persulfate-ultraviolet oxidation, followed by conductometric determination of the released CO_2 on a Technicon autoanalyser.

The surficial sediment samples were thawed and centrifuged to remove excess water; subsamples (equivalent to $\approx$ 1 g dry wt.) were extracted and trace metals were partitioned into the following empirical fractions (Tessier et al. 1985): i) the sediment subsample was extracted for 30 min with 1 N $MgCl_2$; ii) the residue from (i) was extracted for 5 h. with CH_3COONa adjusted to pH 5 with CH_3COOH; iii) the residue from (ii) was extracted for 30 min. at room temperature with 0.1 M $NH_2OH \cdot HCl$ in 0.1 N HNO_3; iv) the residue from (iii) was extracted for 6 h. at 96°C with 0.04 M $NH_2OH \cdot HCl$ in 25% (v/v) CH_3COOH; v) the residue from (iv) was extracted for 5 h. at 85°C with H_2O_2 adjusted to pH 2 with HNO_3, and then at room temperature with 3.2 M NH_4OAc in 20% (v/v) HNO_3; vi) the residue from (v) was digested successively with concentrated HNO_3 (15 min; under reflux; followed by evaporation to dryness), concentrated $HCLO_4$ (4 mL; 60 min under reflux) and HF (15 mL; evaporation to dryness; 12-18 h) and dissolution of the residue was effected in 50 mL of 5% HCL. Fe, Mn, Cd, Cu, Ni, Pb and Zn concentrations in the extracts were determined by flame or flameless AAS, using the appropriate extractant matrices for standards and blanks. Details of these procedures are given in earlier publications (Tessier et al. 1979, 1985). The National Research Council of Canada reference sample of marine sediment MESS-1 has been subjected to the sequential extraction

procedure. We measured, for the sum of the six fractions: 25.2 ± 1.4 μg Cu g^{-1} (N=4; certified value 25.1 ± 3.8 μg Cu g^{-1}), 169 ± 2 μg Zn g^{-1} (N=4; certified value 191 ± 17 μg Zn g^{-1}), 29.6 ± 0.9 μg Pb g^{-1} (N=4; certified value 34.0 ± 6.1 μg Pb g^{-1}). For Cd, and Ni, which showed lower than detection limit values in some fractions, we found the following ranges $0.56 \pm 0.07 < x < 0.72 \pm 0.03$ μg Cd g^{-1} (N=4; certified value 0.59 ± 0.10 μg Cd g^{-1}) and $26.0 \pm 1.5 < x < 28.6 \pm 2.8$ μg Ni g^{-1} (N=4; certified value 29.5 ± 2.7 μg Ni g^{-1}). Sediment organic carbon concentrations, $\{C_{org}\}$, were determined with a CNS analyzer (Carlo-Erba, Model NA1500) after removal of inorganic carbon by acidification with diluted H_2SO_4 (0.5 mol L^{-1}; 15 min., 100 mL/g sediment dry weight).

Each pooled bivalve tissue was homogenized (Brinkman tissue grinder, Model CH-6010). A subsample was then dried to constant weight to determine the wet:dry weight ratio, and a second subsample was digested in a Teflon bomb with concentrated nitric acid (Aristar; 3 mL g^{-1} of tissue dry weight) in a microwave oven at pressures between 5500 and 7000 KPa for $\approx$ 1 min. A certified reference material (lobster hepatopancreas, TORT-1, NRC) was submitted to the same digestion procedure and analyzed for Cd, Cu, Ni, Pb and Zn; we obtained 24.1 ± 0.5 μg Cd g^{-1} (N=5; certified value 26.3 ± 2.1 μg Cd g^{-1}), 385 ± 5 μg Cu g^{-1} (N=5; certified value 439 ± 22 μg Cu g^{-1}), 2.1 ± 0.3 μg Ni g^{-1} (N=4; certified value 2.3 ± 0.3 μg Ni g^{-1}), 9.6 ± 0.7 μg Pb g^{-1} (N=5; certified value 10.4 ± 2.0 μg Pb g^{-1}) and 182 ± 31 μg Zn g^{-1} (N=5; certified value 177 ± 10 μg Zn g^{-1}).

3. RESULTS

The concentrations of dissolved constituents above the sediment-water interface, as obtained with the porewater peepers, are given in Table 2. Dissolved cadmium concentrations vary between 0.04 and 0.25 nmol L^{-1}; these values are much lower than those reported by Hinch and Stephenson (1987) for Beech (3 nmol L^{-1}) and Tock (3 nmol L^{-1}) Lakes. For this latter lake, we measured 0.23 nmol L^{-1}. Campbell and Evans (1991) measured values between 0.2 and 1.25 nmol L^{-1} in the epilimnia of various lakes in south-central Ontario; some of their sampled lakes are in the Muskoka area. We measured dissolved Cu concentrations between 4.6 and 7.0 nmol L^{-1} and Zn concentrations between 17 and 89 nmol L^{-1}; these values are

Table 2. Mean concentrations (±SD) of total dissolved constituents (Ca, Cd, Cl, Cu, Fe, Mn, Ni, Pb, SO_4, Zn, pH, inorganic and organic carbon) above the sediment-water interface, as obtained with the porewater peepers.

Site	pH	Cd	Cu	Ni	Pb	Zn
			(nmol L^{-1})			
BI-01	6.37	0.17[a]	5.5±1.1	<6	<1	44.4±5.9
PA-01	7.13	0.043±0.006	7.0±0.8	<6	<1	16.7±2.4
RI-01	6.02	0.20±0.03	5.2±0.8	<6	<1	89.2±5.1
TO-01	6.43	0.23[a]	6.2[a]	<6	<1	71.2±13.7
WR-01	6.27	0.25±0.01	4.6±1.1	<6	<1	80.8±10.1

Site	Ca	Mg	Na	K	Cl	SO_4
			(μmol L^{-1})			
BI-01	107±37	34.6±1.2	35±7	12±3	15±1	78±6
PA-01	147±36	51.4±0.6	86±5	16±2	83±3	97±3
RI-01	113±11	35.0±2.1	44±0	10±0	35±2	78±4
TO-01	139±40	30.8±1.2	39±0	10±0	41±3	79±3
WR-01	80±17	28.1±4.6	64±7	14±3	58±6	81±7

Site	Fe	Mn	C_{inorg}	C_{org}
	(μmol L^{-1})		(μmol C L^{-1})	
BI-01	1.3±0.9	0.45±0.13	210±60	475±118
PA-01	0.9±0.8	0.11±0.08	130±30	440±34
RI-01	1.8±0.2	0.75±0.15	180±20	473±60
TO-01	0.5±0.3	0.32±0.11	110±50	474±99
WR-01	1.3±0.8	0.60±0.14	110±80	453±63

[a]: mean of two values.

slightly lower than those reported by Hinch and Stephenson (1987) for Beech (16 nmol Cu L^{-1}; 77 nmol Zn L^{-1}) and Tock (16 nmol Cu L^{-1}; 120 nmol Zn L^{-1}) Lakes. The concentrations of dissolved Ni and Pb were below our detection limits (6 and 1 nmol L^{-1} respectively). For these last two metals, multiple injections did not improve detection limits.

Concentrations of sedimentary trace metals obtained in various fractions vary slightly from one lake to another (Table 3). Comparison of sediment trace metal concentrations among lakes or with those obtained by other researchers is difficult, since the sediment samples were obtained from the littoral zone of the lakes, where sediment composition is often patchy. The results show, however, general trends that were observed in other studies (Forstner and Wittmann, 1981). For example, non-residual Cu is found mostly in fraction F4 (between 65% (Paint Lake) and 97% (Little Wren Lake)), which confirms the high affinity of natural organic matter for Cu. Large proportions of non-residual Pb (between 47% (Tock Lake) and 87% (Paint Lake)) and non-residual Zn (between 46% (Ril Lake) and 64% (Paint Lake)) are found in the sum of fractions F3A and F3B; similar results were reported for suspended river sediments (Tessier *et al.*, 1980). The ratio $\{C_{org}\}$:$\{Fe\text{-ox}\}$ in the sediments ($\{Fe\text{-ox}\}$ is the sum of $\{Fe(F3A)\}$ and $\{Fe(F3B)\}$ in Table 3) varies between 10 (Paint Lake) and 130 (Little Wren Lake); this large variation in the ratio explains at least partly variations in metal partitioning observed among lakes. For example, the ratio [Cu(F4)]:([Cu(F3A)] + [Cu(F3B)]) is linearly correlated ($r^2=0.92$; N=5) with the ratio $\{C_{org}\}$:$\{Fe\text{-ox}\}$. This strong correlation suggests a competition between iron oxyhydroxides and organic matter for copper; such a competition has been reported by Luoma (1986).

Concentrations of Cd, Cu, Ni, Pb and Zn in the tissue of *E. complanata* are given in Table 4. We found that cadmium concentrations in the tissues of the bivalve varied between 13 and 26 μg g^{-1}. These values are similar to those reported for *E. complanata* by Servos *et al.*, (1987) for Lake of Bays (12 μg g^{-1}) and by Hinch and Stephenson (1987) for Beech (11 μg g^{-1}) and Tock (15 μg g^{-1}) Lakes. The values obtained for Cu (between 5.9 and 7.3 μg g^{-1}) and Zn (between 170 and 215 μg g^{-1}) are similar to those reported by Hinch and Stephenson (1987) for Beech (7.3 μg Cu g^{-1}; 155 μg Zn g^{-1}) and Tock (10 μg Cu g^{-1}; 130 μg Zn g^{-1}) Lakes.

Table 3. Partitioning[*] of trace metals in the oxic layer of lake sediments and concentration of sedimentary organic carbon. The concentrations are given on a dry weight basis.

Site	{M(F1)}	{M(F2)}	{M(F3)}	{M(F3B)}	{M(F4)}	{M(F5)}	{M}$_T$
{Cd} (nmol g^{-1})							
BI-01	1.12	1.62	0.89	4.80	<0.5	<0.9	8.43
PA-01	0.61	0.82	0.36	0.18	0.71	<0.9	2.67
RI-01	1.00	1.77	1.33	5.16	0.53	<0.9	9.79
TO-01	0.90	3.61	1.69	10.5	1.25	<0.9	17.9
WR-01	0.71	1.05	0.80	7.38	1.25	<0.9	11.2
{Cu} (nmol g^{-1})							
BI-01	1.97	0.27	1.42	5.82	79.6	49.6	139
PA-01	<0.5	2.77	2.05	8.50	24.2	26.8	64.3
RI-01	0.87	1.87	1.42	5.35	79.9	49.6	139
TO-01	<0.5	5.52	1.26	11.3	187	125	331
WR-01	<0.5	<0.2	<0.2	2.68	94.7	27.5	125
{Ni} (nmol g^{-1})							
BI-01	6.88	7.63	<7	35.4	51.1	162	263
PA-01	3.99	7.63	9	25.9	10.2	145	201
RI-01	21.3	6.82	<7	32.7	34.1	153	248
TO-01	23.2	13.1	<7	72.4	129	162	400
WR-01	6.93	<7	2.7	39.0	64.7	145	258
{Pb} (nmol g^{-1})							
BI-01	1.88	27.5	2.08	112	18.3	57.9	220
PA-01	<1	2.7	4.05	33.1	2.90	55.5	98.3
RI-01	16.7	34.2	2.08	85.9	14.5	57.9	211
TO-01	6.56	79.1	2.99	138	75.3	53.1	355
WR-01	3.38	19.8	<2	48.7	26.1	45.8	144
{Zn} (nmol g^{-1})							
BI-01	177	173	78.5	503	97.9	667	1697
PA-01	43.7	108	69.7	283	47.7	531	1083
RI-01	358	182	124	404	82.6	541	1691
TO-01	203	378	190	1361	283	765	3180
WR-01	110	145	82.7	491	135	505	1469

Table 3. (Continue).

Site	{M(F1)}	{M(F2)}	{M(F3)}	{M(F3B)}	{M(F4)}	{M(F5)}	{M}$_T$
			{Fe} (μmol g^{-1})				
BI-01	0.20	8.49	6.59	95.8	10.3	413	534
PA-01	0.20	4.03	6.52	105	3.65	397	517
RI-01	0.04	8.83	9.79	73.9	10.6	380	483
TO-01	0.06	6.79	7.07	113	33.9	544	705
WR-01	0.14	7.72	7.95	63.8	24.9	344	448
			{Mn} (μmol g^{-1})				
BI-01	0.87	1.26	2.29	1.49	0.06	9.56	15.5
PA-01	0.55	2.02	25.3	3.08	0.06	9.65	40.7
RI-01	0.69	1.24	1.97	1.04	0.05	7.88	12.9
TO-01	0.88	1.48	0.87	1.18	0.05	6.19	10.7
WR-01	1.07	0.35	0.07	0.28	0.08	9.08	10.9

	{C$_{org}$} (μmol C g^{-1})
BI-01	4472
PA-01	1107
RI-01	3230
TO-01	9967
WR-01	9358

(*): {M(F1)} ..... {M(F5)} represent metal concentrations in fractions 1 to 6 following the sequence given in the text.

Table 4. Metal concentrations (on a dry weight basis) in the tissues of *Elliptio complanata* from various sampling sites. He, hepatopancreas; Gi, gills; Ma, mantle; Re, remaining; org, whole organisms.

Site	[M(He)]	[M(Gi)]	[M(Ma)]	[M(Re)]	[M(org)]
			Cd (μg g^{-1})		
BI-01	9.40	7.54	16.8	12.9	12.7
PA-01	17.9	8.28	14.9	7.59	10.3
RI-01	17.3	14.0	24.6	12.3	15.4
TO-01	25.9	18.1	47.8	20.3	25.7
WR-01	14.6	17.1	31.6	10.0	15.7
			Cu (μg g^{-1})		
BI-01	10.7	13.2	5.86	5.37	7.14
PA-01	12.2	11.8	6.58	5.31	7.29
RI-01	10.5	13.4	4.92	4.82	6.63
TO-01	12.6	12.8	6.35	4.75	7.32
WR-01	8.05	10.2	3.68	4.85	5.89
			Ni (μg g^{-1})		
BI-01	1.59	2.59	1.46	1.09	1.40
PA-01	0.82	2.88	2.14	0.77	1.34
RI-01	1.68	4.81	3.31	1.82	2.45
TO-01	2.47	2.89	2.46	1.38	1.94
WR-01	1.39	2.86	2.75	0.92	1.63
			Pb (μg g^{-1})		
BI-01	42.0	14.0	51.1	37.2	38.8
PA-01	1.81	1.26	1.97	1.54	1.61
RI-01	20.7	10.5	21.7	13.0	15.3
TO-01	92.4	37.4	102	53.4	65.3
WR-01	27.8	12.2	65.7	25.0	30.7
			Zn (μg g^{-1})		
BI-01	168	234	197	153	173
PA-01	128	289	266	120	173
RI-01	158	356	254	135	187
TO-01	194	330	309	159	215
WR-01	144	282	257	120	175

4. DISCUSSION

4.1 The free-ion activity model.

According to the free-ion activity model (Figure 2), the effects (including bioaccumulation) of a trace metal M on an organism which obtains the trace metal from the water should be predicted by the free ion concentration (or activity) of this metal, $[M^{z+}]$. The concentration of a metal accumulated into an organism, [M(org)], should thus be written (Morel, 1983):

$$[M(org)] \quad = \quad f([M^{z+}]) \tag{1}$$

where f means a function. This model has been developed for explaining (with great success) biological effects of trace metals on unicellular organisms. Laboratory bioassays, conducted with benthic animals exposed to dissolved metals under carefully controlled conditions, have shown that the effects of trace metals on these animals are also related to the free metal ion concentration and not to the total metal concentrations in the animals' environment. For example, mortality of the shrimp *Palaemonetes pugio* exposed to cadmium was shown to be related to $[Cd^{2+}]$ (Sunda *et al.*, 1978). Similarly, short-term (14 d) accumulation of copper in the American oyster *Crassostrea virginica* was found to be related to $[Cu^{2+}]$ (Zamuda and Sunda, 1982). Note, however, that the applicability of the free-ion activity model in the field, where dissolved ligands (e.g. natural organic matter) differ from the synthetic ligands used in the laboratory (e.g. NTA, EDTA), has never been demonstrated.

For the following discussion, we have focused on cadmium; among the metals measured, water, sediment and animal data are more complete for this metal (other metals show many "lower than detection limit" values, especially for the water samples). To enhance the representativity of the study, we include also Cd data obtained for other lakes that we have studied, which are located in the areas of Sudbury (On), Rouyn-Noranda (Qc; mining area; heavily contaminated with Cd), Chibougamau (Qc; mining area), Québec (Qc) and Eastern Townships (Qc). These lakes are distributed over a geographical area of about 350 000 km² and they represent a large gradient of Cd contamination and a wide range of pH values. Since additional measurements are needed to obtain a satisfactory picture of Cd concentrations in *E. complanata* (see below; this section and section 4.3), we also include in the following
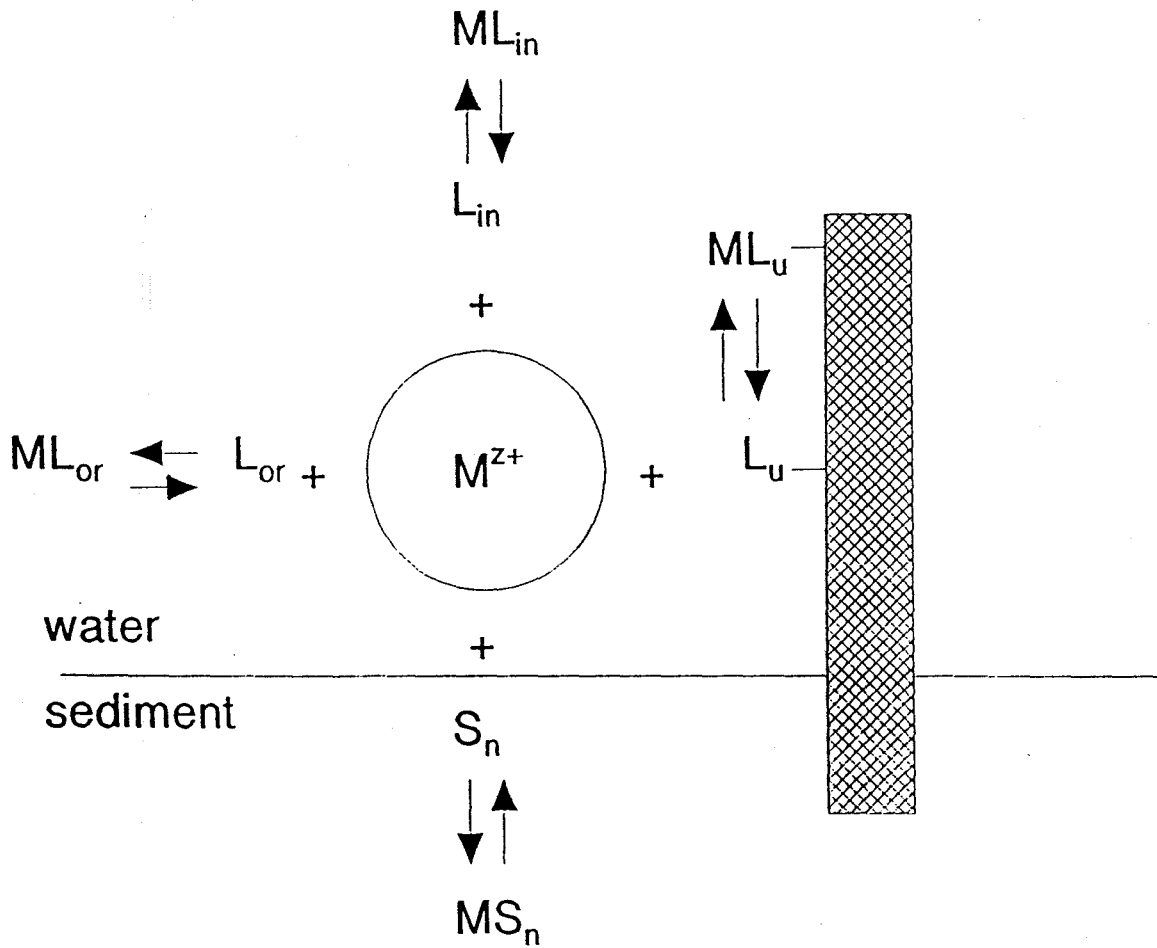
Figure 2. Schematic representation of the various reactions occurring in the water overlying the sediments. M^{z+} is the free metal ion; L_{in} and L_{or} are dissolved inorganic and organic ligands respectively; L_u is a ligand at the surface of an organism or a transport molecule; S_n is a component of the sediment (e.g. iron oxyhydroxides; organic matter) which sorbs the trace metal; ML_{in}, ML_{or}, ML_u and MS_n represent the metal bound to the various ligands or sediment components.

discussion Cd data that we have obtained for another widespread freshwater bivalve, *Anodonta grandis*.

We have plotted in Figure 3 cadmium concentrations in *E. complanata* (Fig. 3a) and in *A. grandis* (Fig. 3b) as a function of $[Cd^{2+}]$. We have calculated $[Cd^{2+}]$ with the equilibrium model HYDRAQL (Papelis *et al.*, 1988), using the total dissolved Cd concentrations ([Cd]; Table 2), the measured concentrations of the inorganic ligands concentrations (Table 2), and the stability constants of the inorganic complexes (Smith and Martell, 1977); the stability constants used for calculating Cd complexation are given in Table 5. Because the thermodynamic equilibrium constants for Cd-DOM (dissolved organic matter) are unknown, possible cadmium complexation by natural organic ligands could not be considered in the calculation.

According to the data in Figure 3b, Cd concentrations in the tissues of *A. grandis* (μg g^{-1}) can be described by :

$$[Cd(org)] \quad = \quad 44 \ (\pm 5) \ [Cd^{2+}] + 10 \ (\pm 15) \qquad\qquad (2)$$
$$(n = 17; \ r^2 = 0.81; \ [Cd^{2+}] \ \text{in nmol L}^{-1})$$

The relationship between cadmium concentration in *E. complanata* and $[Cd^{2+}]$ is, however, not as clear; if data from D'Alembert Lake are removed, it would resemble an hyperbolic function. Additional measurements, especially at sites where dissolved Cd concentrations are high, are needed before a definitive interpretation can be made.

It might be argued that much of the scatter in Figure 3a,b is due to variation in dissolved Cd on short time scales (Tessier *et al.*, 1993). For example, Yan *et al.* (1990) reported a 2-fold change in dissolved Cd concentration in Red Chalk Lake during the ice-free season; this lake is located in the Muskoka area. Dissolved Cd concentrations used in the present study are mean values for a single sampling. Cadmium concentrations in the bivalves are probably not sensitive to short-term variations in dissolved Cd. For example, we have observed that Cd concentrations in the tissues of *A. grandis* specimens transplanted from the unpolluted Lake Brompton (Eastern townships) to the polluted Lake Joannes (Rouyn-Noranda area) had not reached, after three years, the cadmium levels observed in the indigenous specimens from Lake Joannes. The use of time-averaged values of dissolved Cd, instead of the single values
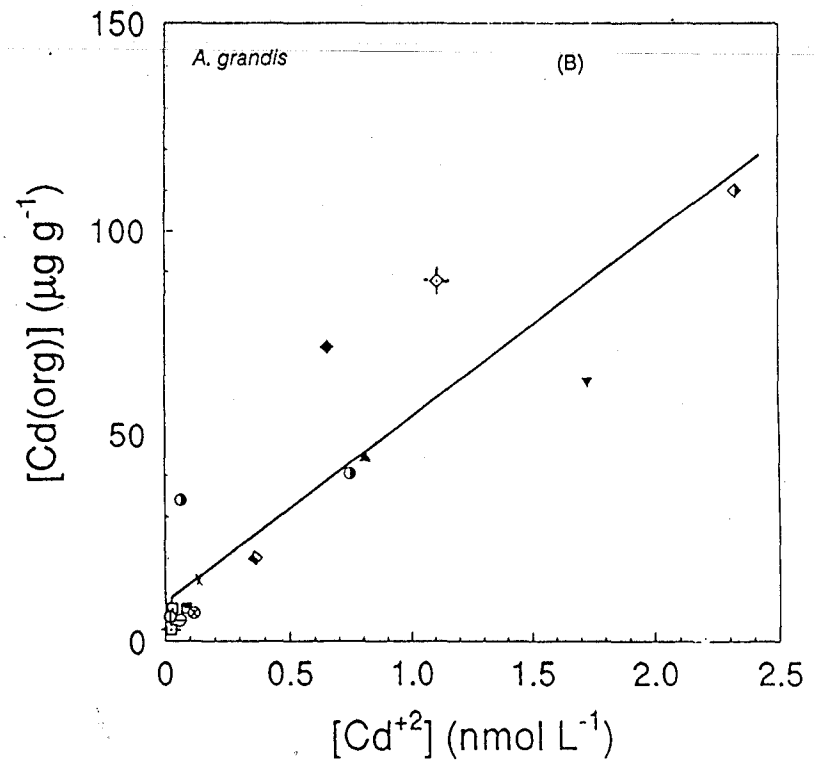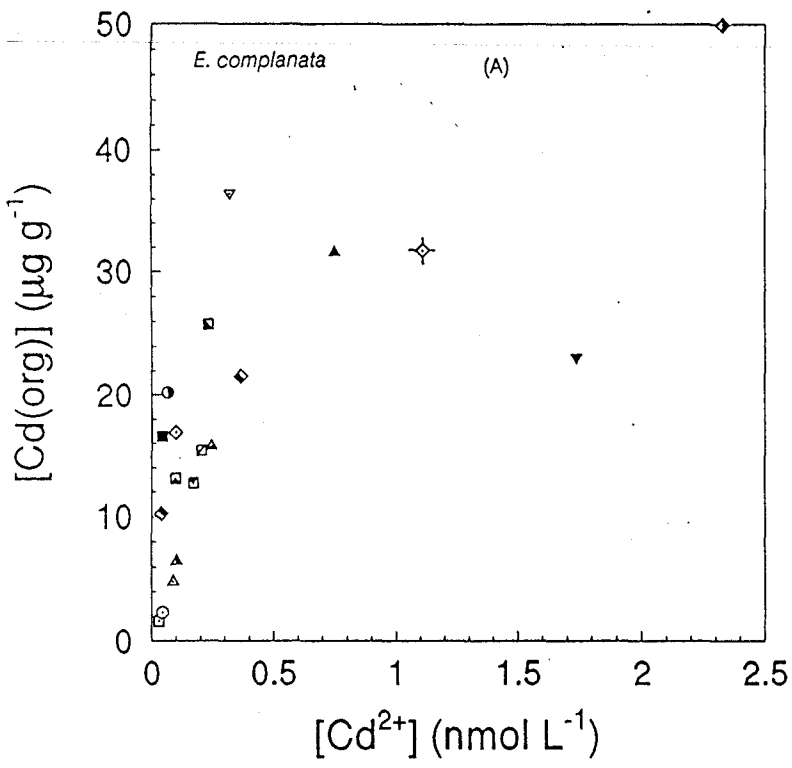
Figure 3. Relationship between cadmium concentration in the tissues (whole organisms) of *E. complanata* (A) or *A. grandis* (B) and the free cadmium ion concentration calculated from total dissolved Cd and inorganic ligands. Symbols represent various sampling sites.

Table 5. Stability constants used in the equilibrium model HYDRAQL (Papelis et al., 1988) for the complexation with inorganic ligands.

Reaction	Log K
$Cd^{2+} + CO_3^{2-} = CdCO_3$	3.20
$Cd^{2+} + SO_4^{2-} = CdSO_4$	2.46
$Cd^{2+} + Cl^- = CdCl^+$	2.00
$Cd^{2+} + 2 Cl^- = CdCl_2$	2.60
$Cd^{2+} + 3 Cl^- = CdCl_3^-$	2.40
$Cd^{2+} + OH^- = CdOH^+$	-10.10
$Cd^{2+} + 2 OH^- = Cd(OH)_2$	-20.40
$Cd^{2+} + 3 OH^- = Cd(OH)_3^-$	-33.00
$Cd^{2+} + 4 OH^- = Cd(OH)_4^{2-}$	-47.35

used here, would improve the predictive power of Eqn (2) and help in choosing the proper function to predict cadmium concentration in *E. complanata* (Fig. 3a). Measurement of temporal changes in Cd concentrations in the tissues of transplanted *A. grandis* specimens suggests that they accumulate metals only during the warm season (e.g. from May to October). For optimum predictive power, the mean $[Cd^{2+}]$ should thus be preferentially obtained for this period.

The data shown in Figure 3 are consistent with the free-ion activity model. It should be noted, however, that very similar relations would have been obtained with total dissolved Cd ($[Cd]$), since its concentration at all sites is close to the computed value for $[Cd^{2+}]$. Given the similarity between $[Cd^{2+}]$ and $[Cd]$ values, and the scatter shown in Fig. 3, it is not possible with the present data to demonstrate unambiguously that the free-ion activity model applies in the field to Cd accumulation in *E. complanata* or *A. grandis*. To do so, one would need a natural setting where the degree of complexation, $\alpha = [Cd]/[Cd^{2+}]$, vary from site to site. Both SO_4 and Cl are known to complex Cd, but it is unlikely that *E. complanata* and *A. grandis* would be found in freshwaters where these inorganic ligands are present in sufficiently high concentrations to complex Cd significantly. An alternative approach to demonstrate the application of the free-ion activity model to Cd accumulation by the two bivalves in the field would be to find sites where natural organic matter complexes Cd significantly, provided of course that we can account for this complexation and correctly estimate $[Cd^{2+}]$.

4.2 Relationship between dissolved and surficial sedimentary Cd.

Cadmium concentrations in the surficial oxic sediments are related to dissolved Cd concentrations in the overlying water, i.e. in the bivalves' aqueous environment. The partitioning of Cd between water and surficial oxic sediments has been interpreted, using surface complexation concepts, in terms of the sorption of this metal to the two following sediment components: organic matter and iron oxyhydroxides. The development of this partitioning model is discussed in detail in the paper by Tessier *et al.*, (1993) given in the Appendix. According to this partitioning model, $[Cd^{2+}]$ can be calculated from the following three expressions:

$$[Cd^{2+}] = \frac{\{Fe\text{-}Cd\}\ [H^+]^x}{N_{Fe}\cdot {}^*K_{Fe\text{-}Cd}\ \{Fe\text{-}ox\}} \tag{3a}$$

$$[Cd^{2+}] = \frac{\{OM\text{-}Cd\}\ [H^+]^y}{N_{OM}\cdot {}^*K_{OM\text{-}Cd}\ \{OM\}} \tag{3b}$$

$$[Cd^{2+}] = \frac{\{Cd\}_T\ [H^+]^{x+y}}{N_{Fe}\cdot {}^*K_{Fe\text{-}Cd}\ \{Fe\text{-}ox\}\ [H^+]^y + N_{OM}\cdot {}^*K_{OM\text{-}Cd}\ \{OM\}\ [H^+]^x} \tag{3c}$$

where:

- $\{Fe\text{-}ox\}$ is the concentration of iron oxyhydroxides in the surficial sediments (nmol g^{-1}) obtained by extracting the sediments with a reducing reagent);
- $\{OM\}$ is the concentration of organic carbon (nmol g^{-1}) in the surficial sediments;
- $\{Cd\}_T$ is the total Cd concentration (nmol g^{-1}) in the surficial sediments;
- $\{Fe\text{-}Cd\}$ and $\{OM\text{-}Cd\}$ are the concentrations of cadmium (nmol g^{-1}) associated with iron oxyhydroxides and organic matter in the surficial sediments, respectively;
- x and y are the average apparent numbers of proton released per Cd^{2+} ion adsorbed on iron oxyhydroxides and organic matter respectively (Honeyman and Leckie, 1986);
- N_{Fe} is the number of moles of sorption sites of the iron oxyhydroxides per mole of iron oxyhydroxides;
- N_{OM} is the number of moles of adsorption sites of the organic matter per mole of organic carbon;
- ${}^*K_{Fe\text{-}Cd}$ and ${}^*K_{OM\text{-}Cd}$ are apparent overall equilibrium constants for the sorption of Cd on iron oxyhydroxides and organic matter respectively.

It should be noted that the values of the geochemical constants x (0.82), y (0.97), $N_{Fe}\cdot {}^*K_{Fe\text{-}Cd}$ ($10^{-1.30}$) and $N_{OM}\cdot {}^*K_{OM\text{-}Cd}$ ($10^{-2.45}$) have been determined experimentally from field geochemical data (see the Appendix).

It should also be noted that any of the three equations (3a, b or c) can be used to estimate $[Cd^{2+}]$, depending on which of the sedimentary variables ({Fe-Cd}, {OM-Cd}, {Fe-ox}, {OM}, {Cd}$_T$) are available and have been measured accurately (in addition to water pH). Some practical examples are given below:

- If {Cd}$_T$, {Fe-ox} and {OM} are available, any of the three equations can be used since {Fe-Cd} and {OM-Cd} can be calculated with the use of the geochemical constants (see the Appendix);

- Eqn (3a) can be used if the ratio {Fe-Cd}/{Fe-ox} is obtained by reductive dissolution of the diagenetic iron oxyhydroxides (and their associated Cd) deposited on Teflon collectors inserted in sediments (Belzile et al., 1989); relatively pure iron oxyhydroxides are obtained with this collection technique, since we get rid of the complex sediment matrix. However, it has been shown that accurate measurements of {Fe-Cd} are difficult to obtain by extraction of a whole sediment sample with a reducing agent (Tessier et al., 1993); use of Eqn (3a) with data obtained in this way is not recommended.

- If only {Cd}$_T$ and {OM} values are available, Eqn (3b) can be used as a first approximation, and with circonspection, by making the approximation {Cd}$_T \approx$ {OM-Cd}; indeed, the association of Cd in oxic lake sediments appears to be dominated by its interactions with sedimentary organic matter (see the Appendix).

- If {Cd}$_T$, {Fe-ox} and {OM} values are available, Eqn (3c) can be used

4.3 Relating cadmium concentrations in the bivalves to sediment characteristics.

We have plotted in Figure 4 cadmium concentrations in *E. complanata* (Fig. 4a) and *A. grandis* (Fig. 4b) as a function of $[Cd^{2+}]$ calculated with Eqn. (3c). According to the data in Figure 4b, Cd concentrations in the tissues of *A. grandis* (μg g^{-1}) can be described by:

$$[Cd(org)] = 59 \ (\pm 7) \ [Cd^{2+}] \ + \ 11 \ (\pm 18) \qquad (4)$$

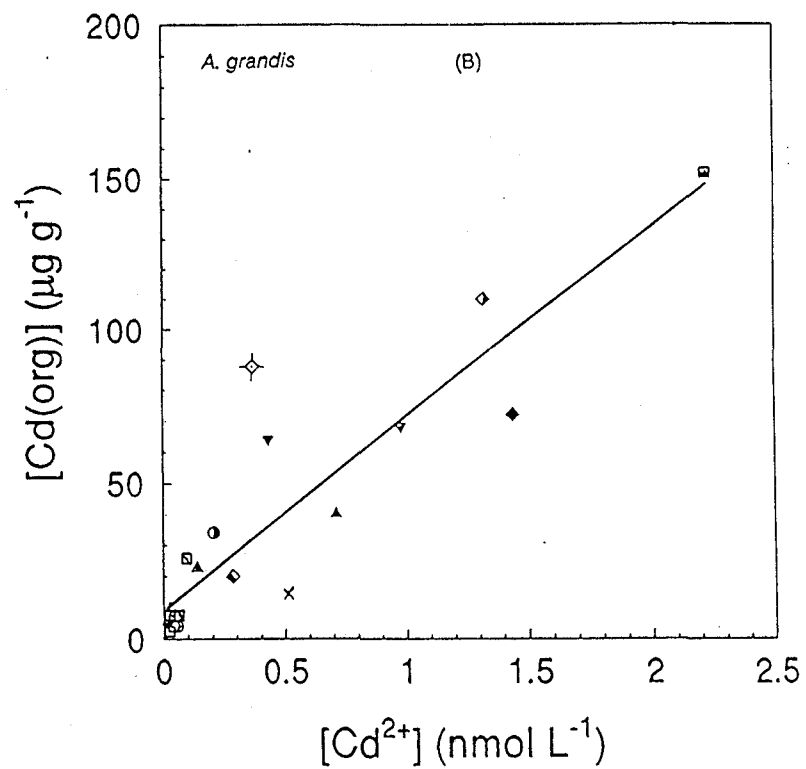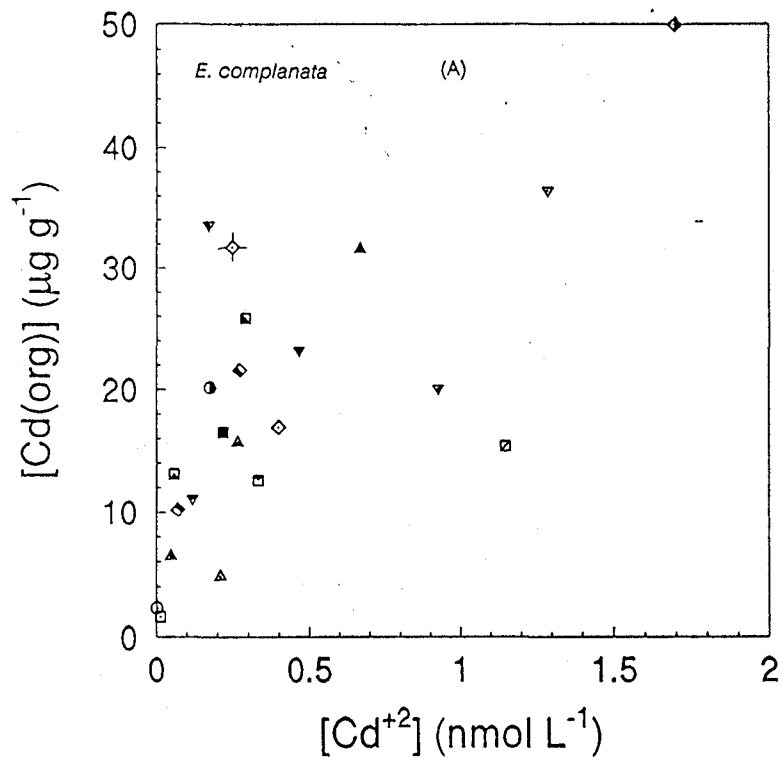$$(n = 19 \ ; \ r^2 = 0.82; \ [Cd^{2+}] \text{ in nmol L}^{-1})$$

Figure 4. Relationship between Cd concentrations in the tissues (whole organisms) of E. *complanata* (A) or A. *grandis* (B) and the free cadmium concentrations calculated with Eqn.(3). Symbols represent various sampling sites.

It should be noted that Eqn. (4) has the same form as Eqn (2), i.e. it is a straight line:

$$[Cd(org)] = F [Cd^{2+}] + [Cd(org)]° \qquad (5)$$

where F is the slope and [Cd(org)]° is the (small) intercept on the y-axis. The function relating Cd concentration in *E. complanata* to [Cd^{2+}] calculated with Eqn. (3c) is not so evident (Fig. 4a). If data from Ril and Dufay Lakes were removed, it would resemble again a hyperbolic function (as in Fig. 3a). Additional measurements are needed before a definitive interpretation can be made concerning *E. complanata*.

Several explanations can be invoked to explain scatter in Figure 4, and the behavior of Ril and Dufay Lakes as outliers. The geochemical model used to partition sedimentary Cd is necessarily crude: i) it assumes that no sediment component other than Fe oxyhydroxides and organic matter can sorb Cd; ii) it assumes that <u>total</u> sedimentary organic matter sorbs Cd - it is conceivable that only certain organic fractions are responsible for sorption, and that the composition of the sedimentary organic matter varies from lake to lake; iii) values of the geochemical parameters N_{Fe}, N_{OM}, $^*K_{Fe\text{-}Cd}$ and $^*K_{OM\text{-}Cd}$ are considered here to be constants, whereas they might be expected to vary with the nature of sedimentary iron oxyhydroxides and organic matter (Luoma and Davis, 1983). It is probable that the nature of these two sediment components present in the top half centimeter of the lake sediments varies among stations. Extraction of iron with $NH_2OH \cdot HCl$ is only moderately selective and will solubilize various iron oxyhydroxide forms; similarly, total organic sedimentary carbon is a very crude estimator of the organic matter active in the sorption process. According to laboratory experiments in well-defined systems, the sorption constants should also vary with the density of adsorption (Benjamin and Leckie, 1981) and with the concentration of particles (DiToro *et al.*, 1986), both of which vary among the studied sites. During collection of the surficial sediment, the oxic layer may have been contaminated by reduced sediments, leading to incorrect estimation of {Cd}$_T$, {Fe-ox} and {OM} present in the oxic surficial sediment. Another source of scatter is the variability in cadmium concentration in the tissues of the bivalves due to biological factors (length or age, reproductive condition). Recommendations are given below (section 5) to improve prediction of Cd (and other trace metals) concentrations in benthic organisms.

Cadmium concentrations in the tissues of the freshwater bivalves are much better related to the parameters appearing in the right-hand side of Eqns (3) than to total sedimentary cadmium, $\{Cd\}_T$ (compare Fig. 4 and 5). Indeed, when cadmium concentrations in the bivalves are compared with $\{Cd\}_T$, no significant relationships emerge (Fig. 5). The same conclusion is reached when Cd concentrations in the bivalves are compared with cadmium concentrations found in any sediment extract, whether or not the extractable Cd is normalized with respect to sediment iron oxyhydroxide or organic carbon concentrations. Such empirical normalizations have been advocated recently for the prediction of As, Cu, Hg and Pb bioaccumulation in bivalves (Table 6: Langston 1980, 1982; Luoma and Bryan, 1978; Tessier *et al.*, 1983; 1984), but they do not seem to be adequate for predicting Cd accumulation in *E. complanata* and *A. grandis* for a large variety of lakes as here.

Prediction of [Cd(org)] with the sedimentary parameters appearing in Eqns. (3) is as good as the prediction with the dissolved [Cd] and the inorganic ligand concentrations (compare Figs. 3 and 4). However, use of sedimentary measurements offers considerable advantages. The measurement of low dissolved Cd concentrations in freshwaters is difficult and requires the use of trace metal-free techniques; possibilities of inadvertent contamination are rampant. An additional problem is the temporal variation of dissolved Cd; considerable effort would be needed to obtain representative mean values of total dissolved Cd at each sampling site. By comparison, the measurement of $\{Cd\}_T$, $\{Fe\text{-}ox\}$, $\{OM\}$ and lake pH is much simpler.

An important point to note is that the geochemical constants x, y, $N_{Fe} \cdot {}^*K_{Fe\text{-}Cd}$ and $N_{OM} \cdot {}^*K_{OM\text{-}Cd}$ determined in this study are specific to cadmium. These types of constants should be metal-specific, and not organism-specific. Once they are determined accurately for a given metal, they could in principle be used for predicting trace metals in any organism that obtains its metal burden from the ambient water. For a specific organism, the only requirement would then be to determine F and $[M(org)]^\circ$ (as in Eqn 5) from a proper calibration. The geochemical constants are in fact used only to estimate $[M^{z+}]$, which is the same for all the organisms at a given site.
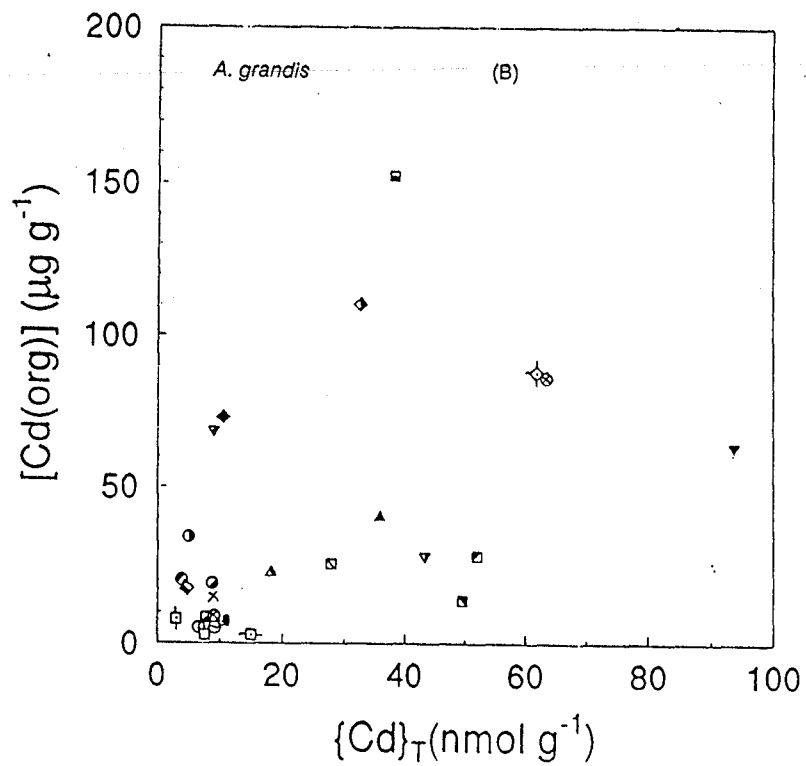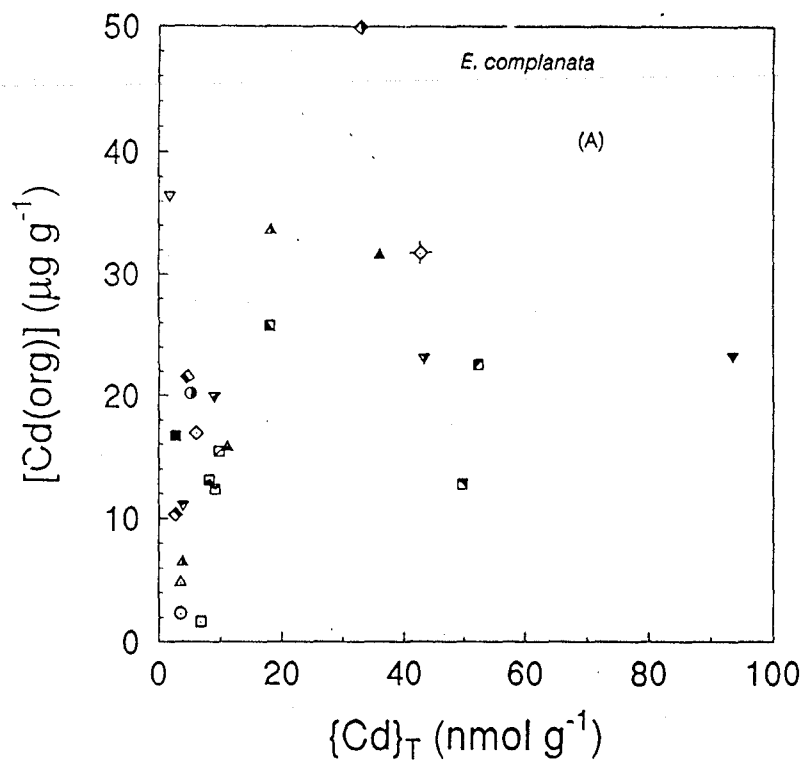
Figure 5. Relationship between Cd concentrations in the tissues (whole organisms) of *E. complanata* (A) and *A. grandis* (B) and total Cd concentrations in the sediments. Symbols represent various sampling sites.

24

Table 6. Prediction of trace metal availability to benthic organisms from sediment characteristics.

Organism	Metal		Prediction		Reference
crobicularia lana	Pb		{Pb} extracted with 1N HCl (r=0.69)	{Pb}/{Fe} extracted with 1N HCl (r=0.99)	Luoma and Bryan, 1978
crobicularia lana	Hg	$\{Hg\}_T$ (r=0.72)	{Hg} extracted with 1N HCl (r=-0.61)	{Hg} extracted with HNO_3/organic content (r=0.80)	Langston, 1982
crobicularia lana	As		{As} extracted with 1N HCl (r=0.80)	{As}/{Fe} extracted with 1N HCl (r=0.96)	Langston, 1980
facoma althica	Hg			{Hg} extracted with HNO_3/organic content	Langston, 1982
lliptio mplanata	Cu	$\{Cu\}_T$ (r=0.79)	{Cu} extracted with $NH_2OH.HCl$ (r=0.94)	{Cu}/{Fe} extracted with $NH_2OH.HCl$ (r=0.97)	Tessier *et al.*, 1984
lliptio mplanata	Pb	$\{Pb\}_T$ (r=0.77)	{Pb} extracted with $NH_2OH.HCl$ (r=0.87)	{Pb}/{Fe} extracted with $NH_2OH.HCl$ (r=0.96)	Tessier *et al.*, 1984
nodonta andis	Cu			{Cu}/{Fe} extracted with $NH_2OH.HCl$ (r=0.92)	Tessier *et al.*, 1983

4.4 Reconciliation with empirical normalization.

In earlier studies, field measurements along trace metal gradients have shown that the prediction of metal concentrations in estuarine and freshwater bivalves, [M(org)], was greatly improved when the trace metal concentration extracted from the sediments was normalized with respect to the iron oxide or organic matter content of the sediments (Table 5). Hence, the ratios {Pb}/{Fe} and {As}/{Fe}, all extracted with 1N HCl, and the ratio {Hg extracted with HNO_3}/{OM} were found to be the best predictors of lead, arsenic and mercury concentrations respectively in the estuarine bivalve *Scrobicularia plana* (Langston 1980, 1982; Luoma and Bryan 1978). Similarly, the best predictors of Cu and Pb in the tissues of the freshwater bivalves *A. grandis* and *E. complanata* were found to be the ratios {Cu}/{Fe} and {Pb}/{Fe} extracted with $NH_2OH \cdot HCl$, a reducing reagent (Tessier *et al.* 1983, 1984). In other words, according to these studies, trace metal concentrations in the organisms are best expressed as:

$$[M(org)] = k \; \frac{\{S_n - M\}}{\{S_n\}} \; + \; [M(org)]^\circ \qquad (6)$$

where k is a proportionality constant; $\{S_n\}$ is the concentration of a sediment component n (which can be Fe oxyhydroxides or organic matter); $\{S_n-M\}$ is the concentration of the trace metal M associated with sediment component n; $[M(org)]^\circ$ is the intercept on the y-axis (which is usually small).

The present study offers a likely explanation for these findings. The studies of Langston (1980, 1982) and Luoma and Bryan (1978) were performed in estuaries, where the pH is relatively constant; the freshwater studies (Tessier *et al.* 1983, 1984) were carried out in three lakes located in a restricted geographical area where the lake pH is relatively constant. In such cases, $[H^+]^x$ and $[H^+]^y$ become approximately constant, and combination of either Eqn. (3a) or (3b) with Eqn. (5) leads to Eqn. (6). The success of sediment Fe or organic carbon as the normalizing factor in these studies could be due to its dominance in the sorption of the particular trace metal investigated. For example, the strong association of Pb (Lion *et al.* 1982; Balistrieri and Murray 1982; Leckie *et al.* 1984) and of As (Aggett and Roberts 1986; Belzile and Tessier 1990) with sedimentary iron oxyhydroxides is well documented; similarly, the affinity of Hg for sediment organic matter (NRCC 1988) is well known.

From the preceding discussion, it follows that the observation of a strong relationship between trace metal levels in a benthic species and sediment characteristics (e.g., extractable metal concentration normalized with respect to the concentration of a sediment component like Fe oxyhydroxides or organic matter) cannot be considered as evidence that the main route of trace metal uptake is via ingestion of particulate material. Such relationships could also be observed for organisms that obtain metal directly from the water, provided that i) the pH is approximately constant over the study area; ii) the dissolved [M] in the water to which the organisms are exposed is in sorptive equilibrium with the sediment component used for normalization. A logical consequence is also that the ratios {M}/{Fe} or {M}/{OM}, although much better predictors than total sediment metal concentrations in some cases, are not "universal" predictors in the sense that their application should be site-dependent (i.e., restricted to a narrow pH range).

5. CONCLUDING REMARKS AND RECOMMENDATIONS

We strongly believe that the development of deterministic models based on sound chemical and biological principles constitutes the most promising approach to the prediction of trace metal burdens in benthic organisms, and eventually to the prediction of metal effects on this community. Provided such models explicitly incorporate the influence of major environmental variables on metal uptake, they should be of general applicability, i.e. they should be able to predict the metal burden of benthos in lakes other than those used for their calibration. In contrast, purely empirical models (black box models), based on statistical relationships only, are useful means of reducing the experimental data but cannot be used to make predictions beyond the original data set. The development of deterministic models has been hindered in the past by our incomplete knowledge of the geochemical and biological processes that control metal accumulation in aquatic organisms. There is no doubt that considerable effort should be devoted to understanding these biogeochemical processes if we are to understand how remedial actions will affect benthic organisms.

The present study represents an attempts to develop a deterministic model of general applicability to predict bioaccumulation of trace metals in aquatic organisms. In the formulation of the model, we use concepts derived from the free-ion model of metal-organism interactions,

and from surface complexation theory, to relate cadmium concentrations in bivalves to those in the water or in the surficial oxic sediments. From a practical point of view, this approach has yielded predictive equations for Cd accumulation in *A. grandis* that require as input geochemical variables readily measured in the bottom waters (pH) and in the sediments ($\{Cd\}_T$, $\{Fe\text{-}ox\}$ and $\{OM\}$). A most important point arising from the study is that relatively little would be needed to establish predictive equations for metal burdens in benthic organisms once the geochemical constants x, y, $N_{Fe} \cdot {}^*K_{Fe\text{-}Cd}$ and $N_{OM} \cdot {}^*K_{OM\text{-}Cd}$ are known accurately for the metals of interest.

Several recommendations arise from our work:

1. **Determination of the geochemical constants.** The approach developed here for Cd could also be extended to other trace metals. Since the geochemical constants x, y, $N_{Fe} \cdot {}^*K_{Fe\text{-}Cd}$ and $N_{OM} \cdot {}^*K_{OM\text{-}Cd}$ are involved in the prediction of cadmium accumulation by (and cadmium effects on) various aquatic organisms, we think that appreciable effort should be devoted to their accurate determination; such an effort would yield a basis for good prediction of cadmium availability to benthic organisms. For example, the following points are suggested:

- Time-averaged values (rather than single grab measurements; see Appendix) of dissolved cadmium concentrations should be obtained at each site for the determination of the geochemical constants.

- Possible means to improve the estimation of the free aquo ion concentration, $[Cd^{2+}]$, should be investigated. In the present study, we have considered only dissolved inorganic ligands; the role of dissolved organic matter in complexing Cd should be assessed and taken into account .

- Our knowledge of the precise sediment components responsible for the sorption of Cd should be improved. Which forms of organic matter are important for Cd sorption? In the present study, we assumed that it is total organic matter, since we use sedimentary organic carbon to estimate $\{OM\}$. Which forms of iron oxyhydroxides are important for Cd sorption? The reagent ($NH_2OH \cdot HCL$; 96 °C) used in the present study to estimate $\{Fe\text{-}ox\}$ extract the sum of amorphous iron oxyhydroxides, ferrihydrite and lepidocrocite. More precise knowledge of the forms of organic matter and iron oxyhydroxides responsible for the sorption, and the development of appropriate methods to measure them, would yield better geochemical

constants. Are other sediment components (e.g. Mn oxyhydroxides) sometimes important for Cd sorption? In the present study, we assumed that only organic matter and Fe oxyhydroxides were important for sorbing Cd.

- The number of sites where Teflon sheets are used to collect diagenetic iron oxyhydroxides (and associated Cd) should be increased; these experimental data are needed to calculate the geochemical constants x and $N_{Fe} \cdot {}^*K_{Fe-Cd}$, and hence indirectly to calculate y and $N_{OM} \cdot {}^*K_{OM-Cd}$ (see Appendix for the details of the calculation). In the present study, only a limited number of sites (8) were investigated with the Teflon collection technique.

2. **Refinement of the geochemical model.** Note that the considerations raised for Cd could also be extended to other trace metals. The prediction of [Cd(org)] from sedimentary measurements depends on how accurately the geochemical model can relate $[Cd^{2+}]$ in the ambient water to sedimentary parameters. The geochemical model used here is still relatively crude, and further work to refine it can be suggested.

- Our understanding of the nature of the sorption processes could be improved. Is it adsorption, surface precipitation, co-precipitation? In the present study, we assumed that $[Cd^{2+}]$ is related to sediment components by overall surface complexation reactions (see Eqn 2 in the Appendix) suggested for adsorption of trace metals on hydrous metal oxides (Benjamin and Leckie, 1981). Identification of the precise processes might lead to better expressions relating $[Cd^{2+}]$ to sedimentary components.

- Effort should be devoted to identify the solid phases responsible for binding [Cd]. Once they are known, better geochemical models could be developed to relate $[Cd^{2+}]$ to sediment components. For example, all the experimental data on the adsorption of Cd on a given iron oxyhydroxide can be described with a set of intrinsic acidity constants, intrinsic adsorption constants for Cd on this solid, density of sites and specific surface area of this solid, and a description of the potential-surface charge relationship (Dzombak and Morel, 1990). Laboratory experiments with pure solid phases have shown that values of these parameters vary from one Fe oxyhydroxide to the other. If the exact forms of Fe oxyhydroxides present in natural sediments were known, we could use these laboratory-derived parameters in a refined geochemical model. Since this information is not yet available, we adopted in the present study a semi-empirical approach where an overall reaction (see Eqn 2 in the Appendix) is used to

describe sorption of Cd on natural Fe oxyhydroxides.

3. **Biomonitors.** Aquatic organisms have been proposed as "biomonitors" for trace metal pollution. Our results raise several points and recommendations for further work.

- Freshwater bivalves have been proposed for biomonitoring purposes (Forester, 1980). According to our results, *A. grandis*, and probably *E. complanata*, do not react rapidly to changes in ambient Cd, Cu and Pb concentrations. For example, *A. grandis* specimens transferred to a polluted lake had not attained, after three years, the metal burdens of indigenous specimens in the polluted lake. Thus, freshwater bivalves will probably be useful for monitoring long-term trends in metal pollution. The suitability of smaller organisms (e.g. insect larvae) should be investigated for monitoring trace metal variations in the environment on a short-term basis.

- Use of organisms for biomonitoring trace metals requires that the relationships between metal concentrations in the organisms (or in a specific tissue) and their external environment: i) be well known; ii) apply to sites other than those used for calibration; iii) apply to environmental conditions other than those used for the calibration. In our opinion, this generality can be obtained only if the relationships between tissue metal concentration and predictive environmental variables are derived from sound biological and chemical principles. This critical point has been overlooked in the past and should be addressed explicitly.

- Figure 3 shows that prediction of Cd concentration in the tissues of *A. grandis* from sedimentary variables is acceptable for a large number of aquatic environments (over a geographical area of about 350 000 km^2 in this case); this is an example of a predictive relationship based on biological and chemical processes. Admittedly, the relationships between [Cd(org)] and the sedimentary parameters could be improved by a better determination of the geochemical constants and a refinement of the geochemical model, as discussed above. Similar approaches to the one developed for the study of Cd in *A. grandis* could be adopted for the study of other trace metals in other aquatic organisms.

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APPENDIX

Article entitled:

Modeling Cd partitioning in oxic lake sediments and Cd concentrations in the freshwater bivalve *Anodonta grandis*.

by A. Tessier, Y. Couillard, P.G.C. Campbell and J.C. Auclair

LIMNOLOGY
AND
OCEANOGRAPHY

Modeling Cd partitioning in oxic lake sediments and Cd concentrations in the freshwater bivalve *Anodonta grandis*

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Abstract

Cadmium concentrations were measured at 49 littoral sites in 38 lakes distributed over 350,000 km^2 in the provinces of Québec and Ontario, both in the abiotic environment (oxic sediments and overlying water, diagenetic iron oxyhydroxide deposits on Teflon collectors) and in the soft tissues of the freshwater bivalve *Anodonta grandis* collected along a Cd contamination gradient. Concentrations of dissolved Cd above the water–sediment interface were highly undersaturated with respect to CdCO$_3$(s). The partitioning of Cd between water and surficial oxic sediments is interpreted in terms of sorption of this metal to sedimentary organic matter and Fe oxyhydroxides, by means of surface complexation concepts. Binding intensity values for the sorption of Cd to Fe oxyhydroxides (K_{Fe-Cd}) and organic matter (K_{OM-Cd}) are estimated from field data (i.e. Cd concentrations in diagenetic Fe deposits, in the sediments, and in the water). The following empirical relationships between binding intensities and lake pH are found: log $K_{Fe-Cd} = 0.82$ pH $- 1.30$ ($r^2 = 0.89$) and log $K_{OM-Cd} = 0.97$ pH $- 2.45$ ($r^2 = 0.78$). Calculated Cd partitioning with these binding intensities indicates that Cd is bound mainly to organic matter in these sediments.

Linear regression analysis indicates that Cd concentrations in the soft tissues of the bivalves, [Cd(Org)] (μg g^{-1} dry wt), are related to dissolved Cd concentrations: [Cd(Org)] $= 44$[Cd^{2+}] $+ 10$ ($r^2 = 0.81$) for [Cd^{2+}] expressed in nmol liter^{-1}. In these lakes, simple normalization of sedimentary extractable Cd with respect to sedimentary Fe oxyhydroxide or organic C concentrations proved inadequate for predicting Cd concentrations in *A. grandis*. Combining surface complexation concepts with the free-metal ion model of trace metal–organism interactions, we show that Cd concentrations in the soft tissues of *A. grandis* can be predicted with similar success as with the dissolved Cd concentration from water pH and sediment chemistry (total sedimentary Cd, Fe oxyhydroxides, and organic C concentrations).

Industrialization has increased fluxes of trace metals from terrestrial and atmospheric sources toward the aquatic environment. An important proportion of these metals is progressively added to the aquatic sediments, where they pose a potential threat to benthic organisms. In principle, remedial actions such as reduction in waste disposal, chemical treatment of in-place contaminants, capping, or dredging can be undertaken; these actions are, however, costly. It is clear that the development of rational, effective, and economical strategies to solve the problem of contaminated sediments will depend greatly on our ability to predict how remedial actions will improve water quality and how these changed conditions will affect aquatic organisms (Wetzel 1991). Important progress in this direction will be made only by understanding the biogeochemical processes governing metal accumulation by benthic organisms under field situations.

Predicting metal bioaccumulation in benthic organisms as a function of environmental variables is not straightforward. Many of these organisms are in contact with both dissolved and particulate trace metals and can in principle accumulate the metals either directly from the water or from food particles (Luoma 1983). Uptake from either source will be influenced by physicochemical factors in the aqueous (e.g. pH, ligand type, and concentrations) and particulate phases (e.g. association of the trace metal with specific sediment constituents). The issue is further complicated by the fact that dissolved metal concentrations in the bottom waters are related to those present in the underlying surficial sediments (Tessier 1992).

Considerable uncertainties remain in our knowledge of the processes responsible for the regulation and cycling of trace metals in lakes. However, comparison of water-column profiles of trace metals and nutrients (Murray 1987) and chemical analysis of material collected with sediment traps (Sigg 1987) suggest that trace metals (Cd, Cu, Pb, Zn) can be removed efficiently by phytoplankton in circumneutral lakes and transported to the bottom sediments by the sinking organisms. Sediment trap measurements suggest that Fe and Mn oxyhydroxides are also important scavengers of trace metals (Cd, Cu, Pb, Zn; Sigg 1987; Sigg et al. 1987) and can carry them to the bottom sediments in lakes. Transport of trace metals to lake sediments is not limited to particulate forms; dissolved metals can also diffuse from the bottom waters into the sediments in acid lakes (Cu, Ni, Zn; Carignan and Nriagu 1985; Carignan and Tessier 1985; Tessier et al. 1989). Release of metals from the sediments back to the overlying waters, following redox processes, may also occur (Morfett et al. 1988). Thus, trace metals in surficial oxic sediments are expected to be associated with sediment components such as organic matter (living organisms, debris, humic acids) and Fe and Mn oxyhydroxides, and the trace metal content of these sediment components can be expected to be related to that in the overlying water.

The above considerations stress the importance of understanding geochemical processes if general models for predicting metal accumulation in benthic organisms are to be developed. In this paper we illustrate the point, taking as an example the accumulation of Cd,

a nonessential trace metal, in the freshwater pelecypod *Anodonta grandis,* a benthic filter feeder, for a large number of lakes over a wide geographical area. We discuss the relationships between concentrations of Cd in oxic sediments and those in the overlying water, by means of surface complexation concepts. We then use these concepts together with the free-metal ion model (Morel 1983) to relate Cd concentrations in *A. grandis* to dissolved and sedimentary Cd concentrations in the animals' environment.

Study area

Oxic sediments, associated pore water, and bivalves (when present) were collected at 49 littoral stations in 38 lakes distributed over a 350,000-km² study area in Québec and Ontario (Table 1). The sites were chosen to represent a gradient of Cd contamination (Cd concentrations in water, sediments, and bivalves) and a wide range of lake pH values and other chemical characteristics (Table 2).

For the lakes in the Eastern Townships of Québec, the bedrock is composed of Ordovician and Cambrian sedimentary rock, covered by unconsolidated deposits of glacial till and marine clays; small-scale mining activities (Cu, Ni, Pb, Zn) occurred until recently. All the other lakes are located on the Precambrian Shield. Lakes in the mining areas of Sudbury (Ni, Cu) and Rouyn-Noranda (Cu, Pb, Zn) are subject to relatively high acid and metal contamination from current mining operations, abandoned mines, and atmospheric deposition from nearby smelters. Lakes in the area of Chibougamau are also affected by ongoing mining operations (Cu). Lakes in the Muskoka area are far from industrial activities (~200 km southeast of Sudbury and 250 km north of Toronto); Lake Tantaré is 40 km north of Québec city, entirely within an ecological reserve.

Materials and methods

Sampling—Water samples were collected in the first few centimeters above the sediment–water interface with in situ samplers (pore-water peepers; 1-cm vertical resolution; Gelman HT-200 membrane; three per site) similar to those described by Hesslein (1976) and Carignan et al. (1985). The peepers consist of Plexiglas sheets (1.3 cm thick) into which com-

Table 1. Sample identification and location of stations.

Site No.	Lake	Area	Location
A-01	Aylmer	Eastern Townships, Québec	45°50'N, 71°20'W
A-02			
BC-01	Blue Chalk	Muskoka, Ontario	45°12'N, 78°56'W
BE-03	Beauchastel	Rouyn-Noranda, Québec	48°10'N, 79°08'W
BI-01	Bird	Muskoka	45°02'N, 79°04'W
BO-02	Bousquet	Rouyn-Noranda	48°13'N, 78°39'W
BR-01	La Bruère	Rouyn-Noranda	48°09'N, 78°56'W
BR-04			
BR-05			
BW-01	Bigwind	Muskoka	45°03'N, 78°50'W
BW-02			
CA-01	Caron	Rouyn-Noranda	47°55'N, 78°58'W
CE-05	Brompton	Eastern Townships	45°25'N, 72°10'W
CE-06			
CH-01	Chub	Muskoka	45°13'N, 78°59'W
CL-03	Clearwater	Sudbury, Ontario	46°22'N, 81°03'W
DA-01	D'Alembert	Rouyn-Noranda	48°23'N, 79°01'W
DF-01	Dufresnoy	Rouyn-Noranda	48°27'N, 79°02'W
DU-01	Dufay	Rouyn-Noranda	48°03'N, 79°28'W
FA-02	Fairbank	Sudbury	46°27'N, 81°25'W
FL-01	Flavrian	Rouyn-Noranda	48°18'N, 79°12'W
GF-01	Gullfeather	Muskoka	45°06'N, 79°01'W
GF-02			
H-01	Harp	Muskoka	45°23'N, 79°08'W
HE-01	Héva	Rouyn-Noranda	48°11'N, 78°19'W
J-01	Joannès	Rouyn-Noranda	48°12'N, 78°40'W
J-02			
LB-01	Lake of Bays	Muskoka	45°15'N, 79°00'W
LD-01	Lac aux Dorés	Chibougamau, Québec	49°55'N, 74°16'W
LD-02			49°49'N, 74°20'W
LD-03			49°55'N, 74°14'W
LD-04			49°54'N, 74°17'W
MA-01	Massawippi	Eastern Townships	45°15'N, 72°00'W
MC-02	McFarlane	Sudbury	46°25'N, 80°57'W
ME-01	Memphrémagog	Eastern Townships	45°05'N, 72°10'W
NO-01	Norhart	Chibougamau	49°29'N, 74°26'W
OP-01	Opasatica	Rouyn-Noranda	48°05'N, 79°18'W
PA-01	Paint	Muskoka	45°13'N, 78°57'W
RI-01	Ril	Muskoka	45°10'N, 79°00'W
SC-01	St. Charles	Sudbury	46°26'N, 81°01'W
SI-01	Silver	Sudbury	46°25'N, 81°01'W
SN-01	St. Nora	Muskoka	45°10'N, 78°50'W
TA-03	Tantaré	Québec, Québec	47°04'N, 71°32'W
TA-04			
TI-01	Tilton	Sudbury	46°22'N, 81°04'W
TO-01	Tock	Muskoka	45°16'N, 78°53'W
VA-01	Vaudray	Rouyn-Noranda	48°07'N, 78°42'W
WA-01	Wavy	Sudbury	46°17'N, 81°06'W
WR-01	Little Wren	Muskoka	45°11'N, 78°51'W

partments (3.3 ml, 1 cm apart in a row, organized in two parallel rows) have been machined. When in storage, the peepers were kept in a dilute H_2SO_4 solution. Before use, they were rinsed with demineralized water (Milli-Q3RO/Milli-Q2 system; Millipore Ltd.); the compartments were filled with demineralized water and deoxygenated by bubbling with nitrogen for at least 24 h in Plexiglas cylinders filled with demineralized water before being inserted vertically in the lake sediments by SCUBA divers. After a 2-week equilibration period in the sediments, the peepers were retrieved by divers and sampled immediately.

Table 2. Mean concentrations of total dissolved Cd ([Cd]), free Cd ([Cd^{2+}]), major ions, alkalinity, and organic C ([C_{org}]) in the overlying waters, and concentrations of total Cd ({Cd}$_T$), Cd associated with organic matter ({OM–Cd}; calculated with Eq. 16), Fe oxyhydroxides ({Fe–ox}), and organic matter ({OM}; μmol C g^{-1}) in the surficial sediments at the various sites studied. (Not measured—NM.)

Site	pH	[Ca]	[Na]	[SO$_4$]	[Alk]*	[C$_{org}$]	[Cd]	[Cd^{2+}]	{Cd}$_T$	{OM–Cd}	{Fe–ox}	{OM}
		\multicolumn{5}{c}{(µmol liter^{-1})}		\multicolumn{2}{c}{(nmol liter^{-1})}		\multicolumn{2}{c}{(nmol g^{-1})}		\multicolumn{2}{c}{(µmol g^{-1})}
A-01	7.25	124	74	57	507	767	0.110	0.108	4.00	3.64	157	1,775
A-02	7.11	128	72	64	453	758	0.089	0.087	3.60	3.41	26.9	575
BC-01	6.82	57	26	65	135	363	0.041	0.041	2.80	2.52	65.6	775
BE-03	7.63	484	NM	NM	680	NM	NM	—	49.8	—	143	NM
BI-01	6.37	107	35	78	109	475	0.170	0.167	8.43	8.09	102	4,472
BO-02	6.34	106	45	82	89	1,217	2.37	2.32	33.0	30.1	207	3,413
BR-01	7.94	395	NM	NM	579	NM	NM	—	52.1	—	94.2	NM
BR-04	7.33	393	NM	NM	687	NM	NM	—	43.6	—	75.1	NM
BR-05	7.33	369	248	241	570	950	0.790	0.743	36.1	33.6	72.9	1,093
BW-01	6.05	94	46	72	145	524	0.350	0.344	5.00	4.86	30.6	1,804
BW-02	6.52	86	52	75	90	625	0.21	0.206	2.33	2.26	24.8	1,200
CA-01	7.05	245	105	181	276	1,108	3.14	3.01	51.2	48.0	92.9	1,707
CE-05	7.16	102	NM	NM	364	NM	NM	—	10.5	—	103	NM
CE-06	7.16	100	39	62	581	453	0.098	0.096	8.29	8.09	97.7	4,617
CH-01	5.50	47	22	71	32	618	0.320	0.314	1.90	1.67	57.7	883
CL-03	4.79	136	94	175	0	343	4.83	4.55	3.87	2.89	757	5,967
DA-01	7.14	197	62	108	267	1,003	1.77	1.72	93.3	91.3	119	6,533
DF-01	7.17	166	NM	NM	NM	NM	NM	—	18.3	17.5	126	3,251
DU-01	6.55	85	NM	NM	NM	NM	NM	—	9.13	8.24	88.0	1,175
FA-02	7.36	163	38	144	246	375	0.036	0.035	3.27	3.07	61.1	1,008
FL-01	7.39	158	NM	NM	NM	NM	NM	—	27.8	27.0	123	4,198
GF-01	5.90	84	43	81	79	858	0.21	0.21	4.19	3.98	46.7	1,601
GF-02	6.07	67	20	86	41	787	0.10	1.10	8.91	8.58	25.9	1,159
H-01	6.93	59	41	67	175	593	0.140	0.138	9.00	8.72	27.5	1,075
HE-01	6.19	52	40	68	40	1,000	0.67	0.66	10.4	9.35	122	1,838
J-01	7.27	176	NM	NM	NM	NM	NM	—	62.8	—	94.9	NM
J-02	7.27	188	35	101	679	784	1.13	0.10	61.9	60.1	120	4,675
LB-01	6.94	64	44	77	128	470	0.090	0.088	6.00	5.59	42.6	733
MA-01	8.10	700	180	108	1,430	398	0.049	0.047	3.40	3.34	117	5,592
MC-02	7.49	410	1,435	227	669	482	0.336	0.285	108	103	371	7,883
ME-01	7.56	380	165	81	882	401	0.032	0.031	6.60	6.43	167	6,642
NO-01	7.09	106	25	31	178	813	0.114	0.113	9.92	9.82	98.2	12,158
OP-01	7.39	280	111	120	494	818	0.37	0.36	4.40	3.76	40.8	262
PA-01	7.13	147	86	97	112	440	0.043	0.042	2.67	2.38	112	1,107
RI-01	6.02	113	44	78	57	473	0.20	0.20	9.79	9.37	83.7	3,230
SC-01	6.88	211	758	197	187	645	0.37	0.33	52.5	50.2	233	6,575
SI-01	4.07	218	1,780	439	0	425	17.5	14.1	1.34	1.10	544	8,375
SN-01	6.80	57	54	66	111	463	0.071	0.069	5.40	5.00	115	1,933
TA-03	5.68	NM	NM	48	NM	NM	0.537	0.537	5.27	3.42	3,212	11,633
TA-04	5.65	NM	NM	50	NM	NM	0.400	0.400	7.15	6.64	482	12,400
TI-01	5.88	97	55	152	37	501	1.93	1.85	8.78	6.93	590	4,042
TO-01	6.43	139	39	79	61	474	0.23	0.22	18.0	17.6	120	9,967
VA-01	6.57	90	NM	NM	NM	NM	NM	—	38.3	34.9	129	1,883
WA-01	4.62	52	28	126	0	420	2.32	2.16	3.31	2.68	683	8,275
WR-01	6.27	80	64	81	50	453	0.25	0.244	11.2	11.1	71.7	9,358
LD-01	7.42	176	30	47	377	462	0.018	0.018	6.92	6.59	165	3,550
LD-02	7.50	224	48	92	401	492	0.062	0.060	9.32	9.13	139	6,883
LD-03	7.47	177	29	48	418	448	0.027	0.027	3.10	3.04	43.7	2,458
LD-04	7.40	200	39	69	404	524	0.024	0.023	15.0	14.9	88.5	16,125

* µeq liter^{-1}; calculated with HYDRAQL, given the inorganic C concentrations and the other chemical characteristics of the lakes.

Samples (1 ml) in the first row were collected from five compartments above the water–sediment interface, and pH was measured in each sample in the field (Carignan 1984) with a combined microelectrode (Microelectrodes, Inc., model MI-710) and a portable pH meter (Radiometer, model PHM80). On several occasions during the summer season, water sam-

ples were also collected at many of the sites (33/49) with a clean polyethylene bottle close to the sediment–water interface for pH measurement. The purpose of this measurement was to calculate time-averaged pH values $[-\log_{10}(\Sigma[H^+]/n)]$ for the summer period. Samples (1 ml) for dissolved sulfate and chloride analysis were removed from the peepers with a syringe from compartments of the same row and injected into prewashed polypropylene tubes; those for inorganic C determinations (1 ml) were also obtained from the same row with a syringe and injected through a septum into pre-evacuated and prewashed glass tubes.

The samples (3.3 ml) for trace metal analysis were collected from the compartments of the second row by piercing the peeper membrane with a Gilson pipette fitted with an acid-cleaned tip: these samples were injected into prewashed and preacidified (30 μl of 1 N Ultrex HNO_3, final pH <2.5) Teflon vials. Additional water was collected from the compartments 6 and 7 cm above the sediment–water interface of each peeper (combined content, 5 ml) for analysis, if necessary, by multiple injection flameless atomic absorption spectrophotometry (AAS, *see below*). Mean concentrations of total dissolved Cd ([Cd]) in the overlying waters are given for each site in Table 2. When sufficiently high (>0.7 nM), the concentrations found in the five compartments of the pore-water peepers immediately above the sediment–water interface (i.e. $3 \times 5 = 15$ values) were used for calculating the means; in the other cases, the values obtained by successive injections (i.e. 3 values) were used for the calculation. Inadvertent contamination of the compartments with Cd, occurring before inserting the peepers into the sediments despite the precautions taken, would have decreased by diffusion out of the cells during the 2-week equilibration period in the lake sediments. A greater possibility of contamination with these devices probably occurs during sampling of the compartments, since small particles (containing Cd) that adhere to the membrane can be taken inadvertently along with the water sample. The low values of [Cd] found in many circumneutral pH lakes (10^{-11} M range; *see Table 2*) argue against important contamination problems.

Sediment cores were collected by divers,

close to the peepers, with Plexiglas tubes (9-cm diam). The tubes were tightly closed to minimize perturbation of the sediments during their transport to the shore. The sediment cores were extruded on shore, and only the uppermost 0.5 cm, containing oxidized sediments, was retained. These samples were placed in 500-ml centrifugation bottles half filled with lake water and kept at ~4°C during transport to the laboratory where they were kept frozen until analysis.

In several of the lakes (sites CE-05, CL-03, DA-01, HE-01, J-02, MC-02, SI-01, and WA-01), Teflon sheets were inserted vertically in the sediments by divers and left in place for more than 10 weeks. In sufficiently reducing sediment layers, Fe(III) oxyhydroxides are reduced to Fe(II) (due to their burial or to fluctuation of the redox transition zone), which is released to the pore water; a portion of the Fe(II) thus produced diffuses upward where it is oxidized in the upper sediment layers and hydrolyzes to form diagenetic Fe(III) oxyhydroxides. The diagenetic Fe(III) oxyhydroxides thus produced can be collected, along with the sorbed trace elements, on inert material such as sheets of Teflon (Belzile et al. 1989; De Vitre et al. 1991).

Fe oxyhydroxide samples obtained by this in situ technique appear as a thin orange-brown band, typically 0.5 cm wide and 5–20 μm thick for littoral sites (Fortin et al. in prep.). The amount of material deposited is small (typically 500 μg per Teflon sheet), but it has the advantage of being relatively free from contamination by the sediment matrix. The Fe particles collected have been characterized by transmission electron microscopy and by electron and X-ray diffraction. Their chemical composition has been determined at a microscopic scale by energy-dispersive spectroscopy and on a macroscopic scale by wet chemical methods (Fortin et al. in prep.). According to these analyses, the crystallinity of the particles is low; crystalline forms identified are poorly ordered ferrihydrite and lepidocrocite. Si, SO_4, Cl, phosphate, Mn, Ca, and Al represent minor components of the Fe-rich particles, whereas organic C (presumably microorganisms, as suggested from transmission electron microscopy observations) is a more abundant component. After retrieval of the Teflon collectors, the areas covered with the Fe oxyhydroxides

were cut out from the Teflon sheet and the deposited material was dissolved at 96°C in a 0.04 M $NH_2OH \cdot HCl$ solution in 25% (vol/ vol) acetic acid. Fe and Cd concentrations in these extracts were determined by AAS as described below for the sediment extracts.

Specimens of *A. grandis* (usually 10 per site; generally ranging from 8 to 10 cm long) were obtained by divers at each site; within a radius of 50 m from the sediment and water collection site. The bivalves were placed in plastic bags with lake water and maintained at ~4°C during transport to the laboratory where they were left to depurate for at least 24 h in aerated lake water. They were then dissected into gills, mantle, hepatopancreas, and remaining tissues, hereafter referred to as "remains." No organisms were gravid, as sampling was undertaken early in summer. For each sampling site, each tissue type of the 10 animals collected was pooled and frozen at −20°C until needed for analysis.

Analyses—The water samples were analyzed for Cd, Fe, Mn, SO_4, Cl, major cations, and organic and inorganic C. The metal concentrations were obtained by flame AAS when possible (Fe, Mn, Ca, Mg, Na, K; Varian Techtron model 575ABQ or model Spectra AA-20) or, otherwise, by flameless AAS (Fe, Mn, Cd; Varian Techtron model 1275 or Spectra AA-30; GTA-95 or GTA-96). When initially measured levels of Cd in the overlying waters did not exceed a concentration threshold of five times the analytical detection limit (0.13 nmol liter⁻¹), its concentration was determined by a multiple injection technique. The subsamples were injected successively and subjected to the preliminary drying steps; the combined sample was then atomized. SO_4 and Cl concentrations were determined by ion chromatography (Dionex AutoIon, system 12); dissolved inorganic C was measured by gas chromatography (Carignan 1984) and dissolved organic C (DOC) by persulfate-UV oxidation, followed by conductometric determination on a Technicon AutoAnalyzer of the CO_2 released. The equilibrium model HYDRAQL (Papelis et al. 1988) was used to calculate ion activities. The calculation of Cd^{2+} activity involved the mean [Cd] in the overlying water (Table 2), the measured concentrations of the inorganic ligands OH^-, CO_3^{2-}, SO_4^{2-} and Cl^-, and the stability constants of the inorganic complexes (Smith and Martell 1977).

The surficial sediment samples were thawed and centrifuged to remove excess water; subsamples (equivalent to ~1 g dry wt) were extracted, and Cd (and Fe) was partitioned into the following empirical fractions (Tessier et al. 1989): (1) the sediment subsample was extracted with $MgCl_2$; (2) the residue from (1) was extracted with an acetate buffer at pH 5; (3) the residue from (2) was extracted at room temperature with $NH_2OH \cdot HCl$; (4) the residue from (3) was extracted with $NH_2OH \cdot HCl$ at 96°C; (5) the residue from (4) was extracted with H_2O_2; (6) the residue from (5) was digested with a mixture of hydrofluoric, nitric, and perchloric acids. Fe, Mn, and Cd concentrations in the extracts were determined by flame AAS with the appropriate extractant matrixes for standards and blanks. Details of these procedures are given elsewhere (Tessier et al. 1979; 1989). Sediment organic C concentrations, $\{C_{org}\}$, were determined with a CNS analyzer (Carlo-Erba, model NA1500) after removal of inorganic C by acidification with H_2SO_4 (0.5 mol liter⁻¹, 15 min, 100 ml g⁻¹ sediment dry wt).

Each pooled bivalve tissue was homogenized (Brinkman tissue grinder, model CH-6010). A subsample was then dried to constant weight to determine the wet : dry wt ratio, and a second subsample was digested in a Teflon bomb with concentrated nitric acid (Aristar; 3 ml per 100 mg of tissue dry wt) in a microwave oven at pressures between 5,500 and 7,000 kPa for ≈1 min. Cd concentrations in the diluted digested samples were determined by flame AAS. A certified reference material (lobster hepatopancreas, TORT-1, Natl. Res. Council Canada) was regularly submitted to the same digestion procedure and analyzed for Cd. We measured 25.7±1.9 µg Cd g⁻¹ ($n = 10$) for TORT-1 (certified value, 26.3±2.1 µg g⁻¹). Unless otherwise indicated, reported variabilities refer to standard error.

Results and discussion

Relationship between dissolved and surficial sedimentary Cd—Table 2 shows that the mean [Cd] varies by nearly three orders of magnitude over the study area. Lakes in the areas of Rouyn-Noranda and Sudbury show the highest [Cd], a probable consequence of the smelting

operations in these areas. There is, however, a general tendency for [Cd] to decrease with increasing lake pH (Fig. 1A), in the absence of local Cd sources. For example, the linear regression between log[Cd] and pH is

$$\log[Cd] = -0.51(\pm0.07)pH - 6.6(\pm0.2) \ (1)$$

with $r^2 = 0.71$ ($n = 26$) if lakes from the Rouyn-Noranda and Sudbury areas, for which the smelters constitute a known anthropogenic source of Cd, are removed.

For all of the lakes studied (pH 4.0–8.4; alkalinity concn between 0 and 1,400 meq liter^{-1}; [PO$_4$] < 0.1 μM; [Si] < 20 μM), CdCO$_3$(s) should be the most stable Cd solid phase. Calculation of the saturation index [SI = log(IAP/K_s), where IAP is the ion activity product and K_s the solubility product] indicates a clear undersaturation of the overlying waters of all the lakes with respect to this solid phase (Fig. 1B). In general, the [Cd^{2+}] calculated by taking into account the inorganic ligands represents >95% of [Cd] (Table 2).

Total Cd concentrations in the sampled sediments vary by more than two orders of magnitude ({Cd}$_T$; Table 2); the highest concentrations are found in lakes in the mining areas of Rouyn-Noranda and Sudbury. Because solubility equilibrium involving pure solid phases cannot explain the presence of this metal in oxic sediments, other reactions including adsorption, absorption, surface precipitation, and coprecipitation must be invoked to relate its concentrations in the overlying water to its concentrations in the surficial sediment (Tessier 1992). The general term "sorption" is used herein, because the different reactions cannot be distinguished in natural waters (Honeyman and Santschi 1988).

There are several indications in the literature that Fe and Mn oxyhydroxides and organic matter are important components for sorbing Cd in sediments. For example, Luoma and Bryan (1981) have shown, by statistical analysis of 50 oxidized surficial estuarine sediments presenting a wide range of sedimentary Cd and sediment component concentrations, that sedimentary Cd was correlated with extractable Fe (0.2 M ammonium oxalate in 0.2 M oxalic acid or 1 M HCl); extractable Fe (presumably Fe oxyhydroxides) was found to be more important than total Fe for binding Cd. Lion et al. (1982) examined the sorption
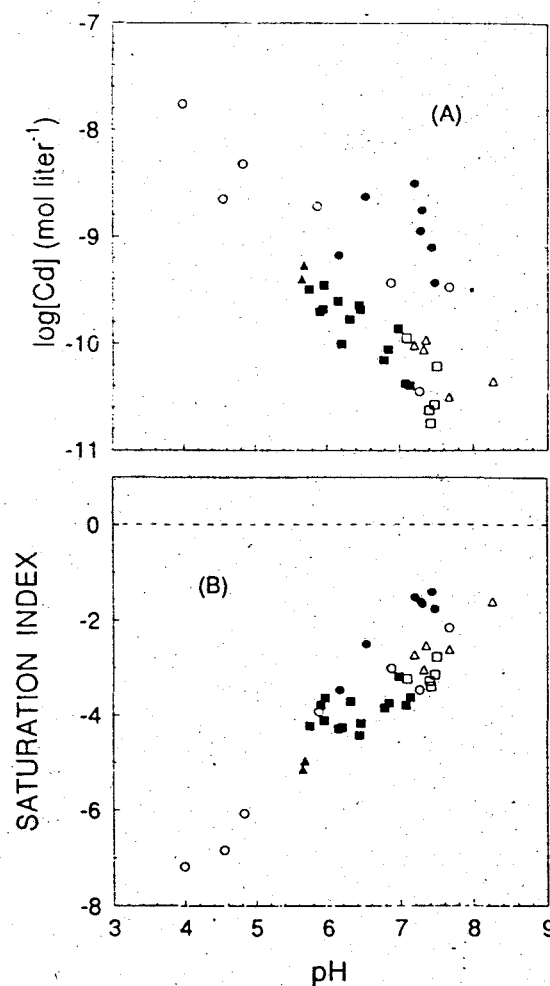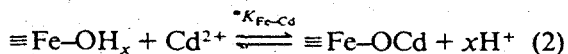

Fig. 1. [Cd] and saturation index as a function of pH for the various sites studied. Different symbols are used for the lakes located in the areas of Sudbury (O), Rouyn-Noranda (●), Chibougamau (□), Muskoka (■), Eastern Townships (△), and Québec (▲). Saturation index is log(IAP/K_s). Dashed line indicates saturation with respect to CdCO$_3$(s).

of Cd on oxidized surficial sediments before and after removing, by chemical attack, various components from the sediments. The major decrease in sorption was observed after removal of organic matter (extraction with NaOH); they thus attributed an important role to organic matter in the sorption of Cd.

In line with the above findings, we assume here that the two main components of oxic sediments that sorb Cd are Fe oxyhydroxides and organic matter, that these components have surface sites for sorption that can be treat-

ed as surface ligands, and that surface complexation concepts developed for simple, well-defined systems in the laboratory can be applied to more complex sediment components. According to surface complexation theory, the adsorption of Cd on Fe oxyhydroxide surfaces can be expressed (Benjamin and Leckie 1981) by

$$\equiv Fe\text{-}OH_x + Cd^{2+} \overset{*K_{Fe\text{-}Cd}}{\rightleftharpoons} \equiv Fe\text{-}OCd + xH^+ \quad (2)$$

$$*K_{Fe\text{-}Cd} = \frac{\{\equiv Fe\text{-}OCd\}[H^+]^x}{\{\equiv Fe\text{-}OH_x\}[Cd^{2+}]} \quad (3)$$

where charges on the solid species are omitted for simplicity, $*K_{Fe\text{-}Cd}$ is an apparent overall equilibrium constant, x is the average apparent number of protons released per Cd^{2+} ion adsorbed (Honeyman and Leckie 1986), and $\{\equiv Fe\text{-}OH_x\}$ and $\{\equiv Fe\text{-}OCd\}$ represent respectively the concentration of free surface sites on the Fe oxyhydroxides and the concentration of sites occupied by Cd. Throughout this paper, the notation "$\equiv$" refers to adsorption *sites*, whereas $\{\cdot\}$ and $[\cdot]$ refer to concentrations of solid and dissolved species respectively.

At low adsorption density (i.e. when the concentration of occupied adsorption sites is small compared to the free site concentration) the condition

$$\{\equiv Fe\text{-}O\text{-}\}_T \approx \{\equiv Fe\text{-}OH_x\} \quad (4)$$

should apply, where $\{\equiv Fe\text{-}O\text{-}\}_T$ is the total concentration of sites. This latter concentration can in turn be expressed as

$$\{\equiv Fe\text{-}O\text{-}\}_T = N_{Fe} \times \{Fe\text{-}ox\} \quad (5)$$

where N_{Fe} is the number of moles of adsorption sites of the Fe oxyhydroxides per mole of Fe, and $\{Fe\text{-}ox\}$ is the analytical concentration of Fe oxyhydroxides. If it is assumed that only one site is occupied by each sorbed metal ion, then

$$\{\equiv Fe\text{-}OCd\} = \{Fe\text{-}Cd\} \quad (6)$$

where $\{Fe\text{-}Cd\}$ is the analytical concentration of Cd associated with the Fe oxyhydroxides. Combining Eq. 3 to 6 leads to

$$K_{Fe\text{-}Cd} = \frac{N_{Fe} \times *K_{Fe\text{-}Cd}}{[H^+]^x}$$

$$= \frac{\{Fe\text{-}Cd\}}{\{Fe\text{-}ox\}[Cd^{2+}]} \quad (7)$$

where $K_{Fe\text{-}Cd}$ is an apparent equilibrium constant which is a function of pH.

By similar reasoning, the following expression can be derived for sorption of Cd on organic matter (OM):

$$K_{OM\text{-}Cd} = \frac{N_{OM} \times *K_{OM\text{-}Cd}}{[H^+]^y}$$

$$= \frac{\{OM\text{-}Cd\}}{\{OM\}[Cd^{2+}]} \quad (8)$$

where by analogy with Eq. 2–7, N_{OM} is the number of moles of sites on the organic matter per mole organic C, and $K_{OM\text{-}Cd}$ and $*K_{OM\text{-}Cd}$ are apparent overall equilibrium constants. Similarly, y is the apparent number of protons released per Cd^{2+} ion adsorbed on organic matter, and $\{OM\}$ and $\{OM\text{-}Cd\}$ are the concentrations of organic matter and of Cd associated with organic matter respectively. Linearization of Eq. 7 and 8 yields

$$\log K_{Fe\text{-}Cd} = x\,pH + \log(N_{Fe} \times *K_{Fe\text{-}Cd}) \quad (9)$$

$$\log K_{OM\text{-}Cd} = y\,pH + \log(N_{OM} \times *K_{OM\text{-}Cd}) \quad (10)$$

and plots of $\log K_{Fe\text{-}Cd}$ or $\log K_{OM\text{-}Cd}$ vs. pH should yield slopes of x and y and intercepts on the y-axis of $\log(N_{Fe} \times *K_{Fe\text{-}Cd})$ and $\log(N_{OM} \times *K_{OM\text{-}Cd})$ respectively.

We have estimated $K_{Fe\text{-}Cd}$ and $K_{OM\text{-}Cd}$ for each sampling site from determinations of the three variables on the right-hand side of Eq. 7 and 8. In the calculation of the first of these variables, $[Cd^{2+}]$ (nmol liter^{-1}; Table 2), only inorganic ligands were considered; because of the lack of relevant equilibrium constants, possible Cd complexation by natural organic ligands could not be considered. The calculated value of $[Cd^{2+}]$ in these waters is very close to that of [Cd]; calculated contributions of $CdSO_4$(aq) and $CdCl^+$ are generally <5%, the only exceptions being for lakes St. Charles (10%), McFarlane (15%) and Silver (19%), all in the Sudbury area.

Estimation of the concentrations of Cd associated with the Fe oxyhydroxides or with organic matter ($\{Fe\text{-}Cd\}$ and $\{OM\text{-}Cd\}$), two of the remaining variables in Eq. 7 and 8, is however not straightforward. Most of sediment Cd was found in extracts (1) 35±20%, (2) 29±10%, (3) 15±10%, and (4) 23±20%; concentrations of Cd in extract (5) were detectable only in a few cases and levels in extract (6) were undetectable for all sediment samples.

Large proportions of sedimentary Cd were thus extracted with relatively mild reagents. In such a situation, it is difficult to decide objectively which portion of this easily extractable Cd was associated with Fe oxyhydroxides or with organic matter in the original sediment.

To overcome this difficulty, we proceeded in the following manner. The ratio $\{Cd\}_c$: $\{Fe\}_c$, obtained from dissolution of the Fe oxide deposit on the Teflon collectors, was assumed to be representative of the ratio $\{Fe-Cd\}$: $\{Fe-ox\}$ prevailing in the sediments. The values of $[Cd^{2+}]$, together with those of the ratios $\{Cd\}_c$: $\{Fe\}_c$ obtained from the Teflon collectors, were then used to calculate K_{Fe-Cd} according to Eq. 7. The plot, corresponding to Eq. 9, is shown in Fig. 2A; linear regression of these data yields

$$\log K_{Fe-Cd} = 0.82(\pm0.08) \text{ pH} - 1.30(\pm0.38)$$
$$(n = 16; \quad r^2 = 0.89). \quad (11)$$

The total sorbed Cd concentration is written

$$\{Cd\}_T = \{Fe-Cd\} + \{OM-Cd\} \quad (12)$$

since we assume that only Fe oxyhydroxides and organic matter bind Cd in sediments. Combining Eq. 7 and 12 allows calculation of $\{OM-Cd\}$ according to

$$\{OM-Cd\}$$
$$= \{Cd\}_T - \frac{N_{Fe} \times {}^*K_{Fe-Cd}\{Fe-ox\}[Cd^{2+}]}{[H^+]^x}. \quad (13)$$

In the calculation of $\{OM-Cd\}$ with Eq. 13, the value of $\{Fe-ox\}$ (mol Fe g^{-1} sediment dry wt; Table 2) was taken as the sum of the Fe concentrations extracted from the sediments in steps (3) and (4) with the reducing reagent $NH_2OH \cdot HCl$. Measurements with pure phases prepared in the laboratory have shown that this reagent dissolves synthetic ferrihydrite and lepidocrocite almost quantitatively (Fortin et al. in prep.), i.e. the Fe oxyhydroxide forms that should be most effective in binding Cd. Together, these two extractions dissolved most (89±7%) of the Fe extractable in the first five extractions. Values of x (0.82) and $N_{Fe} \times {}^*K_{Fe-Cd}$ ($10^{-1.30}$) were taken from Eq. 11. Values of $\{OM-Cd\}$ calculated on this basis with Eq. 13 were used, together with $[Cd^{2+}]$ and $\{OM\}$ (Table 2), to calculate K_{OM-Cd} according to Eq. 8. The values of sedimentary organic C concentrations (mol organic C g^{-1} sediment dry wt) were used as estimates of $\{OM\}$. The plot
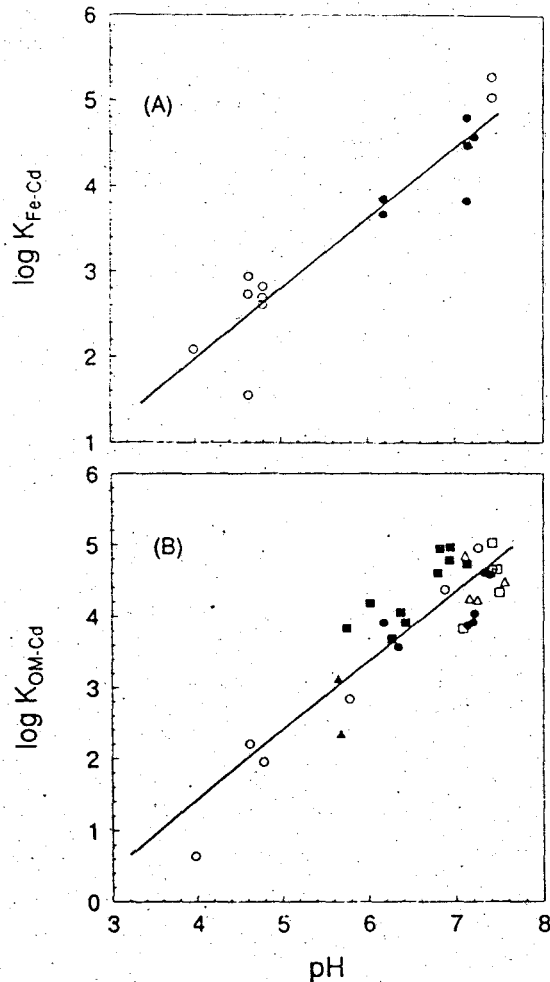

Fig. 2. Apparent overall equilibrium constants for the sorption of Cd on natural Fe oxyhydroxides and organic matter as a function of pH. Symbols as in Fig. 1.

corresponding to Eq. 10 is shown in Fig. 2B and regression of the data yields

$$\log K_{OM-Cd} = 0.97(\pm0.09) \text{ pH} - 2.45(\pm0.46)$$
$$(n = 35; \quad r^2 = 0.78). \quad (14)$$

Sites located in lakes Gullfeather and Bigwind, for which the pore-water profiles showed evidence of anoxic conditions at the sediment–water interface (release of dissolved Fe from the sediment; reduction of sulfate at the interface), were not included in the calculation; station MA-01, consistently an outlier, was also excluded.

$\log K_{Fe-Cd}$ and $\log K_{OM-Cd}$ show pH dependency (Fig. 2), as expected from Eq. 9 and 10; this behavior is consistent with the simple sur-

face complexation model used, despite the crude assumptions that were made. Many factors may contribute to the scatter evident in Fig. 2. The simple model retained does not consider electrostatic interactions for the sorption of Cd on Fe oxyhydroxides and organic matter, i.e. it assumes that the free energy of adsorption is dominated by chemical interactions rather than by electrostatic interactions. Values of the parameters N_{Fe}, N_{OM}, $*K_{Fe-Cd}$, and $*K_{OM-Cd}$ are considered here to be constants, whereas they might be expected to vary with the nature of sedimentary Fe oxyhydroxides and organic matter (Luoma and Davis 1983); it is probable that the nature of these two components present in the top 0.5 cm of the lake sediments varies among stations. Extraction of Fe with $NH_2OH \cdot HCl$ is only moderately selective and will solubilize various Fe oxyhydroxide forms; similarly, total organic sedimentary C is a very crude estimator of the organic matter active in the sorption process. Only two sediment components, Fe oxyhydroxides and organic matter, have been assumed to be responsible for sorption; sorption by Mn oxyhydroxides, which might be important in some high pH lakes, has been neglected. According to laboratory experiments in well-defined systems, the sorption constants should also vary with the density of adsorption (Benjamin and Leckie 1981) and with the concentration of particles (Di-Toro et al. 1986), both of which vary among the sites. Sedimentary Cd concentrations probably do not vary as rapidly as dissolved Cd and H^+ in response to variations in environmental conditions, i.e. the assumed sorption equilibrium might not be fully attained. The concentration (and possibly the nature) of the dissolved organic matter varies among stations (Table 2); in calculating K_{Fe-Cd} and K_{OM-Cd}, possible complexation of Cd by dissolved organic matter was not taken into account.

Some of the scatter in Fig. 2 might also be due to experimental difficulties. The dissolved Cd concentrations are low, especially for high pH lakes; such samples are particularly subject to contamination and the analytical determinations themselves are less precise than at higher concentrations. During collection of the surficial sediment, the oxic layer may be contaminated by reduced sediments, leading to incorrect estimation of $\{Cd\}_T$, $\{Fe-ox\}$, and $\{OM\}$ present in the surficial sediment. The ratio $\{Cd\}_c$: $\{Fe\}_c$ is also assumed to be representative of the ratio $\{Fe-Cd\}$: $\{Fe-ox\}$ prevailing in the oxic sediments. The Teflon sheets, however, collect "young" diagenetic Fe oxyhydroxides; for example, no goethite could be identified in the Fe-rich material collected (Fortin et al. in prep.), whereas there are indications that this crystalline solid can be present in lake sediments (Schwertmann et al. 1987). In addition, chemical analysis of the Fe-rich diagenetic deposits indicated the presence of organic C and Mn (Fortin et al. in prep.); organic matter and Mn oxyhydroxides (for higher pH lakes) could be responsible for binding a fraction of the Cd collected on the Teflon sheets and assumed to be bound to Fe oxyhydroxides.

Comparison of $\{Cd\}_T$ and $\{OM-Cd\}$ in Table 2 indicates that the association of Cd in oxic lake sediments is dominated by its interactions with organic matter. For the lake sediments studied, $\{OM-Cd\}$ and $\{Fe-Cd\}$ represent $92\pm8\%$ and $8\pm8\%$ of $\{Cd\}_T$, respectively. The proportion of each form varies from one site to another, depending on the relative concentrations of sedimentary Fe oxyhydroxides and organic matter in the sediment and on lake pH. It should be noted that similar conclusions were reached by Luoma (1986) for Cu in oxidized estuarine sediments. The values of $\{OM-Cd\}$ calculated with Eq. 13 correspond very closely to the sum of Cd concentrations found in sediment extracts (1), (2), (4), and (5) (slope = 0.95; $r^2 = 0.99$; $n = 35$). Calculated values of $\{Fe-Cd\}$ agree also reasonably well with Cd concentrations found in the remaining extract (3): slope = 1.26; $r^2 = 0.65$; $n = 35$. It is however difficult, at the moment, to rationalize these correlations on a geochemical basis.

The model developed above should prove useful (if our assumptions regarding the calculation of K_{OM-Cd} are valid) for obtaining a rough estimate of the partitioning of Cd between organic matter and Fe oxyhydroxides in oxic sediments of other lakes. Combination of Eq. 7, 8, and 12 leads to

$$\frac{\{Fe-Cd\}}{\{Cd\}_T}$$
$$= (N_{Fe} \times *K_{Fe-Cd}\{Fe-ox\}[H^+]^y)$$
$$\div (N_{Fe} \times *K_{Fe-Cd}\{Fe-ox\}[H^+]^y$$
$$+ N_{OM} \times *K_{OM-Cd}\{OM\}[H^+]^y) \quad (15)$$

$$\frac{\{OM-Cd\}}{\{Cd\}_T}$$

$$= (N_{OM} \times {}^*K_{OM-Cd}\{OM\}[H^+]^x)$$

$$\div (N_{Fe} \times {}^*K_{Fe-Cd}\{Fe-ox\}[H^+]^y$$

$$+ N_{OM} \times {}^*K_{OM-Cd}\{OM\}[H^+]^x). \qquad (16)$$

The only requirement would be to measure $\{Cd\}_T$ (sum of nondetrital forms), $\{OM\}$, and $\{Fe-ox\}$ for the same oxic sediment sample and lake pH; the necessary values of x, y, $N_{Fe} \times {}^*K_{Fe-Cd}$, and $N_{OM} \times {}^*K_{OM-Cd}$ are obtained from linear regressions 11 and 14. The values of $\{OM-Cd\}$ calculated with Eq. 16 for the lakes studied are shown in Table 2.

Relationship between Cd concentrations in water and in A. grandis—Cd concentrations in various soft tissues of the freshwater bivalve *A. grandis* are given in Table 3. Concentrations in the whole organism, [Cd(Org)], were calculated as follows:

$$[Cd(Org)] = \frac{\Sigma[Cd(tissue)]_i W_i}{\Sigma W_i} \qquad (17)$$

where $[Cd(tissue)]_i$ and W_i are the Cd concentration and the dry weight of the ith tissue. Table 3 shows a 50-fold variation in [Cd(Org)] among stations. Concentrations are generally highest in the gills of the bivalve, especially for the more polluted sites. Gills always contained the greatest proportion ($40 \pm 13\%$) of the total Cd burden of whole animals; the mantle, hepatopancreas, and remaining tissues contributed 21 ± 7, 11 ± 8, and $28 \pm 11\%$. Stepwise multiple regression was performed to examine the relationships between [Cd(Org)] as the dependent variable and [Cd^{2+}], [Ca^{2+}], [H^+], and C_{org} as the independent variables. Due to intercorrelations among both pH and C_{org} and pH and [Cd^{2+}], the largest partial regression coefficient, found for [Cd^{2+}], explained most of the variance ($r^2 = 0.80$); addition of pH ($P < 0.08$) increased the explained variance by only 3% ($r^2 = 0.83$).

Figure 3 illustrates the dependence of [Cd(Org)] on the concentration of the free Cd^{2+} ion, as calculated from [Cd] and inorganic ligand concentrations. The linear regression equation found is

$$[Cd(Org)] = 44(\pm 5) [Cd^{2+}] + 10(\pm 15)$$
$$(n = 17; \quad r^2 = 0.81) \qquad (18)$$

with [Cd^{2+}] in nmol liter^{-1}. Regressions be-

Table 3. Cd concentrations (μg g^{-1}) in the tissues of *Anodonta grandis* from various sampling sites. He—hepatopancreas; Gi—gills; Ma—mantle; Re—remaining; Org—reconstituted organisms (calculated with Eq. 17).

Site	[Cd(He)]	[Cd(Gi)]	[Cd(Ma)]	[Cd(Re)]	[Cd(Org)]
BE-03	17.1	44.1	13.3	8.7	14.4
BO-02	93.4	190	96.8	65.3	110
BR-01	22.3	91.3	23.8	15.6	28.2
BR-04	22.3	116	21.1	15.9	28.5
BR-05	28.4	101	46.3	17.8	40.4
CE-05	6.25	9.90	9.96	5.10	6.80
CE-06	7.32	11.3	13.8	6.46	7.73
DA-01	32.3	223	62.7	18.8	63.5
DF-01	20.8	38.3	25.1	15.9	22.7
DU-01	50.4	103	62.5	55.2	68.1
FL-01	20.8	76.1	28.9	10.5	25.6
GF-01	24.5	23.2	41.8	7.30	19.4
GF-02	23.7	25.2	37.3	6.40	17.4
H-01	44.3	18.8	14.5	9.70	14.7
HE-01	68.5	143	75.8	37.8	72.2
J-01	45.1	263	54.4	35.9	86.9
J-02	48.6	248	62.1	32.9	87.7
LD-01	4.50	12.0	8.70	2.40	6.03
LD-02	1.00	8.10	5.80	3.90	4.96
LD-03	8.10	15.9	10.8	2.40	7.82
LD-04	0.20	5.90	3.20	1.70	2.79
ME-01	8.57	7.50	5.19	3.69	4.74
NO-01	3.10	15.1	6.50	5.30	7.22
OP-01	29.5	24.8	25.8	9.30	19.9
SN-01	66.7	49.3	45.3	14.6	34.0
VA-01	95.7	360	137	78.2	152

tween [Cd^{2+}] and Cd concentrations in the tissues are highly significant ($P < 0.001$), except for Cd in the hepatopancreas which is significant (Table 4).

Laboratory bioassays, conducted with marine benthic animals exposed to dissolved metals under carefully controlled conditions, have shown that the effects of trace metals are related to the free-metal ion concentration and not to the total metal concentrations. For example, mortality of the shrimp *Palaemonetes pugio* exposed to Cd was shown to be proportional to [Cd^{2+}] (Sunda et al. 1978). Similarly, short-term (14 d) accumulation of Cu in the oyster *Crassostrea virginica* was found to be proportional to [Cu^{2+}] (Zamuda and Sunda 1982). These laboratory observations are consistent with our field results (Fig. 3; Table 4).

However, we would have obtained similar regression equations with [Cd] since it is close to the computed value for [Cd^{2+}] at all sites. Given the similarity between [Cd^{2+}] and [Cd] values, and the relative uncertainty in the relations given in Table 4, we cannot demon-
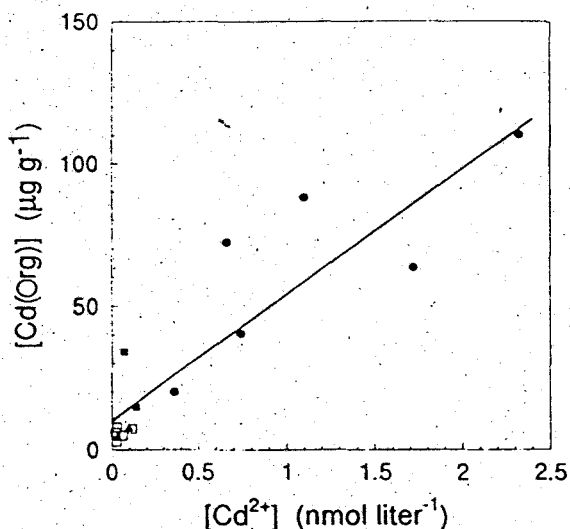
Fig. 3. Relationship between Cd concentrations in the tissues of *Anodonta grandis* and [Cd^{2+}] calculated from total dissolved Cd and inorganic ligands. Symbols as in Fig. 1.

strate unambiguously that the free-ion activity model (Morel 1983) applies to Cd accumulation in *A. grandis*. This model has been shown to apply to various organisms and various metals under laboratory conditions where artificial ligands were used, but has not been validated in the field. It is unlikely that *A. grandis* will be found in freshwaters where inorganic ligands (SO_4, Cl) are present in sufficiently high concentrations to complex Cd significantly; an

alternative approach to demonstrate application of the model to Cd accumulation by *A. grandis* in the field would be to find sites where natural organic matter complexes Cd significantly, provided we can account for this complexation and correctly estimate [Cd^{2+}]. Partial correlation analysis (holding Cd constant) did not show any significant relationship between [Cd(Org)] and DOC ($r = -0.13$; $n = 17$), suggesting that complexation by organic matter did not influence Cd uptake by the bivalves at our sites.

Reasonable predictions of Cd concentrations in the tissues of *A. grandis* can be obtained presently from ambient [Cd^{2+}] values with the regression equations given in Table 4. The predictive power of these equations could however be improved. Much of the scatter in Fig. 3 is probably due to changes in dissolved Cd on short time scales with environmental conditions (phytoplankton biomass, pH, etc.). For example, Yan et al. (1990) observed a twofold change in [Cd] in Red Chalk Lake during the ice-free season; this lake is within our study area (Muskoka). The bivalves would not react rapidly to such changes in [Cd]. Indeed, we have observed that Cd concentrations in the tissues of *A. grandis* specimens transplanted from unpolluted Lake Brompton to polluted Lake Joannès (both included in our present study) had not reached, after 3 yr, the Cd levels observed in the indigenous specimens of Lake Joannès (Tessier unpubl. re-

Table 4. Linear regression equations describing Cd accumulation in various tissues of *Anodonta grandis* as a function of [Cd] or sedimentary variables. Tissues abbreviations: Gi—gills; Ma—mantle; He—hepatopancreas; Re—remains; Org—whole organism. (***: $P < 0.001$; **: $P < 0.01$.)

Dissolved Cd

[Cd(tissue)] = F [Cd^{2+}] + [Cd(tissue)]⁰

[Cd(Gi)] = 108(±15) [Cd^{2+}] + 16(±41)	$n = 17$; $r^2 = 0.77$***
[Cd(Ma)] = 36(±6) [Cd^{2+}] + 17(±16)	$n = 17$; $r^2 = 0.71$***
[Cd(He)] = 27(±8) [Cd^{2+}] + 16(±21)	$n = 17$; $r^2 = 0.45$**
[Cd(Re)] = 21(±3) [Cd^{2+}] + 5(±9)	$n = 17$; $r^2 = 0.74$***
[Cd(Org)] = 44(±5) [Cd^{2+}] + 10(±15)	$n = 17$; $r^2 = 0.81$***

Sedimentary variables

$$[Cd(tissue)] = \frac{F\{Cd\}_T[H^+]^{1.79}}{10^{-1.30}\{Fe-ox\}[H^+]^{0.97} + 10^{-2.45}\{OM\}[H^-]^{0.82}} + [Cd(tissue)]^0$$

[Cd(Gi)] = 123(±24) [Cd^{2+}] + 28(±64)	$n = 19$; $r^2 = 0.61$***
[Cd(Ma)] = 52(±5) [Cd^{2+}] + 14(±14)	$n = 19$; $r^2 = 0.86$***
[Cd(He)] = 41(±6) [Cd^{2+}] + 13(±15)	$n = 19$; $r^2 = 0.77$***
[Cd(Re)] = 33(±3) [Cd^{2+}] + 5(±8)	$n = 19$; $r^2 = 0.87$***
[Cd(Org)] = 59(±7) [Cd^{2+}] + 11(±18)	$n = 19$; $r^2 = 0.82$***

sults). The use of time-averaged values of $[Cd^{2+}]$ (or [Cd]) in the linear regression equations, instead of the single values used here, would undoubtedly improve the predictive power of these equations for Cd concentrations in the tissues of *A. grandis*. Measurements of temporal changes in Cd concentrations in the tissues of transplanted bivalves suggest that they accumulate metals only during the warm season (e.g. from May to October). For optimum predictive power, the mean $[Cd^{2+}]$ values should then be obtained preferentially for this period. Another source of scatter, probably less important, is variability in Cd concentration in the tissues of the bivalves due to biological factors (length or age, reproductive condition); in the present study, we attempted to minimize the influence of such factors by collecting specimens in a narrow size range, at times chosen to avoid the presence of gravid animals.

Relationship between Cd in the sediments and in A. grandis—Since $[Cd^{2+}]$ is difficult to measure, an alternative approach to the use of dissolved Cd to predict [Cd(Org)] would be to consider sedimentary Cd concentrations as possible predictors. When Cd concentrations in the bivalves (Table 3) are compared with $\{Cd\}_T$ in the sediments (Table 2), no relationship is shown (Fig. 4). The same conclusion is reached when the Cd concentration in the whole organism or any soft tissue is compared with Cd concentrations found in any sediment extract, whether or not the extractable Cd is normalized with respect to sediment Fe oxide or organic C concentrations. Such normalizations, based on sound geochemical principles regarding the binding strength of sediment components toward trace metals (Luoma and Bryan 1978), have been useful for predicting As, Cu, Hg, and Pb bioaccumulation in bivalves (Langston 1980, 1982; Luoma and Bryan 1978; Tessier et al. 1983, 1984), but do not seem adequate for predicting Cd accumulation in *A. grandis* from a large variety of lakes as in the present study.

Close examination of the data in Tables 2 and 3 reveals that, at a given ratio of $\{Fe-Cd\}$: $\{Fe-ox\}$ or $\{OM-Cd\}$: $\{OM\}$, the bivalves accumulate much more Cd in their tissue in lakes of low pH than in those of high pH. For example, at site VA-01 ($\{Fe-Cd\}$: $\{Fe-ox\}$ = 2.7
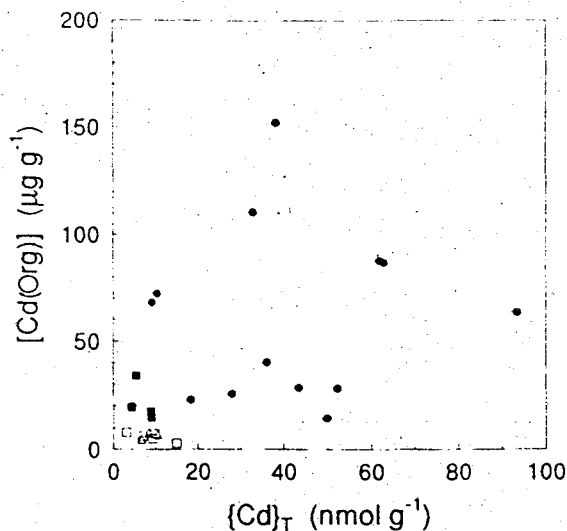

Fig. 4. Relationship between Cd concentrations in the tissues of *Anodonta grandis* and $\{Cd\}_T$ in the sediments. Symbols as in Fig. 1.

$\times$ 10^{-5}; pH = 6.57) the bivalves accumulated 152 μg g^{-1} of Cd whereas at site BR-05 ($\{Fe-Cd\}$: $\{Fe-ox\}$ = 3.4 $\times$ 10^{-5}; pH = 7.33) they accumulated only 40 μg g^{-1}. Similarly, the Cd concentration in the bivalves was much higher at site BO-02 ($\{OM-Cd\}$: $\{OM\}$ = 8.8 $\times$ 10^{-6}; pH = 6.34; [Cd(Org)] = 110 μg g^{-1}) than at site H-01 ($\{OM-Cd\}$: $\{OM\}$ = 8.1 $\times$ 10^{-6}; pH = 6.93; [Cd(Org)] = 15 μg g^{-1}). This pH dependence of Cd bioaccumulation at a given concentration ratio of sorbed Cd : sorbent can be taken into account by combining the surface complexation concepts described above with the free-metal ion activity model, as described below.

If the Cd concentration in the molluscs is assumed to be related to $[Cd^{2+}]$, as suggested by Fig. 3, one can write

$$[Cd(Org)] = F[Cd^{2+}] + [Cd(Org)]^0, \quad (19)$$

which is of similar form to the linear regression 18; F is a proportionality factor between [Cd(Org)] and $[Cd^{2+}]$ whereas $[Cd(Org)]^0$ is the intercept on the y-axis. Combining Eq. 7, 8, 12, and 19 yields

$$[Cd(Org)] = F\frac{\{Fe-Cd\}[H^+]^x}{N_{Fe} \times *K_{Fe-Cd}\{Fe-ox\}}$$
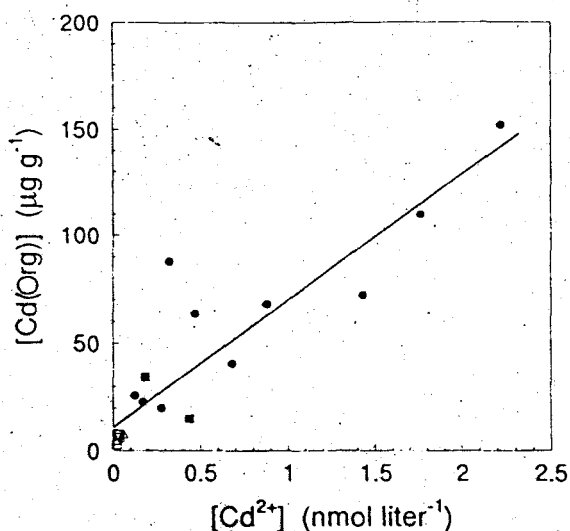
$$+ [Cd(Org)]^0, \quad (20a)$$

Fig. 5. Relationship between Cd concentrations in the tissues of *Anodonta grandis* and the [Cd^{2+}] calculated with Eq. 21c. Symbols as in Fig. 1.

$$[Cd(Org)] = F \frac{\{OM-Cd\}[H^+]^y}{N_{OM} \times {}^*K_{OM-Cd}\{OM\}}$$

$$+ [Cd(Org)]^0, \qquad (20b)$$

and

$$[Cd(Org)] = F \frac{\{Cd\}_T[H^+]^{x+y}}{(N_{Fe} \times {}^*K_{Fe-Cd}\{Fe-ox\}[H^+]^y}$$

$$+ N_{OM} \times {}^*K_{OM-Cd}\{OM\}[H^+]^x)$$

$$+ [Cd(Org)]^0. \qquad (20c)$$

The right-hand quotients in Eq. 20a,b,c can be used to evaluate [Cd^{2+}] without need to measure [Cd], provided that the geochemical constants $x, y, N_{Fe} \times {}^*K_{Fe-Cd}$, and $N_{OM} \times {}^*K_{OM-Cd}$ are known. All three quotients lead to the same value of [Cd^{2+}]. Substituting the values of these constants obtained from linear regressions 11 and 14 into Eq. 20, one obtains

$$[Cd(Org)] = F \frac{\{Fe-Cd\}[H^+]^{0.82}}{10^{-1.30}\{Fe-ox\}}$$

$$+ [Cd(Org)]^0; \qquad (21a)$$

$$[Cd(Org)] = F \frac{\{OM-Cd\}[H^+]^{0.97}}{10^{-2.45}\{OM\}}$$

$$+ [Cd(Org)]^0, \qquad (21b)$$

and

$$[Cd(Org)] = F \frac{\{Cd\}_T[H^-]^{1.79}}{(10^{-1.30}\{Fe-ox\}[H^+]^{0.97}}$$

$$+ 10^{-2.45}\{OM\}[H^+]^{0.82})$$

$$+ [Cd(Org)]^0. \qquad (21c)$$

Similar equations can be written for individual tissues of the organisms. Equation 21 can be used in practice to predict Cd concentrations in the tissues of various aquatic organisms. The first step is to determine the values of F and [Cd(Org)]^0. We have determined these two constants with Eq. 21c for various tissues of *A. grandis* with the values of $\{Cd\}_T$, pH, $\{Fe-ox\}$, and $\{OM\}$ given in Table 2 and the Cd tissue concentrations given in Table 3 (*see Table 4*; Fig. 5). We found that using the sum of Cd extracted in steps (1), (2), (3), and (4) instead of $\{OM-Cd\}$ in Eq. 21b did not change the explained variance (r^2). Substitution of $\{OM-Cd\}$ by $\{Cd\}_T$ in Eq. 21b reduced the value of r^2, but only slightly (e.g. from 0.82 to 0.79 for [Cd(Org)]). This lack of sensitivity reflects the fact that the binding of Cd to the sediment is dominated by organic matter.

The values of F and [Cd(Org)]^0 obtained from the linear regressions could be used to predict Cd concentrations in the tissues of *A. grandis* in other lakes, provided that lake pH and $\{Cd\}_T$, $\{Fe-ox\}$, and $\{OM\}$ have been determined for the same sediment samples from each lake. Equation 21 may be valid to predict Cd concentrations in organisms other than *A. grandis* that obtain Cd from the water (or from food such as phytoplankton, the Cd concentration of which would be related to that in the water); the only requirement would be to determine the values of F and [Cd(Org)]^0, which should be organism-specific. Because the geochemical constants $x, y, N_{Fe} \times {}^*K_{Fe-Cd}$, and $N_{OM} \times {}^*K_{OM-Cd}$ are involved in predicting Cd accumulation by various organisms, their precise determination would yield a better basis for predicting Cd bioavailability to benthic organisms.

Use of sedimentary measurements as in Eq. 21 to predict Cd bioaccumulation offers considerable advantages over direct measurement of dissolved Cd (as in Eq. 18). Measuring low values of [Cd] in freshwaters is difficult and requires the use of trace metal-free techniques; possibilities of inadvertent contamination are rampant. An additional problem is the temporal variation of dissolved Cd; considerable

effort would be needed to obtain representative mean values of total dissolved Cd at each sampling site. By comparison, measuring $\{Cd\}_T$, $\{Fe-ox\}$, $\{OM\}$, and lake pH is simpler.

In earlier studies, field measurements along trace metal gradients have shown that prediction of metal concentrations in estuarine and freshwater bivalves, [M(Org)], was greatly improved when the trace metal concentration extracted from the sediments was normalized with respect to the Fe oxide or organic matter content of the sediments. Hence, the ratios $\{Pb\}:\{Fe\}$ and $\{As\}:\{Fe\}$, all extracted with 1 N HCl, and the ratio $\{Hg$ extracted with $HNO_3\}:\{OM\}$ were found to be the best predictors of Pb, As, and Hg concentrations respectively in the estuarine bivalve *Scrobicularia plana* (Langston 1980, 1982; Luoma and Bryan 1978). Similarly, the best predictors of Cu and Pb in the tissues of the freshwater bivalves *A. grandis* and *Elliptio complanata* were found to be the ratios $\{Cu\}:\{Fe\}$ and $\{Pb\}:\{Fe\}$ extracted with $NH_2OH \cdot HCl$, a reducing reagent (Tessier et al. 1983, 1984). In other words, according to these studies, trace metal concentrations in the organisms are best expressed as

$$[M(Org)] = k\frac{\{S_n-M\}}{\{S_n\}} + [M(Org)]^0 \quad (22)$$

where k is a proportionality constant, $\{S_n\}$ the concentration of sediment component n (which can be Fe oxyhydroxides or organic matter), $\{S_n-M\}$ the concentration of the trace metal M associated with sediment component n, and $[M(Org)]^0$ the intercept on the y-axis (usually close to zero).

The present study offers a likely explanation for these findings. The studies of Langston (1980, 1982) and Luoma and Bryan (1978) were performed in estuaries, where the pH is relatively constant; the freshwater studies (Tessier et al. 1983, 1984) were carried out in three lakes located in a restricted geographical area where the lake pH is relatively constant. In such cases, $[H^+]^x$ and $[H^+]^y$ become approximately constant and Eq. 20a and 20b reduce to Eq. 22. The success of sediment Fe or organic C as the normalizing factor in these studies could be due to its dominance in sorption of the particular trace metal investigated. For example, the strong association of Pb (Lion

et al. 1982; Balistrieri and Murray 1982; Leckie et al. 1984) and As (Aggett and Roberts 1986; Belzile and Tessier 1990) with sedimentary Fe oxyhydroxides is well documented; similarly, the affinity of Hg for sediment organic matter (NRCC 1988) is well known. Thus the simpler normalization approach appears to be applicable only where a pH gradient does not exist.

From the preceding discussion, it follows that the observation of a strong relationship between trace metal levels in a benthic species and sediment characteristics (e.g. extractable metal concentration normalized with respect to the concentration of a sediment component like Fe oxyhydroxides or organic matter) cannot be construed as evidence that the main route of trace metal uptake is via ingestion of sediment particles. Such relationships could also be observed for organisms that obtain metal directly from the water (or from food, the Cd content of which would be related to that in the water), provided that the pH is approximately constant over the study area and that the dissolved [M] in the water to which the organisms are exposed is in sorptive equilibrium with the sediment component used for normalization. A logical consequence is also that the ratios $\{M\}:\{Fe\}$ or $\{M\}:\{OM\}$, although much better predictors than total sediment metal concentrations in some cases, are not "universal" predictors in the sense that their application should be site-dependent (i.e. restricted to a narrow pH range).

Conclusions

The contamination of surficial sediments by metals of anthropogenic origin is of potential ecological importance. Past attempts to relate total metal concentrations in surficial sediments to metal levels in indigenous benthic organisms have generally proven disappointing, as noted by other researchers (Luoma and Bryan 1982; Bryan 1985; NRCC 1988); the present study offers another example of the failure of this approach (*see Fig. 4*). Even when apparently successful within a limited geographical area, such empirical models cannot be used to extrapolate beyond the original data used to develop the underlying statistical relationships.

We submit that a more promising approach

to predicting trace metal concentrations in benthos (and eventually to predicting metal effects on this community) would be to develop deterministic models based on sound chemical and biological principles. Provided such models explicitly incorporate the influence of major environmental variables on metal uptake, they should be generally applicable, i.e. they should be able to predict the metal concentration in benthos from lakes other than those used in calibration. The development of this type of model should be a prerequisite for use of animals as bioindicators of trace metal pollution. Such an approach has been hindered in the past by our incomplete knowledge of the geochemical and biological processes that control metal accumulation in aquatic organisms.

The present study represents an attempt to develop such a deterministic model of general applicability to predict the concentrations of Cd in a freshwater bivalve. In formulating the model, we used concepts derived from the free-ion activity model of metal-organism interactions and from surface complexation theory to relate Cd concentrations in the bivalve to those in the water or in the surficial oxic sediments. From a practical point of view, this approach has yielded predictive equations for Cd bioaccumulation in *A. grandis* that require as input geochemical variables readily measured in bottom waters and sediments (Table 4). The predictive power of these equations is acceptable within the 350,000-km² study area, but they should obviously be tested against Cd accumulation in *A. grandis* in lakes in other geographical areas before their generality can be proclaimed. In principle, this type of model should apply to other trace metals and to other sedentary aquatic organisms.

Refinement of the proposed model, or formulation of better ones, will require better understanding of the geochemical and biological processes involved in bioaccumulation of trace metals by benthic organisms. For example, the nature of the "sorption" reactions that are responsible for the presence of trace metals in oxic sediments is still poorly understood; the identity of the solid phases responsible for binding trace metals is also largely unknown. Similarly, improved knowledge of the feeding strategies and physiology of benthic animals would aid in the development of future models.

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