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Atmospheric loading of Zn, Cu, Ni, Cr, and Pb to lake sediments: The role of catchment, lake morphometry, and physico-chemical properties of the elements

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Abstract. Although catchments have been implicated as an important source of metals to lakes, the catchment contribution of different metals is poorly known, and the anthropogenic contribution is not known at all. We determine the anthropogenic lake sediment burdens of Zn, Cu, Ni, Cr, and Pb for several Quebec and Ontario lakes, not subject to point source loading, to obtain estimates of atmospheric loading and inputs from terrestrial sources. To do this, we first collected multiple cores across 11 lake basins to estimate the whole-lake Pb burdens. As the whole-lake Pb burdens did not differ among lakes that spanned over two orders of magnitude in drainage ratios (drainage basin area/lake area), we conclude that catchment retention of anthropogenic Pb is complete. The anthropogenic Pb burdens were then used as a correction for focusing for the other metals. Among the metals, Cr and Ni were the most readily exported from drainage basins, followed by Cu. Zn showed no increase with drainage ratio, indicating Zn to be effectively retained by catchments. The export coefficients of the Pb corrected metals correlate well with ocean residence time, revealing a similar metal sorption/precipitation sequence in both soils and oceans. Sediment metal burdens provide a relatively easy way to obtain not only metal export coefficients from drainage basins, but also the atmospheric deposition of anthropogenic metals (e.g. Pb: S.E. Quebec, 950 mg*m^{-2}: Laurentians, north of Montreal, 420 mg*m^{-2}). The export coefficients are not only simpler to obtain than by mass balance measurements, but, in addition, identify the anthropogenic component.

Introduction

Atmospheric metal budgets have demonstrated the enormous impact that anthropogenic activity is having on trace metal fluxes. The dominant sources of anthropogenic metal fluxes to the atmosphere are oil, gasoline and coal combustion, smelting, and refuse incineration (Nriagu 1989). Concern about the impact of these emissions has resulted in an upsurge of research on the cycling and fate of trace metals through the biosphere.

On the basis of modeling whole-lake sediment metal burdens as a function of drainage ratio (catchment area:lake area) it has been suggested that catchment contributions of anthropogenically derived Pb (Dillon & Evans 1982), Zn, and Cd (Evans et al. 1983) to lakes are insignificant. Likewise, Schut et al. (1986) described catchments as 'sinks' for both Cu and Pb. Dillon et al. (1988) derived metal budgets for heavily acidified lakes near Sudbury and described catchments to act as a 'sink' for Cu and Zn but as a 'source' for Al, Mn, and Ni. More recently it has been demonstrated that catchment contributions of Hg are highly significant, with 25% of the Hg deposited on catchments exported to lake sediments (Swain et al. 1992).

Mechanistic modeling of metal retention in soils has demonstrated that the degree of retention is a function of the metal's affinity to particles (Tyler & McBride 1982; Evans 1989) as well as soil characteristics. However, the notion that metal chemistry affects catchment retention has not been demonstrated empirically. Several investigators have found that heavy metal partitioning, remobilization, and binding is a function of simple properties of the elements (Jackson et al. 1980; Fisher 1986). In general, a metal's affinity for particulate matter is related to its charge density (Turner et al. 1981). Physico-chemical properties of the elements such as charge density and ionic radius have been related to the biouptake of metals in *Daphnia* (Kaiser 1980), marine phytoplankton (Fisher 1986), *Chironomid* larvae (Krantzberg 1989) and macrophytes (Jackson et al. 1991). Soil parameters that have been shown to exert an influence on the sorption of metals include pH (i.e. Lo et al. 1992; Dillon et al. 1988), the abundance of Fe and Mn oxides (Jenne 1968), surface area, clay content, and cation exchange capacity (Korte et al. 1976).

The purpose of this investigation was to determine whether a variety of transition metals (Fe, Mn, Zn, Cu, Ni, Cr, Pb) differing in their geochemical behaviour also differ in the extent that they are retained by catchments rather than released to lakes. Secondly, to determine if catchment contributions can be predicted as a function of the physico-chemical properties of the elements.

Methods

Study sites

The three regions that were examined in this study were: (1) The Muskoka/Haliburton region of south — central Ontario; (2) the Laurentian region of Quebec, north of Montreal; and (3) the Eastern Township region of Quebec near the Vermont border (Fig. 1). There is a considerable range in the geology across the three regions. Both the Muskoka/ Haliburton region and the Laurentian region are underlain by Precambrian metamorphic, plutonic and volcanic silicate rocks that are overlain by Pleistocene glacial deposits. The Eastern Township region is composed primarily of Paleozoic sedimentary and metasedimentary rocks overlying Lower Ordovician ophiolitic bedrock. Average concentrations of SO_4^{-2} in precipitation for all three regions range between 80—100 μeq L^{-1} (Munger & Eisenreich 1983). All lakes are used for recreation and are not exposed to industrial point sources of pollutants. Lakes were chosen on the basis of obtaining as large a range of catchment sizes as possible since our objective was to assess the effect of the catchment on metal

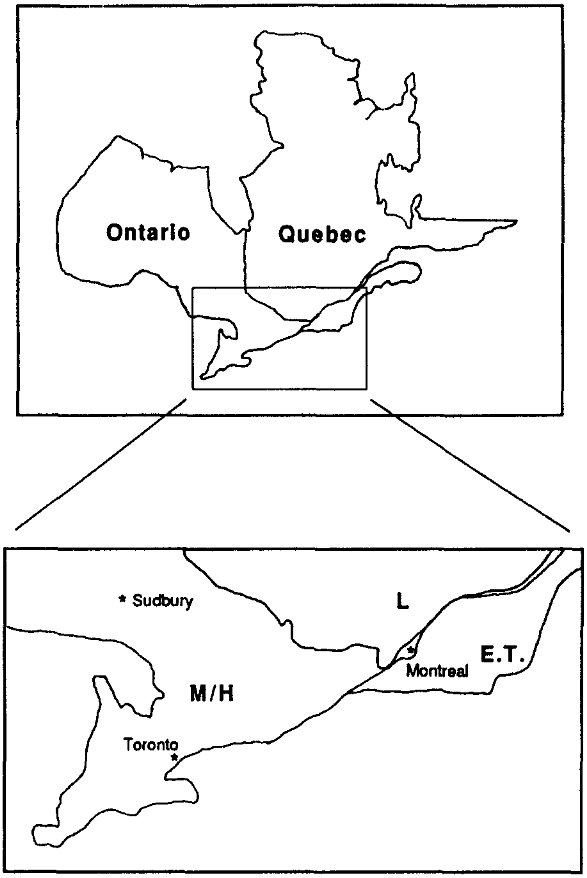

Fig. 1. Map of Quebec and Ontario showing the three study regions: M/H = the Muskoka/ Haliburton region of Ontario; L = the Laurentian region of Quebec; E.T. = the Eastern Townships of Quebec.

loading to lakes. The Muskoka/Haliburton region is located approximately 250 km south east of the smelters at Sudbury. The Eastern Township lakes are about 80 km south west of the mines at Thetford Mines, and 200 km south east of the city of Montreal.

In all, there were 31 lakes involved in the analysis. Limnological data are provided in Table 1. Both lake area (LA) and direct drainage area (DDA) were derived by planimetry of topographic maps. The mean and maximum depths (Z_{mean} and Z_{max}) were derived from bathymetric maps from the Ministère des Richesses Naturelles. Water residence time was derived from Janus & Vollenweider (1981) when available, or according to the following equation:

$$W_{res} = (LA(P - E) + DBA * R) * LVOL^{-1}$$

Where: LA is lake area (m^2), P is annual precipitation (m), E is annual lake surface evaporation (m), R is annual runoff (m), and LVOL is lake volume (m^3) (Schallenberg 1992). These data were all obtained from the Hydrological Atlas of Canada (Fisheries and Environment Canada 1978).

Core collection

Sample collection was divided into two parts. The first consisted of deriving regional deposition values for Pb across the Eastern Townships and Laurentians of southern Quebec. This involved extracting cores along transects in 11 lakes to obtain a complete cross-section of depths across lake basins. At each site, depth was recorded and slope of the basin was determined by echo sounding perpendicular to basin contours. The second part consisted of coring the deepest part of each lake with a modified K-B gravity corer to obtain ratios of the different metals relative to Pb. For this analysis, two cores were extracted at a single site from each lake. The sediment was extruded on shore using a vertical extrusion system, sliced at 1 cm intervals for the first 10 cm, and 2 cm intervals thereafter. Samples were stored in clean, pre-weighed polyethylene vials. In the laboratory, the samples were weighed, oven-dried at 60—80 °C for 1—2 days, and water loss was determined. Sub-samples were ashed at 550 °C for two hours to obtain the loss on ignition (LOI).

Metal analysis

All laboratory equipment used for metal analysis was acid washed in 10% HCl and rinsed at least twice with double distilled water. All reagents used in the analysis were ANALAR grade acids from BDH Inc. Approximately

Table 1. Characteristics of the lakes used in one or more aspects of this study. LA = lake area, DDA = direct drainage area, Z_{mean} and Z_{max} = mean and maximum depths respectively, T_{RES} = annual hydraulic residence time, TOC = total organic carbon, cond = conductivity, alk = alkalinity, lat. and long. are latitude and longitude, respectively.

Lake	LA (km^2)	DDA (km^2)	Z_{mean} (m)	Z_{max} (m)	T_{RES} (year)	pH	colour (mg/L)	TOC (mg/L)	cond μS/cm	alk (mg/L)	lat.	long.
Eastern Townships, Quebec												
Aylmer	29.5	1655	8.5	36.2	0.23	7.4	106.6	—	66	18.3	45°49′	71°20′
Bowker	2.28	9.74	25.9	59	5.1	7.6	6.4	—	48	11.9	45°25′	72°12′
Brome	14.5	199.81	5.8	12.8	0.70	7.6	12.8	—	104	23.9	45°15′	72°30′
Brompton	1.95	115.85	12.5	42.3	1.9	7.2	38.4	—	62	15	45°18′	72°09′
Coulombe	0.78	24.43	5.4	12.2	0.22	7.2	141	—	—	—	45°50′	71°25′
Elgin	4.07	64.02	—	—	—	6.9	—	—	—	—	45°45′	71°20′
Lovering	4.62	48.68	10.3	24.9	1.0	6.9	32.6	—	57	22.3	45°10′	72°16′
Massawippi	17.9	584.2	41.6	85.7	1.5	7.6	13.6	—	140	76.9	45°18′	72°00′
Nicolet	3.97	12.56	17.3	41.5	8.3	7.5	21.2	—	43	11.8	45°50′	71°35′
Orford	1.26	10.62	17.7	48.0	2.29	7.1	6.1	—	265	27.9	49°17′	72°16′
Silver	0.67	10.97	16.3	55.0	1.58	7.4	14.8	—	110	—	45°38′	72°48′
Stukely	3.8	18.67	13.6	32.2	2.5	8.2	12.1	—	49	15.9	45°22′	72°15′
Laurentians, Quebec												
Achigan	5.21	91.03	12.3	26.2	1.6	6.7	23.3	—	57	14.8	45°55′	74°00′
Connelly	1.37	21.35	9.7	17.0	1.2	7.3	22.8	—	96	21.0	45°53′	73°58′
Croche	0.21	1.10	4.43	10.5	1.6	6.9	26.6	—	27	8.3	45°59′	74°00′
Cromwell	0.04	8.8	3.0	9.0	0.07	6.6	56.3	—	32	9.3	45°59′	74°00′

Table 1 (Continued)

Lake	LA (km^2)	DDA (km^2)	Z_{mean} (m)	Z_{max} (m)	T_{RES} (year)	pH	colour (mg/L)	TOC (mg/L)	cond $\mu S/cm$	alk (mg/L)	lat.	long.
Haliburton, Muskoka region, Ontario												
Atkins	0.073	3.55	—	—	4.09	6.41	—	1.65	24	1.1	45°07′	79°14′
Barnum	0.22	11.42	3.2	10.1	6.46	7.18	—	2.85	96	68.5	45°02′	78°32′
Dickie	0.931	5.96	4.9	12.2	1.9	6.50	—	1.33	18	1.5	45°09′	79°05′
Grass	0.809	8.20	3.4	9.5	—	7.44	—	1.10	54	18.7	45°02′	78°33′
Haas	0.417	3.60	1.9	3.7	1.77	7.01	—	4.57	150	47.3	45°12′	78°27′
Kennisis	13.9	32.87	6.8	23.3	0.04	7.24	—	1.93	21	2.0	45°13′	78°38′
L. Dudmun	0.637	3.87	7.1	18.0	0.33	6.60	—	1.60	52	35.1	45°02′	78°21′
Miskwabi	2.57	12.03	19.7	44.2	0.09	6.67	—	1.52	56	—	45°03′	78°19′
Moose	3.19	37.99	16.6	43.9	0.28	7.40	—	0.97	44	16.0	45°09′	78°28′
Pelaw	0.245	3.55	5.7	14.6	1.00	7.51	—	1.44	21	2.3	45°13′	78°33′
Raven	6.27	29.73	8.1	41.8	0.075	6.44	—	2.10	19	1.6	45°12′	78°51′
Tooke	0.221	1.814	3.1	6.1	1.03	5.30	—	2.85	38	2.4	45°11′	79°08′
Twelve mile	3.38	35.1	12.0	27.5	0.48	5.56	—	2.45	29	9.7	45°01′	78°43′
Two Island	0.662	6.397	6.6	23.2	0.57	4.20	—	3.01	84	25.6	45°02′	78°22′

Data sources: Schallenberg (1992), del Georgio (unpublished), Janus & Vollenweider (1981), the Water Resources Branch of the Ontario Ministry of the Environment (OMOE) and Lafond et al. (1990).

0.5 g of sediment was crushed with mortar and pestle, and digested in dilute aqua-regia (3 $HCl:3H_2O:HNO_3$) at 80 °C for one hour. The digestate was brought to a 25 ml final volume with double-distilled water, and metal concentrations were determined with a flame atomic absorption spectrophotometer (Perkin-Elmer 5100). NBS Buffalo River Sediment (NBS # 1572) was used as a reference standard to derive extraction efficiencies and to detect any week to week variations in the analytical procedure. Dilute aqua regia digested Cu, Ni,Zn, Pb, and Mn with a 100% efficiency, whereas Al, Fe and Cr were extracted with 18, 60 and 51% efficiencies, respectively. Extraction reproducibility was within the limits set by the National Bureau of Standards for all elements analyzed.

Data handling

Anthropogenic metal burden was derived for each site using the following equation (after Evans 1980):

$$M_A = \frac{\Sigma\,[M_i - M_B]\,W_D}{a} \qquad (1)$$

where

M_A = anthropogenic metal burden ($\mu g/cm^2$)
M_i = metal concentration at i^{th} section of the core ($\mu g/g$)
M_B = background metal concentration derived at depth in the core ($\mu g/g$)
W_D = dry weight of i^{th} section (g)
a = area of core (cm^2)

These parameters are illustrated in Fig. 2. In some cases, M_B was unusually high for Ni and Cr (>100 ppm) in areas of the Eastern Townships, something also recognized by nineteenth century miners who established small open pit mines in the area. High backgrounds made it impossible to distinguish anthropogenic metal burdens from background noise, since surface concentrations for these metals usually don't exceed 80 ppm. These cores were therefore removed from the analysis (Table 4).

Anthropogenic Pb was determined in 146 cores from 11 lakes in the Eastern Townships, and 20 cores from two Laurentian lakes of Quebec using eq. 1. Each core consisted of a minimum of 15 horizontal slices. With these data, Pb-depth curves were derived for each lake (Fig. 4, Table 2). Whole-lake Pb burdens were calculated by a depth-integrated averaging procedure similar to Evans & Rigler (1985). When asymptotic Pb-depth curves were observed (Fig. 4), they were so plotted. Bathymetric maps were measured by planimetry to determine areas of lake basins at 1

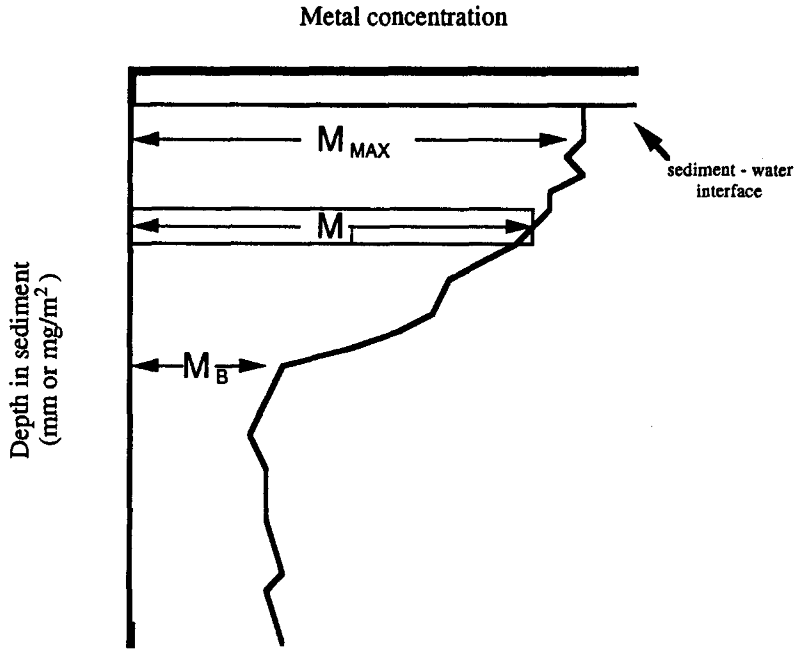

Fig. 2. Core profile parameters used in equation 1.

meter depth intervals. Using these hypsographic data, we derived the amount of Pb deposited at each depth interval and calculated a mean value for Pb burden across the entire basin (Table 3).

Anthropogenic Pb was used as a correction for sediment focusing for

Table 2. Equations used for lakes for which whole-lake Pb burden data were obtained. Lakes Orford and Stukely showed no depth trend so Pb deposition was derived from an average of all cores collected from these lakes.

Lake	Equation	R^2	# of cores
Aylmer	$Pb = 58.5 + 11.55\,(depth) - 0.186\,(depth)^2$	0.71	17
Bowker	$Pb = -35.5 + 8.55\,(depth) - 0.08\,(depth)^2$	0.72	12
Brompton	$Pb = -55 + 136\,(\log depth)$	0.90	12
Coulombe	$Pb = 6.4 + 9.01\,(depth)$	0.48	12
Croche	$Pb = -25.9 + 14.2\,(depth)$	0.66	8
Cromwell	$Pb = -8.65 + 15.06\,(depth)$	0.65	11
Lovering	$Pb = -15.0 + 7.86\,(depth)$	0.71	14
Massawippi	$Pb = -67.2 + 14.23\,(depth) - 0.243\,(depth)^2 + 0.001\,(depth)^3$	0.77	16
Nicolet	$Pb = -165 + 211.5\,(\log depth)$	0.54	12

Table 3. Anthropogenic Pb burdens calculated for the lakes in Table 2.

Lake	Anthropogenic Pb burden (mgPb/m^2)
E. Townships	
Aylmer	1186
Bowker	617
Brompton	770
Coulombe	510
Lovering	603
Massawippi	1285
Nicolet	882
Orford	1619
Stukely	1078
mean	950
Laurentians	
Croche	420
Cromwell	402
mean	411

all other metals. The implicit assumption behind this correction is that all sediment metals will be redistributed to the same extent by turbulence within lake basins. The use of anthropogenic Pb as a correction for focusing has previously been applied to estimate anthropogenic Zn and Cd burdens (Evans et al. 1983). Multiple regressions (SYSTAT) were performed to relate the focus-corrected trace metal burdens to drainage characteristics. Whenever the distribution of data was not homoskedastic, they were logarithmically transformed.

Results and discussion

Sediment metal surface enrichment

Surface enrichment of metals in sediment was observed for all metals studied except Al. Sediment enrichment factors (M_{max}/M_B, Fig. 2) were derived for all metals in each core. The mean enrichments for all the metals are compared in Fig. 3A with atmospheric enrichment factors (i.e. interference factors) derived by global atmospheric metal budgets (Nriagu 1989). A second comparison involved examining the same sediment

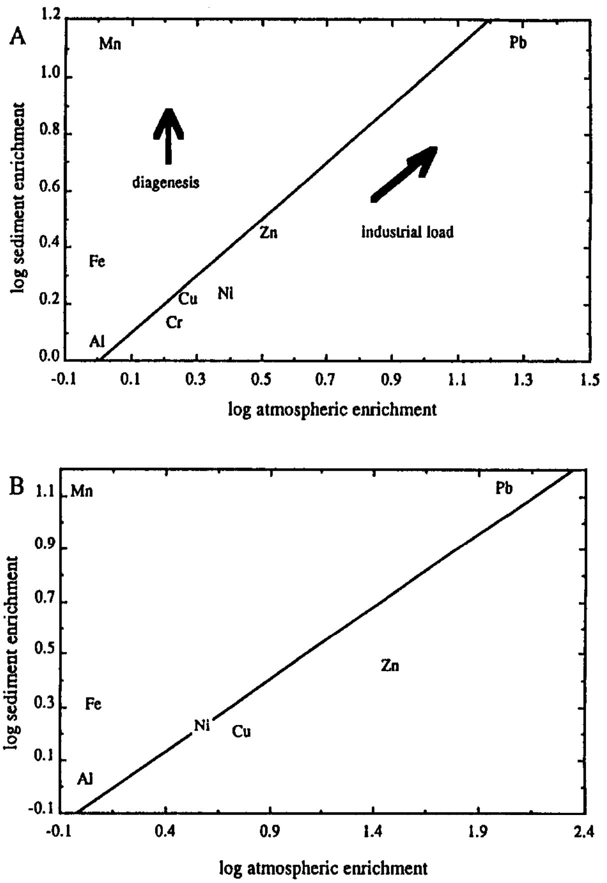

Fig. 3. Log sediment enrichment factors plotted against the atmospheric enrichment factors from (A) the global atmospheric metal budgets of Nriagu (1989), and (B) the atmospheric metal enrichment factors calculated for the Haliburton/Muskoka region of Ontario by Jeffries & Snyder (1981) Note the similarity in relative enrichments.

enrichment factors on a regional scale, as calculated by Jeffries & Snyder (1981) for Southern Ontario (Fig. 3B). The atmospheric enrichment factor is defined as the ratio of industrial to natural metal flux to the atmosphere. The observed sediment enrichment is strongly reflected in atmospheric enrichment for 6 of the 8 metals: Al, Cr, Cu, Ni, Zn, and Pb. This indicates that sediments provide a useful index of industrial load for these particular metals. Both Mn and Fe are positive outliers which can be attributed to surface migration. Such post-depositional mobility for Mn and Fe in sediments is well documented (Emerson 1976; Carignan & Flett 1981).

Whole-lake Pb burdens

The whole-lake anthropogenic Pb burdens averaged out to 950 mg Pb/m^2 +– 349 (SD) for the Eastern Township lakes, and 411 mg Pb/m^2 +– 9 (SD) for the Laurentian region (Table 3). There was no relationship when whole-lake anthropogenic Pb burdens were plotted against drainage ratio (drainage basin area/lake area) (Fig. 5). This indicates that catchment retention of Pb is virtually complete, since no increase in whole-lake Pb burden is observed across lakes that span over two orders of magnitude in drainage ratio. A similar observation was made by Dillon & Evans (1982) for lakes of south central Ontario, Canada.

The regional estimates of Pb deposition in the Eastern Townships were much higher than those reported in other, more remote regions. Evans & Rigler (1985) reported an average of 44 mg/m^2 for Schefferville, in northern Quebec, 330 mg/m^2 for Parc des Laurentides, Quebec, 380 mg/m^2 for Barry's Bay Ontario, and 390 mg/m^2 for Parry Sound, Ontario. The higher Pb deposition levels in the Eastern Townships may be attributable to the relatively close proximity to the City of Montreal, or to the mining activities in the region (Thetford Mines).

We observed the Pb-depth relationships to be non-linear in the deeper lakes (Fig. 4). Lakes such as Massawippi, Aylmer, Brompton, and possibly Nicolet exhibited an inflection in the Pb-depth relationship at a depth of about 20 meters. The Pb-depth relationships previously calculated have always been linear (i.e. Evans 1980; Dillon & Evans 1982; Evans & Rigler 1985), suggesting that sediment resuspension occurs at all depths. The present findings show this to be incorrect for deeper lakes at least. That lake basins can indeed be separated into a shallower zone of sediment erosion, and a deeper zone of sediment deposition was recently demonstrated independently by Rowan et al. (1992). They characterized sediments on the basis of erosional and depositional zones by examining distributions of sediment texture across lake basins. An implication of their work is that sediments do not become resuspended past a threshold depth, which was determined as a function of fetch (exposure) and under water slope. If sediments are not resuspended past a threshold depth as this theory predicts, then we would expect to observe an inflection (asymptote) in metal deposition values as this threshold is reached. The asymptotic nature of the Pb-depth trends that we observed in the deeper lakes support the findings of Rowan et al. (1992).

Catchment retention of Zn, Cu, Ni, and Cr

We examined the efficacy with which Cr, Ni, Cu, and Zn were retained by

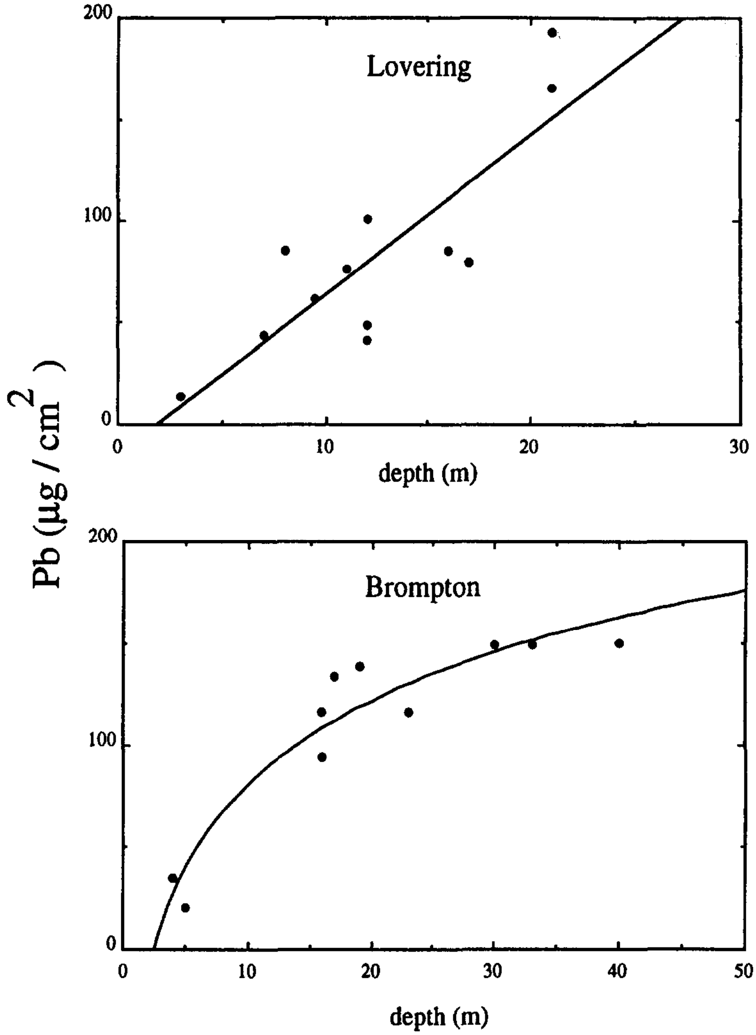

Fig. 4. Typical Pb-depth curves for two of the eleven Quebec lakes.

the drainage basins by normalizing their sediment burdens (1) to Pb burden (Table 4). It is evident that Pb-normalized Cr and Ni burdens increase with drainage ratio until drainage ratio values of about 20 are reached. Beyond this point, the Cr and Ni values start to taper off (Fig. 6). We attribute this to localized sinks in very large catchments that impede the export of metals to lakes. The same non-linear element load — catchment area relationship has been observed in stream mass balances for heavy metals (Dillon et al. 1988) and phosphorus (Prairie & Kalff 1988). Individual element models were constructed on the basis of

Table 4. Sediment metal burdens expressed as ratios to anthropogenic Pb burden for the lakes where Ni, Cr, Zn, and Cu were measured. Asterisks (*) denote cores with elevated background concentrations for Ni and Cr (> 100 ppm). LOI (loss on ignition) is given as % dry mass.

Lake	Ni	Cu	Zn	Cr	LOI (%)
Eastern Townships, Quebec					
Bowker	*	0.074	1.055	0.001	22
Brome	0.137	0.197	1.050	0.133	15
Coulombe	0.490	0.063	0.950	0.009	27
Elgin	*	0.093	1.064	0.105	25
Lovering	0.256	0.112	0.825	0.109	15
Nicolet	*	0.040	0.508	*	27
Silver	0.424	0.105	0.457	0.120	10
Stukely	*	0.018	0.511	*	21
Laurentians, Quebec					
Achigan	0.026	0.034	0.724	0.013	32
Connelly	0.069	0.038	0.972	0.010	37
Croche	0.020	0.044	0.924	0.030	46
Muskoka/Haliburton, Ontario					
Atkins	0.120	0.120	0.992	0.033	37
Barnum	0.08	0.104	1.394	0.049	31
Dickie	0.056	0.088	0.562	0.018	37
Grass	0.111	0.265	1.800	0.035	20
Haas	0.077	0.130	2.413	0.045	63
Kennisis	0.061	0.059	1.382	0.002	21
L. Dudmun	0.060	0.040	1.955	0.010	42
Miskwabi	0.071	0.019	1.953	0.013	28
Moose	0.028	0.031	0.542	0.027	18
Pelaw	0.196	0.030	2.650	0.085	26
Raven	0.054	0.053	0.659	0.006	27
Tooke	0.043	0.085	0.914	0.004	34
Twelve Mile	0.066	0.138	1.809	0.154	13
Two Island	0.023	0.030	1.234	0.040	35

drainage ratios that spanned from 0—20, since metal burdens in this range appeared linear (Fig. 6).

The three Laurentian lakes were outliers in the sediment metal models suggesting a regional effect. For this reason, we derived the individual element models with the Laurentian lakes absent (Table 5A) and present (Table 5B). Both the coefficients of determination (R^2) and the standard deviation of the residuals (SE_{est}) demonstrated a better fit when the

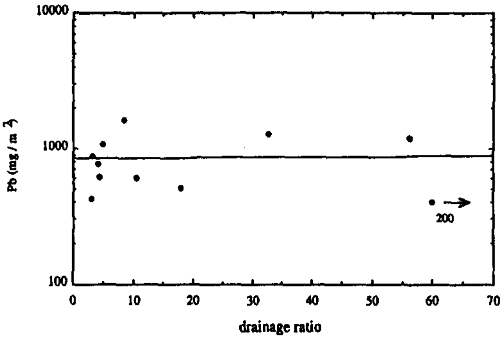

Fig. 5. Total Pb deposition in Quebec lakes as determined by depth — integrated averaging plotted against drainage ratio. The absence of an increase shows a complete catchment retention of Pb.

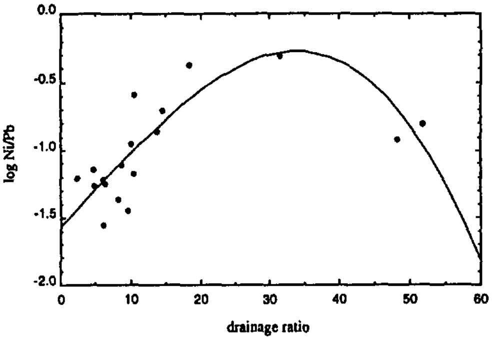

Fig. 6. Log Ni/Pb burden plotted against drainage ratio demonstrating the non-linear relationship between metal burdens and catchment size.

Laurentian lakes were removed (Tables 5A and 5B). It is possible that the metal retention characteristics of drainage basins differ between the steeper sloped, well drained and calcareous basins of the Eastern Townships, and the lower sloped, poorly drained and igneous drainage basins of the Laurentian region.

Cr demonstrated the largest increase with drainage ratio (slope = 0.12, Fig. 7A). The Cr-drainage ratio model appears to form an asymptote at the top right of its distribution, but there are too few points in this region to warrant a non-linear model. Ni likewise showed an increase (Fig. 7B). Cu increased slightly with increasing drainage ratio, but the model was not quite significant ($P = 0.07$). Finally, Zn did not increase at all with increasing drainage ratio (Fig. 7A). The metal export sequence that is reflected in the different slopes (Cr > Ni > Cu > Zn = Pb) has

Table 5. Individual element models for log metal/Pb burden as a function of drainage ratio (DR; range 0—20) with the three Laurentian lakes (A) absent, and (B) present. Standard errors are in brackets.

A

metal burden ratio	model
log Cr/Pb	−2.65 (0.215) + 0.12 (0.022) DR $R^2 = 0.69$, $SE_{est} = 0.348$, $n = 15$, $P < 0.001$
log Ni/Pb	−1.61 (0.137) + 0.058 (0.014) DR $R^2 = 0.57$, $SE_{est} = 0.221$, $n = 15$, $P < 0.001$
log Cu/Pb	−1.54 (0.187) + 0.038 (0.020) DR $R^2 = 0.18$*, $SE_{est} = 0.361$, $n = 18$
log Zn/Pb	−0.028 (0.135) + 0.006 (0.015) DR $R^2 = 0.01$**, $SE_{est} = 0.261$, $n = 18$

* $P = 0.07$, not significant
** $P = 0.67$, not significant

B

metal burden ratio	model
log Cr/Pb	−2.34 (0.248) + 0.074 (0.023) DR $R^2 = 0.39$, $SE_{est} = 0.459$, $n = 18$, $P = 0.005$
log Ni/Pb	−1.48 (0.173) + 0.035 (0.016) DR $R^2 = 0.22$, $SE_{est} = 0.316$, $n = 18$, $P = 0.045$

previously been observed in soil leaching experiments (Korte et al. 1979; Tyler & McBride 1982). Mass balance studies in the Sudbury region have likewise shown Ni retention in soils to be considerably less than that of Zn and Cu (Dillon et al. 1988). Furthermore, Schut et al. (1986) provided mass balance data from two Ontario lakes demonstrating almost complete catchment retention of Cu and Pb, which is consistent with our findings.

We used the slopes of the individual element models to represent the catchment export coefficients. A positive relationship is observed between catchment export and ocean residence time for the five metals (Fig. 8), as

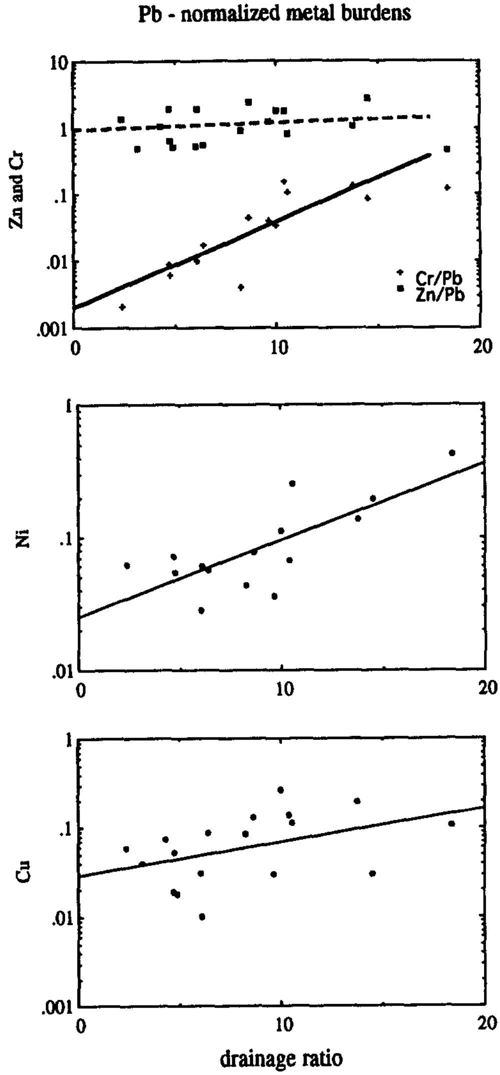

Fig. 7. Pb-normalized (focus corrected) sedment metal burdens as a function of drainage ratio over the range 0—20, with the 3 Laurentian lakes removed. Each point represents an individual lake.

calculated by Broecker & Peng (1983). This trend shows that those metals that settle out most readily in oceans are also the elements that are most effectively retained by catchments. An element's ocean residence time is reflected by its chemical reactivity. Important reactions which may remove elements from the water include: (1) adsorption reactions that involve cation exchange (outer sphere), or ligand exchange (inner sphere); and

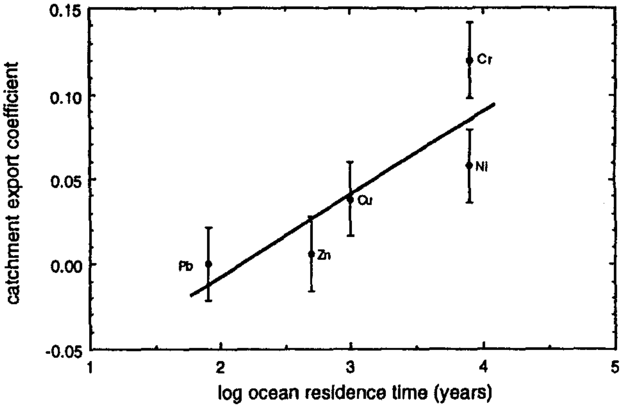

Fig. 8. Catchment export coefficients (slopes of the individual element models) plotted against ocean residence times obtained from Broecker & Peng (1983). Bars represent standard errors.

(2) precipitation reactions of oxides, hydroxides, carbonates, silicates, phosphates, or sulfides (Evans 1989). The relative importance of these reactions is poorly understood, but it is evident that similarities exist in the removal of metals from water in both soils and oceans. Note that both Cr and Ni have identical ocean residence times, but different catchment exports. This may result because Cr forms oxide anions in soils (Korte et al. 1976) which would be repelled by clays and Fe oxyhydroxides thereby enhancing export of Cr from soils. Although only five metals were used in the derivation of this model, we predict that our findings should be applicable to other metals as well. On the basis of ocean residence times measured for other elements, we would predict that catchment export coefficients for some other elements would be as follows: Cd = 0.10; V = 0.12; Co = 0.08; Hg = 0.04, etc.

It has been suggested that DOC is an important vector for catchment metal export (i.e. Tyler 1981). However, the adsorption sequence of metals on organic matter has been shown to exhibit the following sequence at pH 5.8:

Pb = Cr = Cu > Zn > Ni (Evans 1989)

This sequence is not one that we observed in our catchment metal exports. Both Pb and Cr are often well correlated with DOC in rivers (Tyler 1981; Lazerte 1991) yet we found that Pb was most effectively retained by catchments, and Cr was most effectively exported. Both Zn and Ni are considered to have a lower affinity for DOC due to weak electrostatic bonding, but behave very differently in the catchments; Ni is readily exported, and Zn is effectively retained. Therefore the flux of organic matter to lakes is clearly not the only factor governing metal export from soils. Instead, catchment metal retention is probably determined primarily by adsorption and co-precipitation of mineral phases in lower soil layers under alkaline conditions which would better explain the correlation between catchment metal export and ocean residence time. However, the observed catchment metal export pattern may not be universal, but rather a reflection of the study regions, which are characterized as having non-acidified catchments that are relatively poor in humus.

Atmospheric metal load

Atmospheric metal load was estimated from the Y-intercepts of the metal-drainage ratio models which represent the metal load to the lake surface (Table 6). We used the Y-intercepts of Pb normalized metal burden-drainage ratio models in conjunction with the regional whole-lake Pb burdens (Table 3) to estimate atmospheric metal load in mg/m^2 for each of the three regions. The atmospheric load for the different metals follows the order:

Table 6. Individual element models with spatial variables included for the Pb-normalized Cr and Ni sediment burdens.

element	model
log Cr	99 (29.8) + 0.074 (0.024) DR − 0.021 (0.006) lat − 0.001 (0.0001) long $R^2 = 0.65$, $SE_{est} = 0.37$, $n = 18$, $P < 0.001$
log Ni	67 (20.4) + 0.035 (0.016) DR − 0.014 (0.004) lat − 0.001 (0.0001) long $R^2 = 0.57$, $SE_{est} = 0.251$, $n = 18$, $P < 0.001$

$$Cr < Ni < Cu < Zn < Pb$$

Nriagu (1979) observed the identical sequence in metal flux rates to the atmosphere from anthropogenic sources. The primary source of Pb to the atmosphere has been the combustion of leaded gasoline, whereas Zn, Cu, Ni and Cr are derived primarily from coal and oil combustion, smelting, and refuse incineration. The fact that the atmospheric depositions computed from lake burdens (Table 7) agree well with patterns of metal emissions (Fig. 3) indicates that diagenesis of these metals in non-acidified sediments does not obscure historical patterns of heavy metal loading to sediments, something proposed for more acidic environments (i.e. Carignan & Nriagu 1985).

Spatial variables

To assess the influence of spatial variables on the sediment metal models, we included latitude and longitude as independent variables in a stepwise multiple regression (Table 6). Both latitude and longitude were significant in predicting Cr and Ni, and improved the fit substantially. This agrees with the observed regional differences in the atmospheric loading of metals to sediments (Table 7). Latitude carries a negative coefficient (Table 6) which indicates that metal load decreases toward the north. A similar decline in metal deposition to sediments has been observed in Sweden (Johansson 1989), and in Ontario (Dillon & Evans 1982). In all these regions, the industrial centers are to be the south. However, longitude also carried a negative coefficient which indicated that metal burdens are greater in the east. The Eastern Township region lies east of the city of Montreal, and in close proximity to the mining activities of Thetford Mines providing an explanation for the elevated metal deposition values in that area. While spatial variables are clearly an important determinant in sediment metal burdens, drainage basin characteristics are important as well because the drainage ratio remains a significant variable once the spacial variables have been considered.

Table 7. Atmospheric load of metals (mg/m^2) was determined from the Y-intercepts of Fig. 6, multiplied by regional Pb depositions obtained from whole-lake Pb burdens (Table 3). Regional values for the Muskoka/Haliburton region were obtained from Dillon and Evans (1982).

Metal	Region		
	Muskoka/Haliburton	E. Townships	Laurentians
Cr	1	2	1
Ni	9	23	11
Cu	11	27	13
Zn	356	890	412
Pb	380*	950	440

* Calculated in Dillon and Evans (1982)

Unexplained variance

In contrast to drainage ratio, pH of the water column did not explain any of the observed variance in metal load to the sediments. We might expect that at a lower pH, there would be more metals leaching from catchments to lakes and their sediments (i.e. Cronan & Schofield 1979) as well as diffusion of metals from the sediments (Schindler et al. 1980). We suspect that pH did not exert an effect in the present study because all but 3 of the lakes had a pH > 6 in the water column (Table 1).

Schut et al. (1986) calculated lake retention of Pb and Cu in Harp and Dickie lakes, Ontario to be in excess of 96% for Pb and about 50% for Cu. Thus it is likely that retention of Pb in our lakes is almost complete. Such a high retention is unlikely for the other metals because metals with a low particle affinity are least readily scavenged and sedimented (Jackson et al. 1980). As a consequence, those metals that are leached most readily through soils are also the most likely to have the lowest retention in lakes. Despite this, we see an increase in sediment load for these metals (Cr and Ni) with increasing drainage ratio which indicates that the effect of metal load from the catchment is greater than the effect of their loss through the outflow.

Conclusions

In conclusion, this study demonstrated that (1) catchment retention of Pb is virtually complete; (2) anthropogenic metal burdens can be estimated with a relatively small number of cores by 'normalizing' to anthropogenic Pb; and (3) the catchment export of different metals reflects their degree of 'particle reactivity'. That this is the case is evident from the identical sequence of catchment export coefficients and ocean residence time which illustrated this last point. Measures of 'ocean residence time' appear to be a useful parameter in the modeling of catchment metal export because ocean residence time integrates both precipitation and adsorption reactions, both of which are important in catchment metal retention.

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