



Trace metals Geochemistry Continental Shelf Transport Métaux en trace Géochimie Plateau continental Transport

Wm. Berry Lyons, H. E. Gaudette

Department of Earth Sciences, University of New Hampshire, Durham, New Hampshire 03824, USA.

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ABSTRACT

Acid leachates from sixty-three surface sediment samples from Jeffreys Basin, Gulf of Maine have been analyzed for Fe, Mn, Cu, Cr, Zn and Pb. With the exception of Cr, the average concentrations of these metals from the continental shelf sediments are similar to those observed in nearby estuarine sediments. Statistical analysis of the trace metal data indicates a very strong correlation (at the 99.5% confidence level) between the trace metal content of the sediments and the grain size with the highest metal concentrations correlating with the clay size sediment fraction. The data suggest that trace metals are transported to the continental shelf as iron and manganese oxides adsorbed on the finest grain sediment fraction, indicating that fine grained particles dominate the behavior of trace metals in the marine environment as proposed by Turekian (1977).

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RÉSUMÉ

Géochimie des sédiments dans le bassin de Jeffrey, golfe du Maine : transport présumé des métaux en trace

63 échantillons de sédiment superficiel du bassin de Jeffrey, dans le golfe du Maine (plateau continental NE des États Unis) ont été attaqués à l'acide, et analysés pour Fe, Mn, Cu, Cr, Zn, et Pb. A l'exception de Cr, les concentrations moyennes de ces métaux dans les échantillons étudiés sont semblables à celles observées dans les sédiments des estuaires voisins. L'analyse statistique des mesures de concentration des métaux en trace montre une très forte corrélation (au niveau 99,5%) entre la teneur en ces métaux et la granulométrie, avec les concentrations en métaux les plus grandes associées à la fraction de taille des argiles. Les résultats suggèrent que les métaux en trace sont entraînés par les oxydes de Fe et Mn adsorbés sur les sédiments les plus fins, et transportés ainsi vers le plateaù continental. Il semble donc que, comme le proposa Turékian (1977), les particules les plus fines ont un rôle majeur dans le comportement des métaux en trace dans l'environnement marin.

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INTRODUCTION

A meaningful assessment of the effects of trace metals on the biosphere requires a delineation of the pathways and fate of both naturally and anthropogenically introduced trace metal species. A number of studies have pointed out the importance of estuarine sediments as the major reservoir for biologically active elements including trace metals Cu, Zn, Cr, Hg, Ni, Cd (Fitzgerald *et al.*, 1974; Thomson *et al.*, 1975; de Groot *et al.*, 1976). Laboratory studies (Sholkovitz, 1976; Boyle *et al.*, 1977; Sholkovitz, 1978) as well as water column investigations (Boyle *et al.*, 1974; Helz *et al.*, 1975; Benninger, 1978) indicate that in some estuaries the trace metals Fe, Mn, Cu, Ni, Co, Pb may be removed very close to their source. These metals may be cycled internally in estuarine systems so that little dissolved metal escapes to the shelf environment. Assuming that stable metals behave analogously to their radioactive counterparts, the rapid scavenging of metals by particles is undoubtedly very important in this regard (Turekian, 1977).

In contrast, global geochemical balances (Horn, Adams, 1966) and studies of oceanic sediments (Chester, Aston, 1976) indicate that, over geologic time, trace metals are transported into deeper water. Although a percentage of the total metal is undoubtedly transported via the atmosphere (Windom, 1970), the majority of the metal must come from the nearshore areas where initial removal and deposition occurs.

The question arises as to what mechanism(s) may be responsible for transporting trace metals from estuaries onto the continental margins and beyond. If particulate scavenging is an effective tool in trace metal removal, metals escaping the estuarine system should be associated with fine grained particles, organic as well as inorganic in character.

We have previously analyzed surficial sediments from Great Bay, (NH) for various trace metals, organic carbon and grain-size parameters (Armstrong *et al.*, 1976). In this study, we report data from the adjoining continental shelf surficial sediments in an attempt to better understand the mechanisms of trace metal transport from the estuary to the near continental shelf.

Figure 1 Jeffreys Basin, Gulf of Maine, Continental Shelf, Northeastern USA.



METHODS

Sixty-three gravity cores from Jeffreys Basin, Gulf of Maine were utilized for this study (Fig. 1). These cores were taken within the "Merrimack Garnet" province as defined by Ross (1970) and the surficial sediments in this area are assumed to be Recent in age. Cores were obtained using a 8.0 cm i. d. stainless steel gravity corer equipped with polycarbonate core liners. The core liners were soaked in 10% HCl and rinsed with distilleddeionized water before use. The top 1 cm of air dried sediment of each core was gently dissaggregated and sieved with stainless steel sieves to obtain a < 80 mesh fraction. A subsample of this fraction of approximately 1 gm was accurately weighted and then treated to remove what we will term "leachable metals". This was done by heating the $\simeq 1$ gm sediment sample with 50 ml of hot 10% v/v HCl for 15 minutes. The samples were then filtered through 10% v/v HCl cleaned glass fiber filters and brought to 100 ml volume in an acid washed volumetric flask with distilled-deionized water. The final solutions were stored in conventional polyethylene (CPE) bottles which had soaked for 24 hours in concentrated HCl and rinsed at least three times with distilled-deionized water. These solutions were analyzed on a Techtron AA-3 Atomic Absorption Spectrophotometer for Fe, Mn, Zn, Cu, Cr and Pb. The hot HCl treatment dissolves metals on ion-exchange sites, iron and manganese hydroxides and iron monsulfide minerals (i. e. mackinawite and greigite) but does not dissolve pyrite (FeS₂) or significantly leach the crystalline lattice of most silicate minerals (Love, 1967; Berner, 1970). Studies have shown that dilute HCl adequately removes the hydrogenous metal fraction from sedimentary material with little effect on organic matter and lithogenous material (Piper, 1971; Agemian, Chau, 1976; Malo, 1977). This method of leaching was also utilized in the estuarine sediment study (Armstrong et al., 1976) and allows us to compare our results. A second subsample of sediment was analyzed for organic carbon by the method of Gaudette et al. (1974). Standard sedimentological techniques (Folk, 1968) were employed in determining grain size parameters. All < 80 mesh samples were checked by X-ray diffraction for calcitearagonite content; none were detected. The results are summarized in Table 1.

Table	1				
Mean	and	range	for	all	variables

	Jef	freys Basi	n	Great B	ay, N.H.	(a) (b)
Variable	Mean	High	Low	Mean	High	Low
Clay (%)	40.8	69.1	0.9	17.3	39.7	1.3
Iron (%)	2.79	4.36	1.15	-		
Zinc (a)	75.4	102.4	30.7	60.6	212	13.4
Copper (a)	16.4	35.1	2.4	16.4	129	2.9
Chromium (a)	56.3	83.7	20.1	112	594	9.6
Lead (a)	31.2	58.6	9.5	40.7	145	0.8
Manganese (a)	314.0	700.0	194.0	-	_	_
Organic C (%)	3.08	4.85	0.38	4.10	13.2	0.2

(a) Concentration expressed as microgrammes per gramme sample.(b) From Armstrong *et al.* (1976).

RESULTS AND DISCUSSION

Organic carbon content of these sediments appears to correlate with water depth and sediment texture (Flight, 1972) in the sense that higher values occur in the deeper portions of the central basin. Lower carbon values are associated with coarser sediments along the ledges. In addition, low organic carbon values are found to the SE of Boon Island, in the northernmost portion of Jeffreys Basin, and in the deeper water just to the north of Old Scantum Ledge. These are also areas where the sediments are the coarsest.

Comparison of the areal distributions of the metal data from Jeffreys Basin point toward: 1) apparent areas of low concentration south and east of Boon Island, and in areas associated with the shallower water ledge areas which limit the basin to the south and southeast; 2) areas of high concentration of leachable metals located in the deeper water central portion of the basin; 3) an area of higher metal concentration occurring just to the south and west of the shallowest water on the northern part of Jeffreys Ledge.

If these factors are considered with respect to sediment texture and organic carbon content, the areal distributions support traditional ideas (de Groot et al., 1976) that: a) organic carbon content is highest in the finer grained sediments; and b) leachable metal concentrations are highest in finer grained sediments. To test these hypotheses, linear correlations were computed for all the variables under consideration. Table 2 tabulates the correlation matrix for all samples (n = 63) and all the variables for the Jeffreys Basin study. Due to the large sample size, the correlation coefficient (r) is significant at 0.300 for the 99% confidence level and 0.330 for the 99.5% confidence level. The calculations show that the correlation between percentage clay size particles and the various leachable metals are all significant at the 99.5% confidence level. On the other hand, the copper and manganese to organic carbon correlations are not significant at this confidence level. In fact, the leachable metal to clay correlations are more significant than the leachable metal to organic carbon correlations for all the metals under investigation. Because the dilute HCl extraction used in this study has little effect on organic matter present in the

Correlation matrix, Jeffreys Basin samples.

	Clay (%)	Fe (%)	Zn	Cu	Cr	Pb	Mn	С (%)
Clay (%)	1.000			- <u></u>				
Fe (%)	0.663	1.000						
Zn (a)	0.777	0.879	1.000					
Cu (a)	0.460	0.521	0.615	1.000				
Cr (a)	0.653	0.774	0.840	0.354	1.000			
Pb (a)	0.588	0.623	0.725	0.503	0.711	1.000		
Mn (a)	0.609	0.691	0.699	0.431	0.678	0.526	1.000	
C (%)	0.562	0.486	0.681	0.165	0.566	0.483	0.305	1.000

For n = 63; $r \ge .300$ significant at 99% confidence level; $r \ge .330$ significant at 99.5% confidence level.

(a) Concentration as microgrammes per gramme sample.

sediments (Piper, 1971), the organic carbon-leachable metal correlations may be lower than anticipated.

The high significance of the leachable or environmentally available metal to percentage clay fraction correlation provides an important insight into the mode of transport of trace metals within and onto the continental margin. The data suggest that the leachable metal in Jeffreys Basin surficial sediments is associated with very fine grained material, possibly adsorbed onto hydrous oxide coatings of Mn^{4+} and Fe^{3+} (Carroll, 1958; Jenne, 1967) or as mucilaginous organic coatings (Frankel, Mead, 1973; Johnson, 1974).

A statistical summary of the sediment data from Jeffreys Basin is compared to that of Great Bay estuarine surficial sediments (Armstrong et al., 1976) in Table 1. It is apparent that the mean leachable metal concentrations from the continental shelf sediments are very similar to those of the estuarine sediments with the exception of chromium. The difference in Cr content can be explained by abnormally large quantities of Cr that have been introduced into the Great Bay system from industrial sources (Capuzzo, Anderson, 1973; Armstrong et al., 1976). Although previous studies have shown that the majority of trace metals introduced into the marine environment are removed in the estuaries (Boyle et al., 1974; Helz et al., 1975; Sholkovitz, 1976; Sholkovitz, 1978), the data from Jeffreys Basin indicate that hydrogenous or environmentally available metal concentrations of the sediments are not significantly different from the estuarine metal concentrations. At first consideration this would seem to be in contradication with prevalent ideas concerning estuarine trace metal geochemistry. However, the data in Table 1 also demonstrate that the concentration of the clay size fraction of the continental shelf sediments is twice that of the estuarine sediments. We have shown in Table 2 and the subsequent discussion that the leachable metal content is highly correlated to the clay size fraction of Jeffreys Basin sediments at the greater than 99.5% confidence level. This suggests that the mean leachable metal concentrations of Cu, Zn and Pb are similar between the two sedimentary regimes, even though the majority of metal may be removed in the estuary, because the continental shelf sediments consist of a higher percentage of finer grained material.

Little data are available regarding the sediment transport in the Gulf of Maine. In addition to seaward movement of sediment from the estuaries in Maine and New Hampshire, landward movement of bottom water may cause the transport of solids from the outer continental shelf toward the nearshore along the New England coast (Meade, 1969). A large areal extent of the Gulf of Maine sediments is probably dominated by Pleistocene relict sediments deposited through glacial action (Milliman et al., 1972). Radiocarbon dating, however, suggests that there is net sediment deposition occurring at a rate of between 5 and 19 cm per 1 000 years in Jeffreys Basin at present (Flight, 1972). Spencer and Sachs (1970) have suggested that the high concentrations of particulate Cu and Zn, averaging $344 \mu g/g$ and 293 μ g/g respectively, at the surface in nearshore

areas of the Gulf of Maine are due to estuarine input of fine-grained suspended material. This data and that of the radiocarbon measurements indicate that Jeffreys Basin is indeed receiving fine-grained sediment from nearshore areas.

In addition, stable carbon isotope analysis of surficial Jeffreys Basin sediment gave a δC^{13} value of $-23.6^{\circ}/_{\circ\circ}$ (S. Macko, personal communication). This value also indicates that a portion of the organic carbon being deposited in the Basin may be of terrestrial origin (Shultz, Calder, 1976; Gearing *et al.*, 1977).

Physical oceanographic measurements indicate that a significant portion of Gulf of Maine water may originate in the Gulf of Saint Lawrence (Sutcliffe *et al.*, 1976; Brown, Beardsley, 1978). This water is transported from the Gulf of Saint Lawrence over the Scotian Shelf and into the Gulf south of Cape Sable, Nova Scotia. Bigelow (1927) described the mean circulation in the Gulf of Maine and suggested that the counterclockwise surface gyre was probably fed from waters from the Scotian shelf. In addition to the New Hampshire, Maine and northern Massachusetts estuarine source of fine-grained material, this Scotian Shelf water may transport fine-grained material into the Gulf of Maine.

In order to evaluate the contribution of trace metals to the Jeffreys Basin area from both the estuarine and the Gulf of Saint Lawrence source we have constructed a simple two end-member model. Several assumptions are implicit in our model: 1) trace metals are solely transported by fine-grained sediments; 2) the source of this fine-grained material of Jeffreys Basin sediments is only from two sources-the Gulf of Saint Lawrence and the estuaries of New Hampshire and Maine; 3) Great Bay estuarine sediments have trace metal concentrations similar to those of Maine estuarine sediments. This final assumption is reasonable considering that: 1) the basement rocks from which the estuarine sediments are derived are similar in both Maine and New Hampshire; and 2) neither coastal area is highly industrialized and hence affected greatly by trace metal pollution.

The model can then be constructed by "normalizing" the trace metal content of Jeffreys Basin sediments and the two source areas, or end members, to 100% clay size material as illustrated by de Groot *et al.* (1976). This is done by plotting trace metal content vs. percentage clay at each location. The results of these calculations are tabulated in Table 3 along with the concentrations of non-detrital Cu, Zn and Pb observed

Table 3

Average trace metal content of Great Bay and Gulf of Maine normalized to 100% clay size fraction and non-detrital pelite concentrations from Gulf of Saint Lawrence.

	Cu (µ/g)	$Zn \ (\mu/g)$	Pb (µ/g)
Great Bay Estuary	95	350	235
Jeffreys Basin	46	144	74
Gulf of Saint Lawrence (a)	3	8	35

(a) From Loring (1978).

by Loring (1978) in Gulf of Saint Lawrence pelite sediments. If the Gulf of Saint Lawrence pelites and the 100% clay fraction of Great Bay sediments are used as end memebers, the amount of Cu, Zn and Pb in the Jeffreys Basin sediments contributed from each endmember can be determined. This is done by assuming that the concentrations of Cu, Zn, and Pb observed in Jeffreys Basin sediments are due to the mixing of fine-grained materials from these two source areas. The results are shown in Table 4.

Although this is a rather simple-minded approach to an undoubtedly complex problem, it allows us a first order assessment of transfer pathways of trace metals onto the near continental shelf. The data suggest that the estuarine areas of northern New England supply between 30-50% of the metal-rich fine-grained sediment into the nearshore basins while the rest is transported from a possible "upstream" source area. This upstream source seems reasonable based on hydrographic and physical oceanographic considerations.

Although the majority of the trace metal input into the estuarine system may be removed within the estuary itself, it appears that the fine-grained sediments of the estuary act as a "leaky sink" of trace metals to the continental margin and ultimately to the oceanic environment. In northern temperate estuaries this transport is undoubtedly accomplished by tidal action with the help of high wind stress events due to winter low pressure areas (Bohlen, 1975) yet their effect on mass transfer may be small. Large wind stress events cause long wind waves which resuspend sediments, particularly in shallow water areas. The mean currents can then transport large quantities of fine-grained material from the estuary onto the continental margin (Milliman et al., 1972; Soutar et al., 1977). Once this material has been deposited on the shelf, it is undoubtedly reworked by tidal action and finally deposited in bathymetric lows similar to Jeffreys Basin. In addition, hydrographic data suggest that sediment is transported into the basins of the Gulf of Maine from the Scotia shelf and/or the Gulf of Saint Lawrence. Although this has been inferred by many authors, our data give added support to the hypothesis that the transfer of fine-grained sediment from the estuary onto the continental shelf is of considerable importance in effecting trace metal transfer as well.

CONCLUSIONS

Table 4

This investigation has shown that the mean acid leachable Cu, Zn and Pb content of Jeffreys Basin surficial sediments are very similar to that of Great

Table 4			
Percentage of fine-grained sediment Basin sediments.	source that	contributes	to Jeffreys

	Cu (%)	Zn (%)	Pb (%)
Estuarine Source	50	40	30
"Upstream" Source	50	60	70

Bay estuary surficial sediments. High correlations exist between leachable metal and fine-grained sediment percentages implying not only that the environmentally available metal is associated with the fine-grained sediment fraction but that the metal may be transfered from the estuary associated with this fine grained material. Our conclusions concerning trace metal transport from the nearshore environment support the idea that particles dominate the behavior of dissolved species in the aquatic environment (Turekian, 1977) and that estuarine fine-grained sediments act as a "leaky sink" for metals to the oceanic environment.

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