Composition and Reactivity of Some River Sediments from the Mackenzie Valley, N.W.T., Canada

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ABSTRACT / Sediments from the Mackenzie Valley-two suspended and one river bottom-were analyzed for major and minor elements, mineralogy, particle size, and ability to release trace metals when subjected to mild leaching.

Copper and zinc in suspended sediments and cadmium in bottom sediment occurred largely (70 to 84 percent for Cu, 72 to 98 percent for Zn, 75 to 81 percent for Cd) in a form that could not easily be separated from the sediments by 0.1M HC1 and EDTA solutions. Cadmium was present in suspended sediments in low concentrations, and was present totally in sorbed leachable form. Iron, manganese, cobalt and chromium were separable from the particulate phase by mild leaching. It was found that approximately 70 hours were required for an apparent steady state concentration to be attained in such leachings.

Reaction of these sediments with Beaufort Sea water (salinity 22.3 parts per thousand) indicated that both iron and manganese were released from sediments to sea water to a very small degree. Copper, lead, and zinc, however, were absorbed by sediments from sea water.

Introduction

The postulation of a steady-state model for the chemical composition of the world ocean requires that the dissolved and particulate chemical load of rivers flowing to the sea be removed from sea water and added to the ocean sediments or the atmosphere (Mackenzie and Garrels 1966a and b). A partial elucidation of this mechanism requires knowledge of the composition and sorption behavior of bottom and suspended river sediments. Darby (1975), Naidu and others (1970) and Carroll (1970) studied the mineralogy of Beaufort Sea sediments, and MacDougall and Harris (1969) studied the geochemistry of an arctic watershed. The chemical and mineralogical composition of suspended sediments of the world's major rivers is poorly known (Garrels and Mackenzie 1971). Campbell and others (1975) and Brunskill and others (1975, 1973) give some information on trace metals in suspended sediments of the Mackenzie River and a number of its tributaries, as well as rates of transport of elements, mineralogy, and composition of sediments. Angino and others (1974) and Gibbs (1973) give information on some trace metals in suspended sediments of selected streams in Kansas and the Amazon and Yukon rivers respectively.

Sorption and ion-exchange by sediments and minerals have been studied with regard to major cations, the radionuclides strontium and cesium (Mathews 1973; Lorrain and Souchez 1972; Sayre and others 1963; Eden and Briggs 1967), and phosphate and silicate (Edzwald and others 1976; Buckley 1973; Helgeson 1971; Wang 1974). Additional related investigations are by Reid and others (1974, 1975) who studied the leaching of river bank soils in the Mackenzie basin area, Reeder and others (1972) who studied the hydrogeochemistry of surface waters in the same area, and Murthy and Ferrell (1973) who studied the distribution of major cations in estuarine sediments.

Krauskopf (1956) showed that sea water is undersaturated with regard to most trace metal ions and suggested that removal of such ions from solution by sorption to sediments must take place. Gardiner (1974) studied the adsorption and desorption of cadmium on river muds and humic solids. O'Connor and Kester (1975) and O'Connor and Renn (1964) studied the adsorption of copper and cobalt onto illite and other substrates, and zinc on river sediments respectively. Scrudato and Estes (1975) studied the adsorption of lead on clay minerals as a function of pH. Kharkar and others (1968) studied the sorptive properties of some clay minerals and oxides of manganese and iron toward cobalt, silver, selenium and molybdenum; Guy and others (1975) studied the adsorption of copper, cadmium and zinc on similar oxide substrates. Gibbs (1973) has shown that suspended river sediments carry variable proportions of "tightly-bound" and "loosely-bound" trace metals which are released to the solution phase on leaching with selected solvents.

In the present paper we present data on (1) the quantity and composition of suspended and bottom sediments being transported to the Beaufort Sea and the Arctic Ocean by the Mackenzie River, (2) the ion-exchangeable and acid labile fraction of trace elements in these sediments, and (3) the release and uptake of some trace elements by these sediments when suspended in Beaufort Sea water.

Materials and Methods

Water containing suspended sediments used in the leaching experiments was taken from the Redstone River near the confluence with the Mackenzie River (latitude 67° 27', longitude 138° 48') on August 1, 1972, and from the East Channel of the Mackenzie River Delta (latitude 68° 29', longitude 135° 55') on September 21, 1974; bottom sediment was collected also at this location in the East Channel. Suspended sediment concentrations were 1,375 *mg/I* and 110 *mg/l* in the Redstone River and the East Channel respectively at the time of collection. Water for suspended sediments, taken with 20/, polyethylene carboys, was centrifuged (continuous, flowthrough) at 15,000 r.p.m. The sediments were dried at 80° C for one hour, homogenized by grinding very lightly in an agate mortar, and then were stored in plastic vials for further use; the bottom sediment was treated in the same way.

Leaching involved shaking $0.5 - 1g$ of sediment in 125 ml polyethylene bottles on an Eberbach reciprocating shaker for 2, 30, 66, 100 and in one instance 150 hours with 30-60 ml of the following solutions: 0.1 M hydrochloric acid, a saturated solution (0.50 g/l) of ethylenediaminetetraacetic acid (EDTA), 0.1 M ammonium acetate solution, and Beaufort Sea water from a sampling station 12 km east of Pullen Island seaward from the Mackenzie Delta (see Table 4). All leachates were filtered through $0.2 \mu m$ pore-size membranes prior to analysis. The membrane filters were first soaked in the respective leaching solutions for 6 to 8 hours, rinsed by filtering distilled water and then stored in the leaching solution till used. The whole filtering apparatus was rigorously cleaned and rinsed with copious quantities of distilled water before filtering the leachates and blanks. The filtered leaching solutions had the following pH at the end of leaching: HCl-leachate, 1.1- 1.9 (depending on duration of leaching and type of sediment); EDTA-leachate, 2.9 - 3.5; ammonium acetate-leachate, 7.0-7.7; sea water-leachate, 7.8.

Trace metals were determined by flameless atomic absorption (graphite tube furnace) using a Perkin Elmer HGA-70 atomization unit and a 403 spectrophotometer. Leachates other than sea water were analyzed directly by injecting the leachate into the atomization cell after filtration. Metals in sea water-leachates were complexed with ammonium pyrollidine dithiocarbamate (APDC) at pH 4, and extracted repeatedly with carbon tetrachloride. The solvent $(CC1₄)$ was then removed by slow evaporation under partial vacuum al 55° C, the residue was oxidized with concentrated nitric acid, made up to volume, and this aqueous solution was then analyzed. Sediments were digested with a mixture of nitric and hydrofluoric acid at 135°C in a Parr bomb with teflon lining. After addition of boric acid, the metals were determined as described above. Calibration standards made up with the corresponding leaching solutions were used in direct analysis of leachates. Distilled water standard solutions with the same quantity of nitric acid added as was used to decompose the extracted residue were used in the analysis of seawater and sediments. The high-purity acids used in all operations were redistilled in teflon containers. All solid reagents, except ammonium ace. tate (reagent grade used) were purified by recrystallizing the reagent grade brand from distilled water in quartz containers. The water used in all operations excepting sea water was doubly distilled in quartz. Background contamination was relatively constant, and was accounted for by blanks of solutions with. out sediment subjected to the same procedures as the solutions with sediment. The tightly-bound fraction of metal ("crystalline") was calculated from the difference in trace metal concentration in the sediment as a whole, and the blankcorrected concentration in the leachate. The concentration of trace metals in the sample of Beaufort Sea water used in this investigation was higher than normally expected for sea water, but this was analytically advantageous since only the relative concentration-that is, the difference in concentration before and after addition of sediment-was of interest in this investigation.

The major elements in sediments (Si, A1, K, Ca, Fe and Mn) were determined simultaneously with a multichannel ARL X-ray spectrometer (Wilson and others 1965). The method consisted essentially of fusing the sample with lithium tetraborate and lanthanum oxide at 1100°C, grinding the fused bead with

The Mississippi data are from Garrels and Mackenzie (1971, p. 106).

*-means not **measured.**

boric acid, and pressing the mixture into discs that were then analysed. Sodium and magnesium were determined by conventional flame atomic absorption.

Total carbon and nitrogen in sediments were determined with a Carlo Erba model 1100 CHN-analyser, and inorganic carbon was determined by

Table 2 Concentration on a Dry Weight (110°C) Basis of Whole Sample of Heavy Metals in Suspended Sediment from the Redstone and Mackenzie (East Channel, Delta) Rivers and in Bottom Sediment from the Mackenzie (East Channel, Delta) River

	μ g/g							
Sediment	Cd	Co	Cr	Cu	Pb	Zn		
Redstone River Suspended Sediment	0.25	17	-*	29	4.4	17		
Mackenzie River East Channel (Delta, Bottom Sediment)	5.2	11	7.5	23	2.5	112		
Mackenzie River East Channel (Delta, Suspended Sediment)	0.81	14	8.5	42	24	126		

"- = not **determined.**

gas-chromatography according to the method of Stainton (1973). Organic carbon in sediments was calculated by subtracting inorganic carbon from total carbon. Minerals were identified by X-ray diffraction with a Phillips diffractometer model PW 1010-PWI 1352/10, with automatic sample changer and graphite monochromator, using unfiltered Curadiation (40 KV, 20 MA). Particle size distribution was determined with a Coulter Counter, model TA II, equipped with plotter, using standard-sized particles for calibration. The method is described by Walker, Woodyer and Hutka (1974).

Results

The elemental composition of a sample of suspended sediment from the East Channel of the Mackenzie River Delta, the Redstone River, and of bottom sediment from the East Channel of the Mackenzie River Delta is given in Tables 1 and 2. The concentration of silicon, aluminium and iron in these sedi-

Table 3 Mineralogy of River Sediments of the Mackenzie Valley

The most abundant mineral is at the top, and the least abundant at the bottom.

ments brackets the concentration of these elements in most other sediments from sampled rivers in the Mackenzie Valley (Campbell and others, 1975), and the concentrations in these and other sediments are similar for other elements. The mineralogy of the sediment samples is given in a semi-quantitative manner in Table 3. Mineralogically these are simi-

lar to other sediments from some rivers in the Mackenzie Valley (Brunskill and others 1973; Campbell and others 1975). The particle size distribution in these sediments is given in Fig. 1. In all three sediments, particle size covered the range of clay, silt, sand, with a small preponderance of particles with a size of 2 to 6 μ m in suspended sediments, and 8

Figure 2. Dependence of iron and manganese concentration in EDTA (saturated) leaching solution on leaching time, and type of sediment: Redstone and Mackenzie Delta suspended sediment, and bottom sediment from a Mackenzie Delta Channel.

to 40 μ m in bottom sediment. The percent fraction of particles with size smaller than 0.6 μ m was always less than 5 percent.

The sediments were leached with the various solutions for 2 to 150 hours. In Figs. 2- 8, the concentrations of metals in the leachate (minus the blank concentration) are shown as a function of leaching time. The concentration of metal in the leachate is necessarily zero at time zero, but this is not shown in these figures because of the condensed time scale used. Tables 5, 6, and 7 give the fraction of each metal leached by the three solvents. Table 8 gives the results of leaching Mackenzie sediments with Beaufort Sea water of the composition shown in Table 4.

Figure 1. Particle size distribution based on Coulter Counter (TAll) analysis of suspended sediments from the Redstone River, the East Channel of the Mackenzie Delta, and bottom sediment from the East Channel of the Mackenzie Delta.

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Figure 3. Dependence of iron and manganese concentration in 0.1 M hydrochloric acid leaching solution on leaching time and type of sediment: Redstone River suspended sediment and Mackenzie Delta Channel bottom sediment,

Figure 4. Dependence of cadmium, cobalt, copper, lead and zinc concentration in EDTA (saturated) leaching solution on leaching time: Mackenzie Delta Channel bottom sediment.

Figure 5. Dependence of cadmium, cobalt, copper, lead and zinc concentration in EDTA (saturated) leaching solution on leaching time: Redstone River suspended sediment.

Figure 6. Dependence of cadmium, cobalt, copper, chromium and lead concentration in 0.1 M hydrochloric acid leaching solution on leaching time: Mackenzie Delta Channel bottom sediment.

Discussion

The different slopes of the concentration-time curves and the different maximum quantities of a metal leached with the same leaching agent indicate that the different sediments responded differently to the same leaching solution. For example, less iron was leached at a slower rate from Redstone River suspended sediment than from Mackenzie River suspended or bottom sediment (Figs 2 and 3). Two hours of leaching at room temperature was too short to attain a relatively constant concentration of metal in the leachate with any of the leaching agents used. Additional quantities of metal were leached after 2 hours (Tables 5 and 6), but after 70 hours the maximum concentration was apparently attained for copper, cadmium and zinc.

Figure 7. Dependence of cadmium, cobalt, copper, chromium and lead concentration in 0.1 M hydrochloric acid leaching solution on leaching time: Redstone River **suspended** sediment.

Figure 8. Dependence of cadmium, cobalt, copper, lead and zinc concentration in EDTA (saturated) leaching solution on leaching time: Mackenzie Delta Channel suspended sediment.

The leaching of lead appeared to proceed differently from that of copper, zinc and cadmium; however, the scatter in the lead data is too great to draw any conclusions. Similar difficulties with lead were encountered by Catanzaro (1975, 1976). Concentration of all metals increased initially in leaching solutions other than sea water but iron, cobalt, chromium and to a lesser extent manganese continued to increase with time, 2 and did not attain a constant concentration within 100 hours. In one particular experiement, the EDTA-leaching time was extended to 150 hours, and the concentration of iron, manganese, cobalt, and chromium in the leachate was again higher than in the leachate of 100 hours (Figs. 2, 4, and Table 5). This can best be explained by a mechanism of actual solid phase dissolution rather than desorption alone. The minerals that are probably most prone to dissolution under these conditions are calcite, dolomite, amorphous iron hydroxide, and possibly other iron minerals. Because iron, manganese and probably cobalt and chromium can be incorporated in small amounts in the crystal structure of dolomite and to some extent calcite (Barber 1974), these metals could therefore be released simultaneously with dissolution of these minerals. Taht calcite and dolomite were actually being dissolution of these minerals. That calcite and dolomite were actually being dissolved calcium and magnesium in leachate which increased in concentration with leaching time. Leaching with 1 M ammonium acetate for 100 hours (Table 7) released from these sediments one tenth of the cobalt, and much less of iron and chromium compared to that released by 0.1 M HC1 or EDTA leachates during the same time (Tables 5 and 6).

The identification of phases releasing the iron and the manganese was not attempted. Iron was shown (by elemental analysis) to be present in these sediments to the extent of 4 to 6 percent (by weight as $Fe₂O₃$, Table 1); X-ray diffrac-

Table 4 Composition of Beaufort Sea water (from 12 km E. of Pullen Island) Used in Leaching Experiments

*After storage of the sample in the laboratory. For pH values of Beaufort Sea water see Brunskill and others 1975.

Sulfate concentration was calculated using a concentra**tion-chlorinity** ratio of 0:1414 (Home 1969) whereas all other concentrations were measured using **"Standard** Seawater" (Denmark 1970) as a calibration standard.

tion, however, did not yield a diffractogram belonging to any specific iron mineral. The iron could be present in the sediments as amorphous iron hydroxide,

Table 5 Trace Metals Leached from Redstone River Suspended Sediment: (1) Mackenzie Delta Channel Bottom Sediment (2) and Mackenzie Delta Channel Suspended Sediment (3) into a Saturated Solution of EDTA (0.5 g/ℓ) for Various Leaching Times and a Final pH of 2.9- 3.5 in the Leachate

***-total metal content was not determined.**

"-total metal content **was not** determined.

as a guest constituent in a crystalline host mineral (dolomite, calcite, feldspar and some clay minerals) without much altering the structure of the host mineral, and partly also as a crystalline iron mineral not detected by X-ray diffraction since the detection limit by this method is only 2 to 3 percent by weight of crystalline material. Some investigators have postulated that iron and manganese are present in suspended river sediments mainly in the form of a "precipitated coating" on other mineral particles (Whitney 1975; Gibbs 1973; Hem 1970).

The metals Cu, Zn, and Cd, showed

distinctly different leaching behaviour from Fe and Mn, in that a plateau was obtained in their concentration-time curves (Figs. 4-7). This leaching behavior is more characteristic of a sorption-desorption mechanism. The time required to attain a steady state concentration in the leachate, as indicated by the onset of the plateau, was approximately 70 hours for copper and zinc, and less for cadmium. Similar equilibrium times have been reported for other systems: for example, 72 hours for adsorption of hafnium species on glass powder (Stryker and Matijevic 1968), several hours for a number of metal cations on

Table 7 Trace Metals Leached from Mackenzie Delta Channel Bottom Sediment with 1 M Ammonium Acetate for Various Leaching Times and a Final pH of 7.0-7.7 in the Leachate

Hours Leached	% of metal in sediment leached into solution									
	Cd	Co	Сr	Cu	Fe	Mn	Pb	Ζn		
2	9.0	1.0	\simeq Bik	10	< 0.001	26	\simeq Blk	$=$ Blk		
30	13	2.8	\simeq Blk	9.0	< 0.001	77	$=$ Bik	\simeq Blk		
66	14	1.8	≃Blk	6.0	< 0.001	53	\simeq Bik	0.1		
100	25	4.5	\simeq Blk	2.0	< 0.001	91	\simeq Bik	0.7		

*= Blk = Concentration in leachate not significantly different from concentration in blank.

manganese oxide (Murray and others 1968), 3 to 12 hours for cobalt on silica (Healey and others 1968). Considerably more than 12 hours apparently were required to attain a steady concentration of zinc in solution when it was desorbed from "river mud" and humic solid (Gardiner 1974). By introducing an enriched 65Cu spike and using isotope dilution, Catanzaro (1976) determined an equilibration time of 20 days for Cu sorption-desorption on suspended river sediment in "highly acidified" Hudson River water. The process of adsorption itself is known to be rapid (see as an example Vermeulen 1958), and the relatively long equilibration times undoubtedly reflect the rate at which mass transfer can proceed by diffusion in pores and channels of the solid particles. Equilibration time will naturally vary from substrate to substrate depending on its surface area and physical properties such as particle size, porosity, and composition (Lagache 1976; O'Connor and Kester 1975). The shapes of some of the curves in Figs. 1-7, are similar to those obtained by Busenberg and Clemency (1976) for the release of major cations and silicate from feldspars. This suggests that the kinetics for the release of these trace metals (Cd, Cu, Zn) are similar to those for the release of major ions.

The Redstone River and Mackenzie River suspended sediments contain very little, cadmium (Table 2). All of this appears to be sorbed, because cadmium can be removed by mild leaching agents. (Table 5). This implies that the cadmium in these suspended sediments is not incorporated in the lattice structure of the minerals, whereas 75 to 81 percent of the cadmium in the bottom sediment sample appeared to be a structural part of mineral latices, and was not all removed by the leaching agents. Similarly, 70 to 84 percent of the copper, and 72 to 98 percent of the zinc was structurally incorporated in minerals resistant to dissolution, and was not easily removed by these leaching agents in any of the three sediments. In comparison, suspended sediments from the Amazon and Yukon

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Rivers (Gibbs 1973), contain 80 percent and 90 percent copper, respectively, in this form (crystalline) when recalculated to the basis of copper content in sediments alone.

The leaching agents employed here, aside from sea water, were much more acidic and had far greater complexing power for heavy metals than the natural aquatic environment. Dissolved organic carbon varied from 3.5 to 16 *mg/l* (Brunskill, unpublished) in Mackenzie East Channel waters, and pH varied between 5.9 and 9.0 over the season in the major rivers of the lower Mackenzie Valley. The action of these leaching agents on sediments must therefore be considered drastic when compared with that of natural aquatic environments.

The effects of changing ionic strength (0.0013-0.45) were also determined directly by leaching Mackenzie sediments with Beaufort Sea water. No significant difference in concentration of Cd, Co, Cr, and in the case of suspended sediment also Pb, and Zn, was detected between sea water blanks and sea water leachates after various times of leaching

(Table 8). These metals were not measurably released from or sorbed to sediments in sea Water. Iron and manganese in the sediment phase were released to sea water to a small but measurable degree (see Table). Copper, on the other hand, was consistently lower in concentration in the leachates (48 to 68 percent) than in the blanks. This indicated that there was a net uptake of copper from sea water by both Redstone River and Mackenzie River Delta sediments. Zinc and lead were scavenged from sea water by Mackenzie River Delta sediment, but not by Redstone River sediment. After two hours of sea water leaching, the quantity of any metal excepting manganese sorbed or released by sediments did not vary in any systematic way with increasing leaching time. However, the fraction of manganese released to sea water increased with increasing leaching time (Table 8).

O'Connor and Kester (1975) have shown that seawater-copper is sorbed to illite in the pH-range of natural sea water. They also showed that desorption of trace metals from sediments occurs first

Table 8 Trace Metals Scavenged from Beaufort Sea Water by Sediments or Released to Beaufort Sea Water by Sediments for Different Leaching Times at pH, 7.8, using Redstone River Suspended Sediment (1), and Mackenzie River Delta Bottom Sediment (2)

"At a sediment concentration of 17 g/ℓ .

"" =BIk = No release or uptake of metal.

to some extent when the salinity of fresh water increases by 10% by mixing with sea water, but that in the pH-range of natural waters, this fraction of metal desorbed is relatively small. Our sample of Beaufort Sea water had an initial pH of 7.9 and a salinity of 22.3% . Over the 1971-74 seasons, the pH varied from 7.4 to 8.3 in the vicinity of our sampling station in the Beaufort Sea; salinity varied from 1 to 25‰ (Campbell and others 1975; Brunskill and others 1973). Our work shows that a small fraction of the total iron and manganese was released from river sediments to sea water, but the potentially exchangeable fraction of the metals Cd, Co, Cr, Cu, Pb, and Zn was not released. Some of these metals (Cu, Pb, Zn) were sorbed to sediment from sea water. Our results also suggest that acid, EDTA and $NH₄ - exchange$ able metals on Mackenzie River sediments-do not contribute greatly to the supply of dissolved trace metals to the Beaufort Sea.

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