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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 ($K_{\text{Fe-Cd}}$) and organic matter ($K_{\text{OM-Cd}}$) 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: $\log K_{\text{Fe-Cd}} = 0.82\ \text{pH} - 1.30$ ($r^2 = 0.89$) and $\log K_{\text{OM-Cd}} = 0.97\ \text{pH} - 2.45$ ($r^2 = 0.78$). 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)] ($\mu g\ g^{-1}$ dry wt), are related to dissolved Cd concentrations: $[\text{Cd(Org)}] = 44[\text{Cd}^{2+}] + 10$ ($r^2 = 0.81$) for $[\text{Cd}^{2+}]$ 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.

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

		[Ca]	[Na]	$[\mathrm{SO_4}]$	[Alk]*	$[\mathrm{C_{org}}]$	[Cd]	$[\mathrm{Cd}^{2+}]$	$\{\mathrm{Cd}\}_T$	{OM–Cd}	{Fe–ox}	{OM}
Site	pH	(μmol $\mathrm{liter^{-1}}$)					(nmol $\mathrm{liter^{-1}}$)		(nmol $\mathrm{g^{-1}}$)		(μmol $\mathrm{g^{-1}}$)	
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 $\mathrm{liter^{-1}}$; 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 samples 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 porewater 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

$$\log[\mathrm{Cd}] = -0.51(\pm 0.07)\mathrm{pH} - 6.6(\pm 0.2) \quad (1)$$

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}; $[\mathrm{PO_4}] < 0.1\ \mu\mathrm{M}$; $[\mathrm{Si}] < 20\ \mu\mathrm{M}$), $\mathrm{CdCO_3(s)}$ 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 $[\mathrm{Cd}^{2+}]$ 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 ($\{\mathrm{Cd}\}_T$; 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).

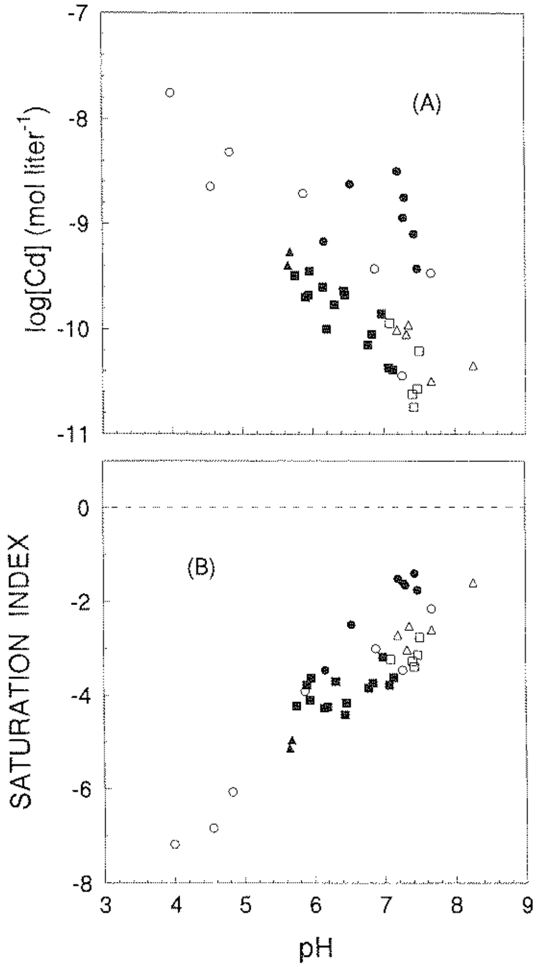

Fig. 1. [Cd] and saturation index as a function of pH for the various sites studied. Different symbols are used for the lakes located in the areas of Sudbury (○), Rouyn-Noranda (●), Chibougamau (□), Muskoka (■), Eastern Townships (△), and Québec (▲). Saturation index is log(IAP/K_s). Dashed line indicates saturation with respect to $\mathrm{CdCO_3(s)}$.

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 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 treated 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

$$\equiv\text{Fe–OH}_x + \text{Cd}^{2+} \xrightleftharpoons{{}^{*}K_{\text{Fe–Cd}}} \equiv\text{Fe–OCd} + x\text{H}^+ \quad (2)$$

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

where charges on the solid species are omitted for simplicity, ${}^{*}K_{\text{Fe–Cd}}$ 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 $\{\equiv\text{Fe–OH}_x\}$ and $\{\equiv\text{Fe–OCd}\}$ 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 "≡" 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

$$\{\equiv\text{Fe–O–}\}_{\text{T}} \approx \{\equiv\text{Fe–OH}_x\} \quad (4)$$

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

$$\{\equiv\text{Fe–O–}\}_{\text{T}} = N_{\text{Fe}} \times \{\text{Fe–ox}\} \quad (5)$$

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

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

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

$$K_{\text{Fe–Cd}} = \frac{N_{\text{Fe}} \times {}^{*}K_{\text{Fe–Cd}}}{[\text{H}^+]^x} = \frac{\{\text{Fe–Cd}\}}{\{\text{Fe–ox}\}[\text{Cd}^{2+}]} \quad (7)$$

where $K_{\text{Fe–Cd}}$ 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):

$$K_{\text{OM–Cd}} = \frac{N_{\text{OM}} \times {}^{*}K_{\text{OM–Cd}}}{[\text{H}^+]^y} = \frac{\{\text{OM–Cd}\}}{\{\text{OM}\}[\text{Cd}^{2+}]} \quad (8)$$

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 $K_{\text{OM–Cd}}$ and ${}^{*}K_{\text{OM–Cd}}$ 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–Cd} are the concentrations of organic matter and of Cd associated with organic matter respectively. Linearization of Eq. 7 and 8 yields

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

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

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

We have estimated $K_{\text{Fe–Cd}}$ and $K_{\text{OM–Cd}}$ 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, $[\text{Cd}^{2+}]$ (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 $[\text{Cd}^{2+}]$ in these waters is very close to that of [Cd]; calculated contributions of $\text{CdSO}_4\text{(aq)}$ 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–Cd} and {OM–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 $K_{Fe\text{–}Cd}$ according to Eq. 7. The plot, corresponding to Eq. 9, is shown in Fig. 2A; linear regression of these data yields

$$\log K_{Fe\text{–}Cd} = 0.82(\pm 0.08)\ \mathrm{pH} - 1.30(\pm 0.38) \quad (n = 16; \quad r^2 = 0.89). \tag{11}$$

The total sorbed Cd concentration is written

$$\{Cd\}_T = \{Fe\text{–}Cd\} + \{OM\text{–}Cd\} \tag{12}$$

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

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

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 $N_{Fe} \times {}^*K_{Fe\text{–}Cd}$ ($10^{-1.30}$) 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 $K_{OM\text{–}Cd}$ 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 corresponding to Eq. 10 is shown in Fig. 2B and regression of the data yields

$$\log K_{OM\text{–}Cd} = 0.97(\pm 0.09)\ \mathrm{pH} - 2.45(\pm 0.46) \quad (n = 35; \quad r^2 = 0.78). \tag{14}$$

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.

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

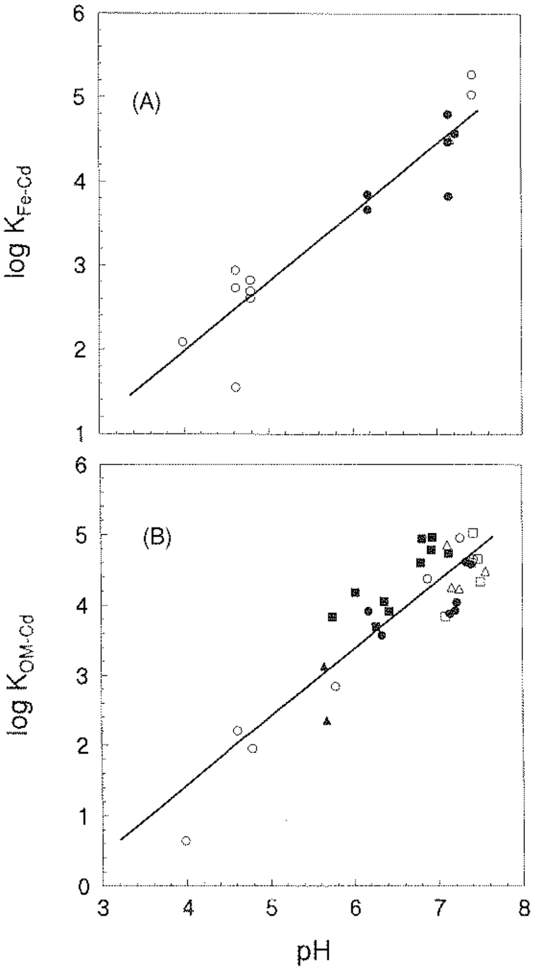

Fig. 2. Apparent overall equilibrium constants for the sorption of Cd on natural Fe oxyhydroxides and organic matter as a function of pH. Symbols as in Fig. 1.

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}, $*K_{Fe\text{–}Cd}$, and $*K_{OM\text{–}Cd}$ are considered here to be constants, whereas they might be expected to vary with the nature of sedimentary 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 $K_{Fe\text{–}Cd}$ and $K_{OM\text{–}Cd}$, 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 $\{Cd\}_T$, $\{Fe\text{–}ox\}$, and $\{OM\}$ present in the surficial sediment. The ratio $\{Cd\}_c : \{Fe\}_c$ is also assumed to be representative of the ratio $\{Fe\text{–}Cd\} : \{Fe\text{–}ox\}$ 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 $\{OM\text{–}Cd\}$ 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, $\{OM\text{–}Cd\}$ and $\{Fe\text{–}Cd\}$ represent 92±8% and 8±8% 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 $\{OM\text{–}Cd\}$ 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 $\{Fe\text{–}Cd\}$ 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 $K_{OM\text{–}Cd}$ 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

$$\begin{aligned}\frac{\{Fe\text{–}Cd\}}{\{Cd\}_T} &= (N_{Fe} \times *K_{Fe\text{–}Cd}\{Fe\text{–}ox\}[H^+]^y) \\ &\quad \div (N_{Fe} \times *K_{Fe\text{–}Cd}\{Fe\text{–}ox\}[H^+]^y \\ &\quad + N_{OM} \times *K_{OM\text{–}Cd}\{OM\}[H^+]^x)\end{aligned} \tag{15}$$

$$\frac{\{\mathrm{OM{-}Cd}\}}{\{\mathrm{Cd}\}_T} = (N_{\mathrm{OM}} \times {}^*K_{\mathrm{OM{-}Cd}}\{\mathrm{OM}\}[\mathrm{H}^+]^x) \div (N_{\mathrm{Fe}} \times {}^*K_{\mathrm{Fe{-}Cd}}\{\mathrm{Fe{-}ox}\}[\mathrm{H}^+]^y + N_{\mathrm{OM}} \times {}^*K_{\mathrm{OM{-}Cd}}\{\mathrm{OM}\}[\mathrm{H}^+]^x). \qquad (16)$$

The only requirement would be to measure $\{\mathrm{Cd}\}_T$ (sum of nondetrital forms), {OM}, and {Fe–ox} for the same oxic sediment sample and lake pH; the necessary values of x, y, $N_{\mathrm{Fe}} \times {}^*K_{\mathrm{Fe{-}Cd}}$, and $N_{\mathrm{OM}} \times {}^*K_{\mathrm{OM{-}Cd}}$ 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:

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

where $[\mathrm{Cd(tissue)}]_i$ 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±13%) of the total Cd burden of whole animals; the mantle, hepatopancreas, and remaining tissues contributed 21±7, 11±8, and 28±11%. Stepwise multiple regression was performed to examine the relationships between [Cd(Org)] as the dependent variable and $[\mathrm{Cd}^{2+}]$, $[\mathrm{Ca}^{2+}]$, $[\mathrm{H}^+]$, and C_{org} as the independent variables. Due to intercorrelations among both pH and C_{org} and pH and $[\mathrm{Cd}^{2+}]$, the largest partial regression coefficient, found for $[\mathrm{Cd}^{2+}]$, 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

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

with $[\mathrm{Cd}^{2+}]$ in nmol liter^{-1}. Regressions between $[\mathrm{Cd}^{2+}]$ and Cd concentrations in the tissues are highly significant ($P < 0.001$), except for Cd in the hepatopancreas which is significant (Table 4).

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

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 $[\mathrm{Cd}^{2+}]$ (Sunda et al. 1978). Similarly, short-term (14 d) accumulation of Cu in the oyster *Crassostrea virginica* was found to be proportional to $[\mathrm{Cu}^{2+}]$ (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 $[\mathrm{Cd}^{2+}]$ at all sites. Given the similarity between $[\mathrm{Cd}^{2+}]$ and [Cd] values, and the relative uncertainty in the relations given in Table 4, we cannot demon-

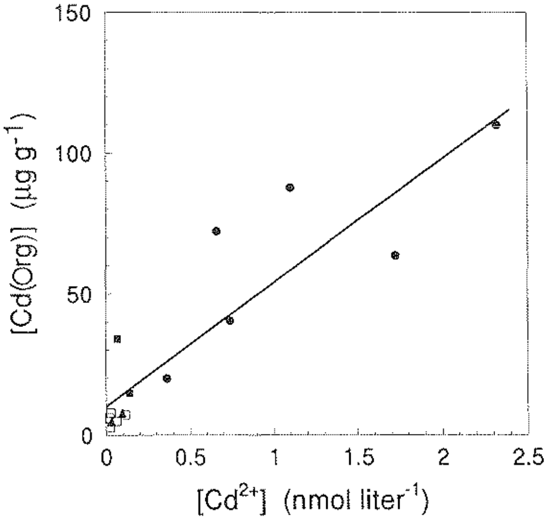

Fig. 3. Relationship between Cd concentrations in the tissues of *Anodonta grandis* and $[Cd^{2+}]$ calculated from total dissolved Cd and inorganic ligands. Symbols as in Fig. 1.

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	
$[\mathrm{Cd(tissue)}] = F\,[\mathrm{Cd}^{2+}] + [\mathrm{Cd(tissue)}]^0$	
$[\mathrm{Cd(Gi)}] = 108(\pm 15)\,[\mathrm{Cd}^{2+}] + 16(\pm 41)$	$n = 17$; $r^2 = 0.77$***
$[\mathrm{Cd(Ma)}] = 36(\pm 6)\,[\mathrm{Cd}^{2+}] + 17(\pm 16)$	$n = 17$; $r^2 = 0.71$***
$[\mathrm{Cd(He)}] = 27(\pm 8)\,[\mathrm{Cd}^{2+}] + 16(\pm 21)$	$n = 17$; $r^2 = 0.45$**
$[\mathrm{Cd(Re)}] = 21(\pm 3)\,[\mathrm{Cd}^{2+}] + 5(\pm 9)$	$n = 17$; $r^2 = 0.74$***
$[\mathrm{Cd(Org)}] = 44(\pm 5)\,[\mathrm{Cd}^{2+}] + 10(\pm 15)$	$n = 17$; $r^2 = 0.81$***
Sedimentary variables	
$[\mathrm{Cd(tissue)}] = \dfrac{F\{\mathrm{Cd}\}_T[\mathrm{H}^+]^{1.79}}{10^{-1.30}\{\text{Fe–ox}\}[\mathrm{H}^+]^{0.97} + 10^{-2.45}\{\mathrm{OM}\}[\mathrm{H}^+]^{0.82}} + [\mathrm{Cd(tissue)}]^0$	
$[\mathrm{Cd(Gi)}] = 123(\pm 24)\,[\mathrm{Cd}^{2+}] + 28(\pm 64)$	$n = 19$; $r^2 = 0.61$***
$[\mathrm{Cd(Ma)}] = 52(\pm 5)\,[\mathrm{Cd}^{2+}] + 14(\pm 14)$	$n = 19$; $r^2 = 0.86$***
$[\mathrm{Cd(He)}] = 41(\pm 6)\,[\mathrm{Cd}^{2+}] + 13(\pm 15)$	$n = 19$; $r^2 = 0.77$***
$[\mathrm{Cd(Re)}] = 33(\pm 3)\,[\mathrm{Cd}^{2+}] + 5(\pm 8)$	$n = 19$; $r^2 = 0.87$***
$[\mathrm{Cd(Org)}] = 59(\pm 7)\,[\mathrm{Cd}^{2+}] + 11(\pm 18)$	$n = 19$; $r^2 = 0.82$***

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.

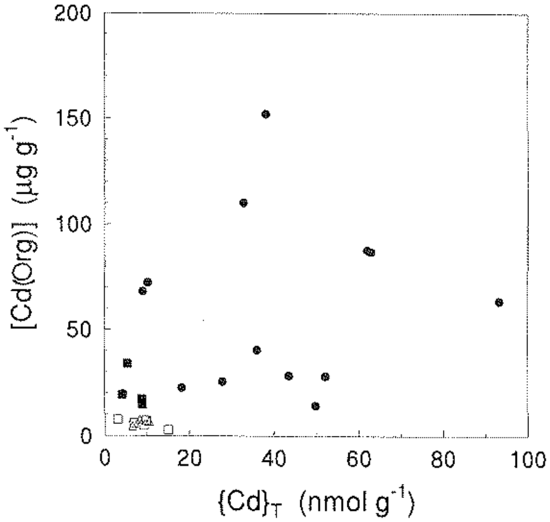

Fig. 4. Relationship between Cd concentrations in the tissues of *Anodonta grandis* and $\{Cd\}_T$ in the sediments. Symbols as in Fig. 1.

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} = 2.7×10^{-5}; pH = 6.57) the bivalves accumulated 152 µg g^{-1} of Cd whereas at site BR-05 ({Fe–Cd} : {Fe–ox} = 3.4×10^{-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} = 8.8×10^{-6}; pH = 6.34; [Cd(Org)] = 110 µg g^{-1}) than at site H-01 ({OM–Cd} : {OM} = 8.1×10^{-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

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

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

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

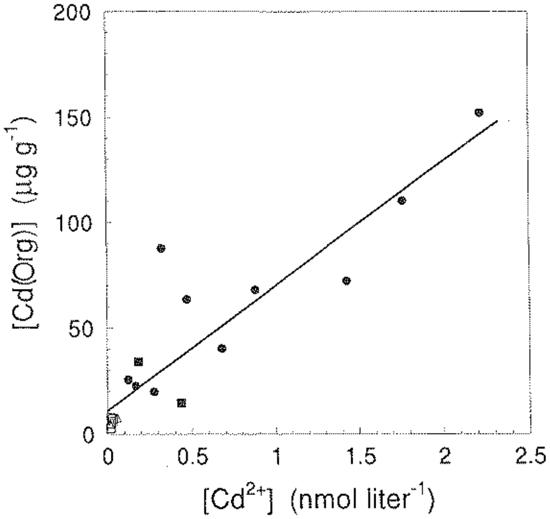

Fig. 5. Relationship between Cd concentrations in the tissues of *Anodonta grandis* and the $[Cd^{2+}]$ calculated with Eq. 21c. Symbols as in Fig. 1.

$$[\mathrm{Cd(Org)}] = F\frac{\{\mathrm{OM{-}Cd}\}[\mathrm{H}^+]^y}{N_{\mathrm{OM}} \times {}^*K_{\mathrm{OM-Cd}}\{\mathrm{OM}\}} + [\mathrm{Cd(Org)}]^0, \tag{20b}$$

and

$$[\mathrm{Cd(Org)}] = F\frac{\{\mathrm{Cd}\}_{\mathrm{T}}[\mathrm{H}^+]^{x+y}}{(N_{\mathrm{Fe}} \times {}^*K_{\mathrm{Fe-Cd}}\{\mathrm{Fe{-}ox}\}[\mathrm{H}^+]^y + N_{\mathrm{OM}} \times {}^*K_{\mathrm{OM-Cd}}\{\mathrm{OM}\}[\mathrm{H}^+]^x)} + [\mathrm{Cd(Org)}]^0. \tag{20c}$$

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

$$[\mathrm{Cd(Org)}] = F\frac{\{\mathrm{Fe{-}Cd}\}[\mathrm{H}^+]^{0.82}}{10^{-1.30}\{\mathrm{Fe{-}ox}\}} + [\mathrm{Cd(Org)}]^0, \tag{21a}$$

$$[\mathrm{Cd(Org)}] = F\frac{\{\mathrm{OM{-}Cd}\}[\mathrm{H}^+]^{0.97}}{10^{-2.45}\{\mathrm{OM}\}} + [\mathrm{Cd(Org)}]^0, \tag{21b}$$

and

$$[\mathrm{Cd(Org)}] = F\frac{\{\mathrm{Cd}\}_{\mathrm{T}}[\mathrm{H}^+]^{1.79}}{(10^{-1.30}\{\mathrm{Fe{-}ox}\}[\mathrm{H}^+]^{0.97} + 10^{-2.45}\{\mathrm{OM}\}[\mathrm{H}^+]^{0.82})} + [\mathrm{Cd(Org)}]^0. \tag{21c}$$

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 $[\mathrm{Cd(Org)}]^0$. 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 $[\mathrm{Cd(Org)}]^0$ 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 $[\mathrm{Cd(Org)}]^0$, 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 $\{\mathrm{Cd}\}_T$, {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 $\mathrm{HNO_3}$} : {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 $\mathrm{NH_2OH \cdot HCl}$, 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

$$[\mathrm{M(Org)}] = k\frac{\{S_n\text{–M}\}}{\{S_n\}} + [\mathrm{M(Org)}]^0 \qquad (22)$$

where k is a proportionality constant, $\{S_n\}$ the concentration of sediment component n (which can be Fe oxyhydroxides or organic matter), $\{S_n\text{–M}\}$ the concentration of the trace metal M associated with sediment component n, and $[\mathrm{M(Org)}]^0$ 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, $[\mathrm{H^+}]^x$ and $[\mathrm{H^+}]^y$ 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-km^2 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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