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TRACE METALS IN FLUVIAL SEDIMENTS OF THE MADEIRA RIVER WATERSHED, AMAZON, BRAZIL*

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ABSTRACT

Sediment samples from 10 rivers of the Madeira River watershed, Amazon, were analyzed for major and trace element composition. Differences among river classes (white, clear and black water) were detected, in particular regarding the organic matter content, the concentration of bioelements, and the trace metals Fe, Mn, Cu and Zn. This shows that the classical differentiation of Amazon rivers based on water chemistry is also confirmed by sediments. Sequential extraction of trace metals showed that the lithogeneous and reducible fractions of sediments are the principal substrates of trace metal transport in these fluvial systems.

INTRODUCTION

Amazonian waters have been the subject of many hydrochemical studies, which resulted in the classical classification of white, black and clear water rivers. The first study was carried out by Sioli (1950), followed by others (Junk and Furch, 1980; Furch et al., 1982).

White water rivers are rich in suspended matter, have neutral pH and present elemental concentrations similar to the mean of world rivers. Both the Amazon and the Madeira are white water rivers originating in the Andes, where steep topography exposes sedimentary rocks. Black and clear water rivers are formed in the Amazon Basin itself, where heavily weathered soils are dominant and rock outcrops are virtually absent. They have acidic pH, very low content of suspended solids and low concentration of dissolved elements (Sioli, 1950; Junk and Furch, 1980, 1985).

Although the water chemistry of Amazonian rivers has been fairly well documented (Stallard and Edmond, 1981, 1983), few studies have focussed on fluvial sediments. Most scientists have devoted their studies to suspended sediments composition rather than bottom sediments (Gibbs, 1967, 1973; Schorin et al., 1985; Stallard, 1985).

The present paper reports the distribution and geochemical partitioning of

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trace elements in bottom sediments of white, clear and black water rivers of the Madeira River watershed, to assess the validity of the classical river classification when applied to sediments, and the geochemical substrates responsible for trace element transport in river bottom sediments.

MATERIAL AND METHODS

Sediment samples were collected from 10 rivers of the Madeira River watershed. Sampling points were located preferentially close to the mouths of the rivers, therefore integrating the major biogeochemical processes occurring in each sub-basin (Fig. 1).

Major water physico-chemical parameters (pH, temperature and electrical conductivity) were determined in the field with portable electrodes. In the laboratory, samples were oven-dried (80°C to constant weight), sieved (< 63 μm) and analyzed for chemical composition (in triplicate) by atomic absorption

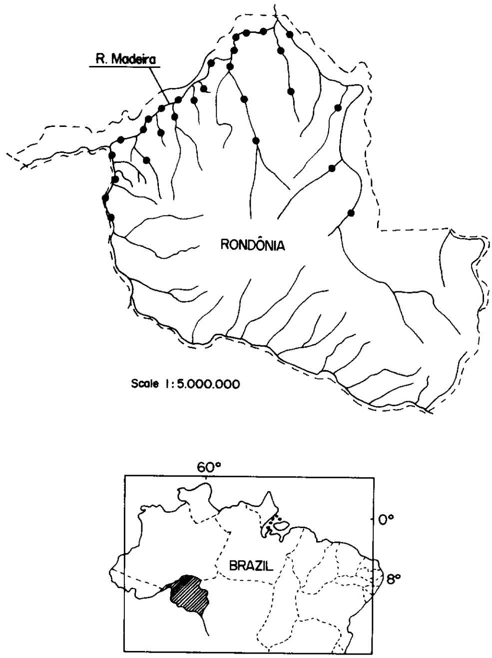

Fig. 1. Map of study area showing sampling locations.

spectrophotometry (AAS) with background correction, after acidic digestion ($HCl + HNO_3$ + conc. HF) in Teflon bombs. Mercury was analyzed by cold vapor-hydride generation AAS according to Pfeiffer et al. (1989).

Sub-samples of sieved sediments from white, clear and black water rivers were used for sequential extraction analyses of trace elements. For comparison, we referred to the scheme that Gibbs (1973) used to analyze Amazon River suspended sediments.

Organic matter content was determined in the bulk sample gravimetrically, after combustion (450°C, 16 h).

Typology of the rivers sampled followed Sioli (1950).

RESULTS AND DISCUSSION

Table 1 shows water pH and electrical conductivity and organic matter content of sediments of the three different kinds of rivers. The data clearly show the hydrochemical differences among them. Sediment organic matter increased from white water (3.9%) to clear water (5.2%) to black water (9.0%), but with high variability in the latter two.

Sediment chemical composition was also different among the white, black and clear water rivers, although certain elements [e.g. P (Table 2); Cr, Pb, Co

TABLE 1

Major physico-chemical parameters of rivers in the Madeira River watershed, Brazil

	White water rivers (n = 17)	Clear water rivers (n = 5)	Black water rivers (n = 8)
pH	6.7 ± 0.3	5.7 ± 0.6	5.7 ± 0.7
Conductivity ($\mu S\,cm^{-1}$)	99 ± 14	13 ± 7	5.8 ± 0.7
Sediment organic matter content (%)	3.9 ± 1.2	5.2 ± 2.8	9.0 ± 4.4

TABLE 2

Major macro-element concentrations in sediments (fraction < 63 μm) of rivers in the Madeira River watershed, Brazil

	White water rivers (n = 17)	Clear water rivers (n = 5)	Black water rivers (n = 8)
P (ppm)	433 ± 56	390 ± 91	376 ± 75
Fe (%)	4.94 ± 0.81	6.64 ± 2.15	2.72 ± 0.99
Mn (ppm)	409 ± 76	1092 ± 938	293 ± 97
Na (%)	0.86 ± 0.09	0.43 ± 0.32	0.58 ± 0.28
Ca (ppm)	160 ± 30	29.7 ± 28.4	30.2 ± 25.4
K (%)	1.62 ± 0.30	1.01 ± 0.59	0.95 ± 0.36
Mg (%)	0.41 ± 0.07	0.23 ± 0.27	0.19 ± 0.19

TABLE 3

Trace element concentrations ($\mu g\, g^{-1}$ dry wt) in sediments (fraction < 63 μm) of rivers in the Madeira River watershed, Brazil

	White water rivers (n = 17)	Clear water rivers (n = 5)	Black water rivers (n = 8)
Cr	52 ± 9.8	33 ± 6	46 ± 15
Pb	24 ± 7.1	43 ± 23	39 ± 20
Co	29 ± 5.5	28 ± 6	22 ± 5
Ni	3.8 ± 0.8	0.9 ± 1.4	3.2 ± 1.8
Cu	27 ± 24	12.4 ± 10.1	276 ± 250
Zn	101 ± 30	194 ± 110	223 ± 168
Hg	0.33 ± 0.81	0.13 ± 0.08	0.49 ± 0.69

and Ni (Table 3)] were fairly constant among them. The most striking differences occurred for Fe and Mn concentrations, the bioelements Na, K, Ca and Mg, and the trace elements Cu, Zn and Hg. Iron and Mn were highest in clear water rivers and lowest in black water rivers. In the clear water rivers, the occurrence of Fe–Mn hydroxide colloidal layers on the sediment surface, and along small drainages of forest soils, was common. This phenomenon has been observed in other forest rivers in the Amazon Basin (Schorin et al., 1985). The higher oxidizing capacity of clear water rivers can readily precipitate soluble Fe^{2+} and Mn^{2+} reaching these rivers from adjacent soil solution. On the other hand, black water rivers with high sediment organic matter content could remobilize both Fe and Mn back into the water column. Junk and Furch (1980) have also attributed higher soluble Fe and Mn concentrations in black water rivers to the high organic matter content of these environments.

All bioelements, particularly Ca, had lower concentrations in clear and black water rivers than in white water rivers. This phenomenon has already been observed by Furch et al. (1982), and is probably related to the strong control on the cycling of such elements by the forest itself (Jordan et al., 1979). Interesting to note are the high concentrations of Fe and Mn, when compared with bioelements such as P and Ca. The over-abundance of these elements reflects the heavily weathered conditions of the Amazon Basin soils, leaving behind less mobile elements such as Al, Fe and Mn (Stallard, 1985).

The trace elements Zn, Cu and Hg had extremely variable concentrations, both among rivers of differing classes and among rivers of the same class. At present the mining activities along the Madeira River watershed presumably contribute large amounts of trace elements (Pfeiffer and Lacerda, 1988; Lacerda et al., 1989; Pfeiffer et al., 1989). In areas with heavy mining activities, concentrations as high as 3000 ppm Cu and 1000 ppm Zn have been reported (de Paula, 1989).

Geochemical partitioning of trace elements is shown in Fig. 2. The results confirm those reported by Gibbs (1973) for suspended sediments in the Amazon River; the residual, lithogeneous fraction, and the reducible, Fe–Mn oxy-

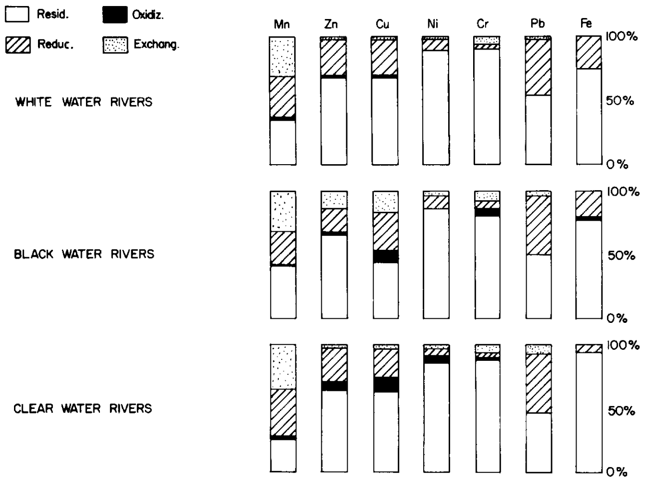

Fig. 2. Geochemical partitioning of trace elements in sediments of the Madeira River watershed.

hydroxide, are the dominant geochemical substrates for all metals, except Mn, in all river classes. Forstner and Salomons (1980) have also found these two geochemical fractions to be the main substrates for trace metals in bottom sediments of the Orinoco and Magdalena Rivers in the northern part of South America.

However, differences among the mobile fractions occurred between white water and clear and black water rivers. The oxidizable and exchangeable fractions become important geochemical substrates for certain elements, in particular Cu and Zn, in clear and black water rivers.

Since clear and, particularly, black water rivers are richer in sediment organic matter content, and the metals in these rivers are derived mostly from the adjacent forest soil solution, more mobile elements such as Zn and Cu could adsorb to organic substrates on entering the rivers.

CONCLUSION

In conclusion, our results confirm that the classical classification of Amazonian rivers based on hydrochemical parameters can also be applied to bottom sediments, for most of the elements analyzed, but could not be applied to phosphorus, Cr, Pb, Co and Ni. The great variability of Cu, Zn and in particular Hg, seems to reflect the present intense mining activity along the watershed. Further studies on this watershed are in progress because of the region's ecological importance. Finally, the geochemical association of trace metals in bottom sediments found in this study confirms that the lithogeneous and reducible (oxy-hydroxides of Fe and Mn) sedimentary phases are the major geochemical supports of trace elements. Also, exchangeable and oxidizable phases can be important, particularly in organic-rich black water rivers.

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