WHAT FRACTION OF THE TOTAL METAL FLUX INTO LAKES IS RETAINED IN THE SEDIMENTS?

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Jerome O. Nriagu and Henry K.T. Wong

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Perspective-gestion

Nriagu, J.O. et H.K.T. Wong. Pourcentage de la charge totale en métaux dans les lacs qui est retenue par les sédiments. Article à présenter dans la publication <u>Water, Air and Soil Pollution</u>.

Les sédiments fournissent souvent des indices qui permettent d'interpréter les changements antérieurs dans les charges de métaux polluants des lacs. En effet, on suppose en général que la plus grande partie des métaux déversés dans les lacs sont retenus par les sédiments. Or, jusqu'à maintenant, cette hypothèse n'a été confirmée par aucune analyse sur le terrain.

On a déterminé les concentrations et les taux de précipitation de métaux polluants (Pb, Cu, Zn, Ni et Cd) et de métaux des terres rares dans les sédiments et les particules en décantation d'un grand lac isolé (lac Opeongo), situé dans la parc provincial Algonquin (Ontario). À l'aide d'un modèle de conservation des masses basé sur les métaux des terres rares, on a pu déterminer que seulement 40 à 60 p. 100 de la quantité totale des métaux déversés dans le lac sont retenus par les sédiments. Étant donné ce faible taux de rétention, on peut mettre en doute l'utilité de faire appel à des modèles de comportement des métaux pour évaluer les récentes augmentations de dépôts de polluants transportés sur de longues distances.

POURCENTAGE DE LA CHARGE TOTALE EN MÉTAUX DANS LES LACS

QUI EST RETENUE PAR LES SEDIMENTS

Jerome O. Nriagu et Henry K.T. Wong Institut national de recherche sur les eaux C.P. 5050 Burlington, Ontario, Canada L7R 4A6

Résumé

On a déterminé les concentrations et les taux de précipitation de métaux polluants (Pb, Cu, Zn, Ni et Cd) et de métaux des terres rares dans les sédiments et les particules en décantation d'un grand lac isolé (Lac Opeongo), situé dans le parc Algonquin (Ontario). À l'aide d'un modèle de conservation des masses basé sur les métaux des terres rares, on a pu déterminer que seulement 40 à 60 p. 100 de la quantité totale des métaux déversés dans le lac sont retenus par les sédiments. Ce faible taux de rétention pourrait donc expliquer les différences très fréquemment observées de teneur des sédiments en métaux entre les bassins et entre les lacs; il faudra en tenir compte lorsque l'on utilisera les modèles de comportement des métaux pour évaluer les changements environnementaux antérieurs associés aux pluies acides.

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RETAINED IN THE SEDIMENTS?

Jerome O. Nriagu & Henry K.T. Wong National Water Research Institute Box 5050 Burlington, Ontario L7R 4A6, Canada

<u>Abstract</u>. The concentrations of, and deposition rates for, the pollutant metals (Pb, Cu, Zn, Ni, and Cd) and the rare earth elements are reported for the sediments and settling particulates in a large, remote lake (Lake Opeongo) in the Algonquin Provincial Park, Ontario. Using a mass conservation model based on the rare earth elements, it is estimated that only 40-60% of pollutant metals getting into the lake is retained by the sediments. The low retention rate may explain the widely reported intra-basin and intra-lake differences in metal contents of sediments and casts some doubt on the use of pollutant metal profiles in retrospective assessment of the human contribution to the metal flux into many lake basins.

1. Introduction.

Sediments provide an historical record of past changes in the loading of metal pollution into lakes (Forstner and Wittmann, 1981; Salomons and Forstner, 1984; MARC, 1985). The reading of such a record occasionally presupposes that most of the metal inputs into a lake is retained in the sediments. Such an assumption has not been validated by actual field measurements. The rare earth (RE) elements as a group represent a conservative non-pollutant in lakes and a study of their mass conservation can potentially provide some insight into the retention of metals by the sediments. In this report, we compare the behaviors of the RE and pollutant metals in a large softwater lake (Lake Opeongo) in Central Ontario and conclude that the pollutant metals are more mobile than has hitherto been realized. Increased lake acidification thus is expected to accentuate the mobilization of pollutant metals stored in sediments of such lakes.

2. <u>Materials and Method</u>

Lake Opeongo is a large softwater, oligotrophic lake with a maximum depth of 50m and mean depth of 15m. The major physical properties and chemical characteristics of this lake are summarized in Table I; additional data are presented elsewhere (Wong et al., 1984; Wong and Nriagu, 1985).

The settling particulates in the water column were collected using sediment traps or particle interceptors (Wong and Nriagu, 1985). The traps were deployed at depths of 3.0 m. below the air-water interface and about 3.0 m. above the sediment-water interface at each of the sampling stations in the lake. The traps were tapped every 28 days in June, July, August and September, 1983 and the seston flux was calculated from the solid matter in the freeze-dried samples and the quantity of material intercepted per unit time.

The sediments were sampled by the lightweight coring device (Williams and Pashley, 1979). The cores were obtained at the same sampling sites as the sediment traps. These were located at the deepest parts of the four basins in the lake, each of which has a relatively flat bottom as determined by echo sounding. Four traps were deployed at different depths across one of the basins (South Arm), and the data presented below represent the averages for the stations. The sediment accumulation rate was determined by Pb-210 geochronology (Robbins, 1978; Nriagu <u>et al</u> 1979). Total metal concentrations were determined by atomic absorption spectrometry following the wet digestion of the samples with aqua regia and HClO3 (Nriagu, et al., 1982; Wong et al., 1984). The rare earth elements were measured by neutron activation while the standard dry combustion method (Perkin Elmer Elemental Analyzer) was used in determining the carbon and nitrogen contents of the freezedried samples.

3. <u>Results and Discussion</u>

The lakewide average concentrations of Cu, Ni, Pb, Zn, organic C and N in suspended particulates collected between May and October, 1983 are shown in Table II. A notable feature is the high concentration of lead in the seston; lakes in Central Ontario are known to receive highly elevated inputs of anthropogenic lead (Evans and Rigler, 1985). The high particulate Zn content may reflect the high background levels in this watershed, the average Zn concentration in the precolonial sediment layers being about 100 ug g^{-1} (Figure 2). By contrast, the average Cu, Ni and Pb concentrations in the precolonial layers are only 21, 16 and 12 ug g^{-1} respectively. The average concentrations of the rare earths (RE) in the seston are also shown in Table II. One can assume that most of the RE in seston are derived from the surrounding bedrock and, indeed, the data compare favourably with the average abundance (in ug g^{-1}) of the RE in the Precambrian shield of Canada: La=32, Ce=65, Nd=26, Sm=4.5, Eu=0.94, Tb=0.48, Yb=1.5, and Lu=0.23 (Shaw et al., 1976). Notice also that the relative ratios of the RE in the seston are very similar to those of the shield rocks suggesting that there is no unusual behavior or supply of any particular RE element to the watershed (e.g., see Crocket and Kabir, 1981; Olmez and Gordon, 1985).

The downcore profiles (Figure 1) show the characteristic enrichment of the pollutant metals in the most recent sediments. Accumulation of excess metal burden in the surficial sediments has been reported in many parts of Europe and North America and is generally attributed to the recent influx of metal pollution into lakes in these areas (see MARC, 1985 for a recent review). By contrast, there is no discernable enrichment of the RE in the most recent sediment (Table III); industrial activities apparently do not now release large quantities of these elements into the environment (Olmez and Gordon, 1985).

The ratios of the concentrations of individual RE elements in the sediments to their concentrations in the suspended particulates $(R_{s/p})$ vary from 2.4 to 3.1 (Table II) and average about 2.7±0.26. In other words, the ratios are relatively constant. Such an enrichment of the RE in sediments in relation to the seston can be regarded as a natural lake phenomenon which may be attributed primarily to the biodegradative removal of the sestonic biomass. This point is emphasized by the $R_{s/p}$ for particulate organic carbon which is 0.35, or roughly the reciprocal of that for the RE. The organic matter content itself varies from well over 50% in the seston (Table II) to under 20% in the surficial sediments (Wong and Nriagu, 1985). Other factors which can also contribute to the relative enhancement of the RE in sediments include (a) addition of weathered and fractionated material from the bluff and bedrock, and (b) diagenetic processes which pump the mobile components out of the sediments. The relative importance of the latter two processes is unkown at the present time. It is, however, worth noting that $R_{s/p}$ values above 2.0 seem to be characteristic of other conservative components in these lakes. For example, Al has an $R_{s/p}$ value of 2.6, which is similar to the RE values, while the expectably more mobile Fe has a slightly lower $R_{s/p}$ of 2.2.

The $R_{s/p}$ values for the pollutant metals are also fairly constant but with a range of only 1.2 to 1.6 (Table II) and a mean of 1.4. In other words, there is also a fractionation of the pollutant metals between the sediments and the seston. The interesting feature however is the marked difference in the $R_{s/p}$ values of the pollutant metals and those of the conservative elements. The RE and Al in the sediments come from the runoff and river inputs, the weathering of bluff and bedrock materials, and

from atmospheric fallout into the lakes. On the other hand, the pollutant metals are believed to come primarily from the atmosphere, and one can envisage a complex source-driven model to explain the observed disparity in the $R_{s/p}$ values. We do, however, prefer the simple explanation which follows.

Pending strong evidence to the contrary, we believe that the reduced $R_{s/p}$ for pollutant metals is due to their leakage out of the sediments. If the pollutant metals were totally conserved in the sediments, just like the RE and Al, the $R_{s/p}$ values close to 2.6 would also be expected. A deviation from this value should give a rough estimate of the regenerative loss of the pollutant metals from the lake sediments. On the basis of this assumption, it is estimated that only 50 to 65% of the total metal input into Lake Opeongo is retained by its sediments. The low retention figure is contrary to the general belief that sediments are the sink for most of the pollutant metal flux into a lake (see Salomons and Forstner, 1984; MARC, 1985). This partial retention/loss may explain some of the common (peculiar) features of trace metal distribution in lake sediments, including the inter-basin and inter-lake differences in the rates of metal accumulation (Forstner, 1977; Nriagu <u>et al.</u>, 1979, 1982; Norton et al., 1981; Evans and Dillon, 1983; Dillon and Smith, 1984). The low retentivity also emphasizes the need for caution in the use of trace metal profiles in retrospective assessment of recent changes in rates of pollutant input into a given watershed.

Possible mechanisms involved in the release of pollutant metals from sediments are not difficult to find. Several studies show that the downward flux of seston (and particulate metals) increases exponentially with depth towards the sediment-water interface of many lakes (Chambers and Eadie, 1981; Rosa <u>et al</u>., 1983, Charlton, 1983). This implies that the turnover time for particles at the sediment-water interface is only a few days. The massive resuspension of sediments, orchestrated by bioturbation and bottom currents, represents the basic physical process that drives the metal release. In addition, the dissolution or desorption of sediment-bound metals results in elevated levels of the pollutant metals in the porewaters (Carignan and Tessier, 1985; Carignan and Nriagu, 1985). The continuous out-flux of the metal-enriched porewaters (due to diffusion and bioturbation) also contributes to the selfcleansing of metal pollution from the sediments. Studies of porewater profiles for trace metals indeed show that the regeneration of pollutant metals is a common feature in sediments of many lakes in Ontario (Carignan and Tessier, 1985; Carignan and Nriagu, 1985).

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	WATER CHEMIS	TABLE I TRY DATA F	OR LAKE OPEONGO	
Ca (mg 1 ⁻¹)	ω ω		PH	6.8
ВW	1.2		Alkalinity(mg 1 ⁻¹) as CaCO_	4.6
Na	1.1		ر (Conductivity (uS cm ⁻¹	42
~	0.62		Lake Area (ha)	5900
SO4	8.6		Maxium depth (m)	43
Al	10.018		Lake volume (m ³ x10 ⁶)	856
			Watershed area (ha)	34609
* Ontario Ministry	of Natural	Recourses	Ficheries Aridification 1	c+ch meanoa

(1982) uy ur natural Nesources Fisheries Acidification Program data

			TABLE II		
	ARTICULATE METAL CON	NCENTRATIONS	AND ENRI	CHMENT FACTORS IN LAKE	OPEONGO
Element	Concentration in seston*	R** S/p	Element	Concentration in seston*	R** s/p
2	38±14 (n=41)	्र अ	ТЪ	2.5 (n=4)	2.4
Ĩ	31 <u>+</u> 10 (n=43)	1.2	La	18 (n=4)	2.7
РЬ	108 <u>+</u> 24 (n=46)	1.6	Ce	31 (n=4)	2.6
Żn	146±435 (n=44)	1.4	Nd	1:6 (n=4)	3.0
Fe	1.6 <u>+</u> 0.6%(n=44)	2.2	Sm	3.1 (n=4)	ω. 1
Al	1.7±0.4%(n=53)	2.6	Eu	0.75(n=4)	2.4
Org. C	28 %(n=45)	0.35	Тb	0.32(n=4)	2.9
			ÝЪ	0.82(n=4)	3.0
				0.14(n=4)	2.6
*Concent of data	crations are in μg g. points averaged; the	-1 (dry wt.) ne <u>+</u> error f	unless o unction s	therwise stated; n= the hown is the standard de	e number eviation
** R_/_ i	is the ratio of conce	entration in	sediment	s to the concentration	л. п

7

"s/p is the facto of concent suspended particulates.

					(uq					
우 		5.4	42	72	40	7.9	1.6	0.8	2.2	0.30
1- 2	1.4	5.6	42	75	38	7.9	1.7	0.8	2.2	0.31
3-4	0.9	6.5	46	84	50	9.0	1.6	0.8	2.4	0.35
6-7	1.3	6.6	45	81	49	8.8	1.8	0.9	2.4	0.35
9-10	1.2	6.3	49	81	49	9.6	1.7	0.9	2.5	0.37
14-15		6.7	50	84	48	9.8	2.2	1.2	2.5	0.38
20-22	٦.4	5.8	53	81	50	11.0	2.0	0 . 9	2.7	0.40
28-30	<u>.</u>	5.5	54	77	53	11.0	1.7	1.0	2.7	0.40
13-45	1.4	<u>6.</u> 0	56	87	54	11.0	1.7	1.1	2.8	0.42

Figure Captions

- Figure 1. Profiles of Ni and Zn in Lake Opeongo sediments showing recent changes in rates of pollutant metal input.
- Figure 2. Profiles of Cd, Pb and Cu in Lake Opeongo sediments showing recent changes in rates of pollutant metal input.



