

Trace elements distribution in the Andean sub-basins of the Madeira river : role of the weathering processes in the freshwaters geochemistry

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Abstract. The distribution of trace elements was investigated in surface waters in two upper Amazonian basins. Three main factors of the geochemical characterisation of the rivers explained mainly by weathering and dilution processes, are : substrate lithology, mining activities, and organic matter content. The dissolved elements reflects the lithological differences between the Mamore and Beni basins. Andean tributaries of the Mamore R. are characterised by high concentrations of Mn, Sr, Mo, Ba and U while high concentrations of As, Zn, Cd and Cs characterise tributaries of the Beni R. Dissolved Sr, Ba, Mo, Rb, U correlate with major ions and appear to be predominantly derived from soluble rocks. Influence of the shale erosion explain the high concentrations of V, Zn, Cu and Pb measured in Beni tributaries. The high values of Co, Ni and Mn reflects the Palaeozoic detritical series from the drainage basins of the Tipuani and Challana rivers. The higher content of Mn in the Ichilo river may reflects the predominance of carbonate rocks. Regarding to the anthropogenic influence, the high Zn, As, and Cd concentrations measured in the Taquesi river can be explained by important mining activities.

INTRODUCTION

Most published trace element budgets and oceanic residence time (Martin and Meybeck, 1979) rely on few possibly unrepresentative data while the widespread use of clean techniques has in many cases substantially decreased estimates of trace element concentrations, especially those of the transition elements, in rivers (Shiller and Boyle, 1985; Albers et al., 1990). According to Zhang and Huang (1993), weathering and erosion exert a major control on dissolved trace metal concentrations in the Huanghe river. Dupre et al (1996) conclude that U, Rb, Ba and Sr in the Congo river are controlled by the dissolution of the main rock types while the abundance of Rare Earth Elements or transition elements are controlled by the presence of colloids. The partitioning of elements between the dissolved and solid phases may also influence trace element concentrations in large river systems, but few recent studies (Dupré et al, 1996) have focused on this aspect. In order to improve the knowledge of processes which govern trace element distributions in rivers and to better constrain budgets, it is necessary to produce more data sets on relatively small drainage basins encompassing the diversity range of lithology, climate and relief. This paper focuses on trace elements (V, Mn, Co, Ni, Cu, Zn, As, Rb, Sr, Mo, Cd, Sb, Cs, Ba, Pb, and U) in both dissolved and suspended matter for the Mamore and Beni watersheds in the Bolivian part of the Amazon basin. Data are used to investigate trace element behaviour in a tectonically active area within the humid tropics. Because they represent an important part of the largest world river basin and also because it is a relatively pristine region where the contribution of the atmospheric marine source is limited (Stallard and Edmond, 1981), the Mamore and Beni basins are ideally suited to assess the different factors that control trace element transport by rivers (Elbaz et al., 1999).

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DESCRIPTION OF THE STUDY AREA

Bolivian Amazonian basin with the Mamore and Beni sub-basins (Fig.1) represents the Andean headwaters of the Madeira River, one of the 4 most important tributaries of the Amazon River. This region provides most of the yield of the Amazon river for both dissolved loads and sediments (Roche and Fernandez, 1988; Guyot, 1993). These highly turbid rivers flowing out from the Andes correspond to white water rivers. The Bolivian part of the Madeira drainage basin reaches $0,9 \cdot 10^6 \text{ km}^2$, with 25% in Andes, 27% on Brazilian shield and 48% in plain. Andean tributaries of the Beni and Mamore river drain both semi-arid areas of high altitude, from 6400 m, and areas of tropical humid forest of the piedmont. Andean rivers export an average of $500 \cdot 10^6 \text{ t}$ of sediments by year, and the half of this burdens is transported by the Beni River in Rurrenabaque (Guyot 1993). The Andean tributaries of the Beni river drain intrusive granitic rocks covered by thick sedimentary deposits from the Ordovician dominated by grey-green to dark shales and sandstone with ages ranging from the lower Palaeozoic to Tertiary. Devonian sequences with marine sediments are well represented in the drainage basins of the Ichilo, Chimore, Yapacani and Grande rivers. Carbonate rocks and evaporite formations from abundant outcrops in the Mamore sub-basin, especially in the Grande river catchment whereas intrusive granites, associated with sulfide mineralization exist in the Beni sub-basin.

MATERIALS AND METHODS

Sampling Procedures

Water samples were collected in April 1994 at the end of the rainy period. Samples for trace elements were collected in acid-clean high density polyethylene bottles (washed successively with aqua regia, hydrochloric acid, nitric acid, and finally filled with sub-boiled 1% nitric acid in Milli-Q water until sampling). The last conditioning work was done under a laminar air flow (class-100, US norms). Dissolved and suspended phases were separated immediately after collection by vacuum filtration through pre-weighed and acid washed $0.22 \mu\text{m}$ Teflon filters (Millipore). The filtrate was transferred to acid-cleaned low density polyethylene Nalgene bottles and acidified to pH2 using sub-boiled nitric acid 12N until analysis. Filtration blanks were run on the field. Contamination was generally negligible except for Zn and Cd which are more subjected to contamination than other traces.

Samples Treatments

For trace element determination, the SPM on the membranes was dried at 60°C for 24 hours. A $\text{HNO}_3\text{-HF-HClO}_4$ digestion was carried out in sealed Teflon (FEP) beakers. The membranes were removed and the solution was evaporated to near dryness. The residue was dissolved in sub-boiling distilled HNO_3 and then diluted with sub-boiled Milli-Q water prior to analysis. HF and HClO_4 were Merck Suprapur grade acids. Digestions were performed under a laminar air flow clean bench. Blanks were negligible when compared to sample concentrations.

Analytical Determination

Analysis of digested SPM and water samples were performed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). Concentrations were established by calibrating peak intensity acquired in peak jump mode with standards solutions. For dissolved samples Indium was used as an internal standard to correct for changes in peak intensities due to instrumental drift. However, ICP-MS may produce spectral interferences and thus analytical errors according to elements and matrix composition (Shao and Horlick, 1991). This problem is systematically evaluated for each analytical sequence. The trace element data presented in this paper are

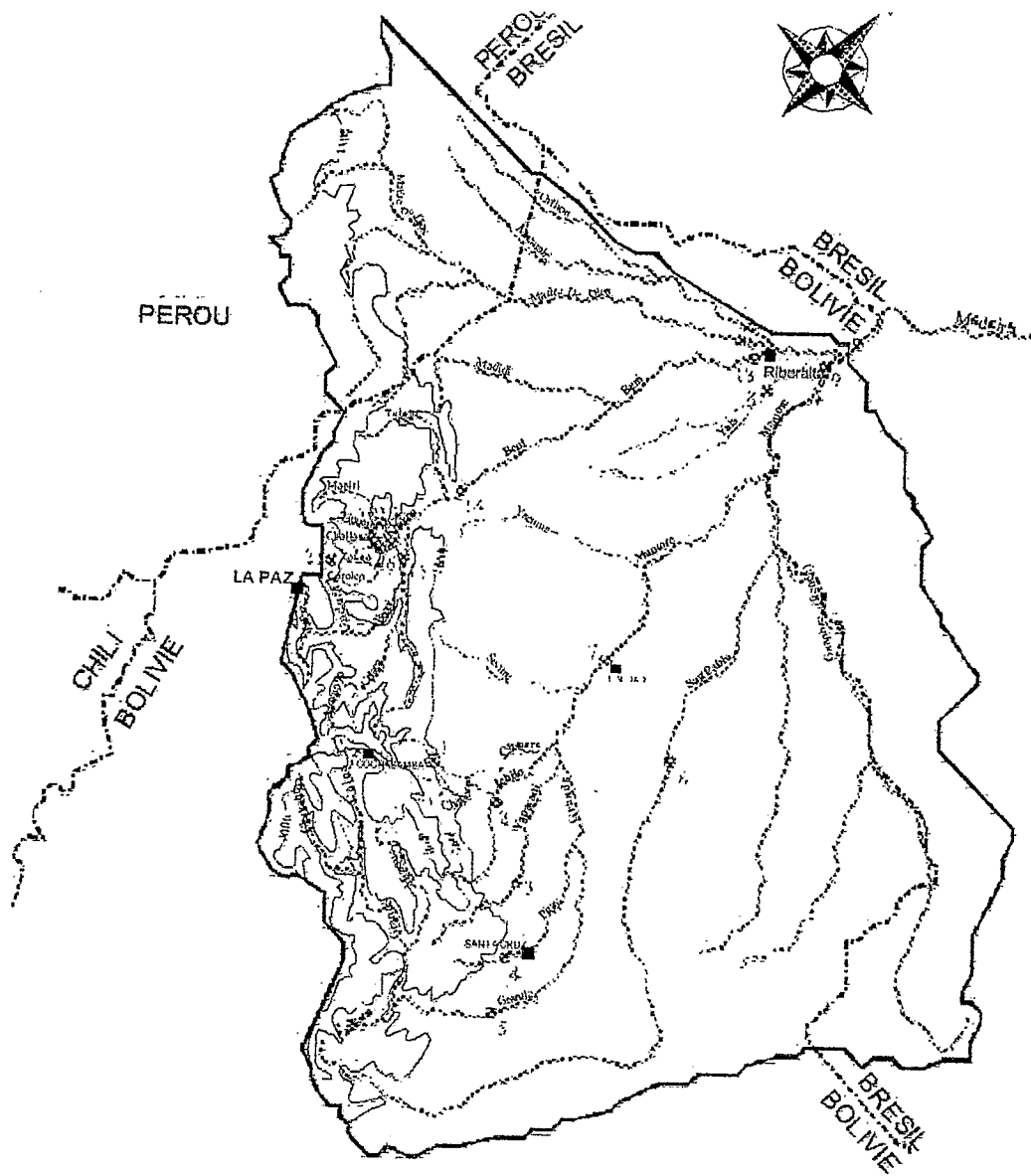
devoid of interferences. The exceptions are Ni and Cu. Calcium oxide strongly affect ^{60}Ni and ^{65}Cu , rendering useless these two isotopes. The determinations have been carried out using ^{62}Ni and ^{63}Cu . The accuracy and the precision of the analytical methods were tested using SLRS-2 (Riverine Water Reference Material for Trace metals certified by the National Research Council of Canada) as standard for the dissolved load and the GBW07310-GSD certified by the National Research Center for Reference Materials of Beijing, P.R. China, for the sediments. A generally good agreement is observed between our data and the certified values.

RESULTS AND DISCUSSION

Three main factors of the geochemical characterisation of the studied rivers explained mainly by weathering and dilution processes, are: i) substrate lithology, ii) mining activities, and iii) organic matter content. Using statistical methods (PCA), the combined use of this geochemical data with geological information on each watershed demonstrates the fundamental role of the weathering processes on the trace chemistry of the Andean rivers.

Dissolved trace elements

The geochemistry of dissolved elements reflects the lithological differences between the Mamore and Beni basins. Andean tributaries of the Mamore R. are characterised by high concentrations of Mn (55 to 4290 nM), Sr (894 to 1943 nM), Mo (2.5 to 20.3 nM), Ba (99 to 399 nM) and U (0.3 to 3.9 nM) while high concentrations of As (1.9 to 310.6 nM), Zn (3.8 to 218.5 nM), Cd (0.03 to 1.66 nM) and Cs (0.06 to 2.57 nM) characterise Andean tributaries of the Beni R with maximum values measured in the Taquesi R. (Figure 2). Compared to the already available data from the Amazon basin (Furch, 1984; Gibbs, 1977; Konhauser et al, 1994) Cd and Zn concentrations are significantly higher probably as a result of sulfide mineralization. The range of U data (0.019 to 7.548 nM) is larger than that measured by Palmer and Edmond (1993) in the same drainage basin (0.010 and 1.06 nM). This discrepancy is the result of the high values observed in the Grande river which had not been investigated by these authors. Otherwise most trace elements are present with concentrations in the range established as normal for other large rivers. Dissolved Sr, Ba, Mo, Rb, U and to a lesser extend Zn and Cd correlate with major ions and appear to be predominantly derived from soluble rocks (carbonates, evaporates or sulphides essentially contained in shales). Influence of the shale erosion from Silurian and Devonian series explain the high concentrations of V, Zn, Cu and Pb measured in Beni tributaries. Additionally, the high values of Co, Ni and Mn reflects the Palaeozoic detrital series from the drainage basins of the Tipuani and Challana rivers. Uranium is strongly correlated with alkalinity (Figure 3), excepted in the Tipuani, Challana and Taquesi rivers in agreement with U inorganic speciation which is dominated by carbonate-complexes. The exceptions correspond to rivers where pyrite drainage is likely occurring and which have also Zn, Cd and Cu anomalies. The higher content of Mn in the Ichilo river may reflect the predominance of carbonate rocks in this Mamore sub-basin. Regarding to the anthropogenic influence, the high Zn, As, and Cd concentrations measured in the Taquesi river can be explained by important mining activities. High values of V measured at the end of the dry season in plain rivers ('black waters') can be correlated with the decreasing of the phytoplankton biomass.



Water sampling points (April, 1994)

IRD (ex ORSTOM) Bolivia

Figure 1. Sampling points in the Bolivian Amazonian basin.

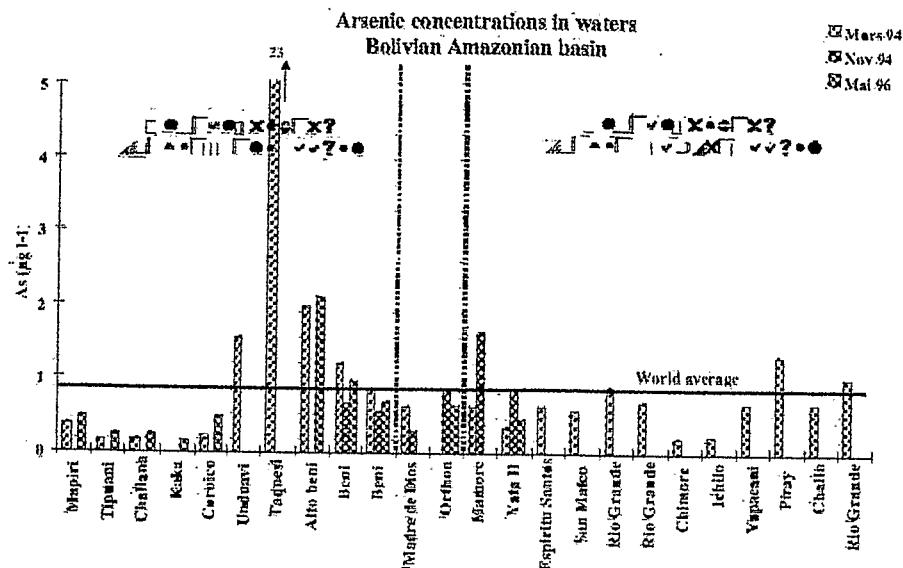


Figure 2. Arsenic concentrations measured in Andean tributaries of the Madeira river, the Beni and Mamore basins.

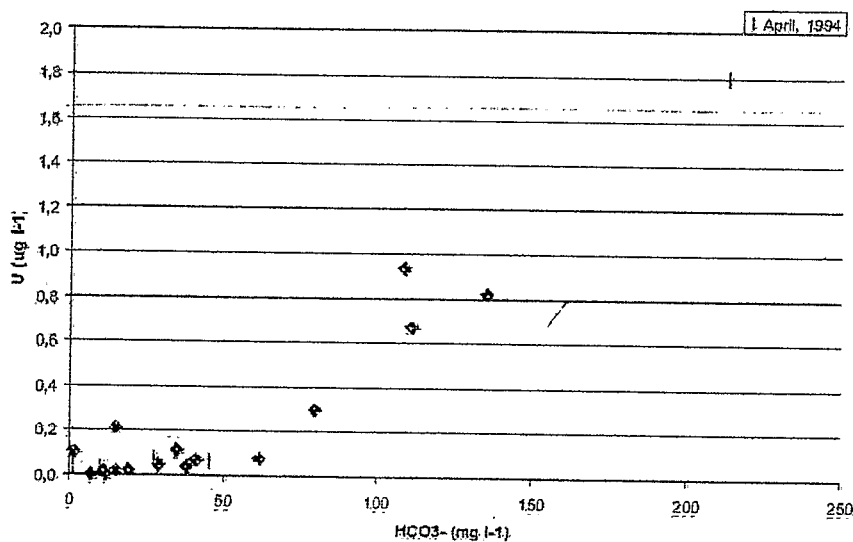


Figure 3. Distribution of U with alkalinity in Andean tributaries of the Madeira river.

Suspended Particulate Material (SPM)

Detailed evaluation of the mineralogy and major element chemistry of SPM have been already undertaken (Guyot, 1993). SPM is made up of clays (57 to 76%) and quartz (15 to 33%) with subordinate amounts of plagioclase and K-feldspar. Illite (53%), kaolinite (20%), chlorite (18%) and smectite (9%) are the main clay minerals in the Madeira basin. No obvious difference has

been detected between the Beni and Mamore sub-basins. The major element chemistry of SPM is dominated by Si, Al and K which represent more than 95% of the total amount. Furthermore the solid load is enriched in K over Na and Mg over Ca in agreement with the abundance of clay minerals. Otherwise the negative correlation between Si and Al indicates that the mineral composition of SPM is dominated by varying proportion of quartz and clay minerals. Although highly variable, the trace element concentrations do not show any relationship with the location of the samples and no significant difference is observed between the two basins. The trace element concentrations in SPM are similar to those of varzea sediments and soils (Konhauser et al 1994) except that the concentrations of Sr and to a lesser extent Ba are relatively low. The fractionation of trace elements in SPM has been attributed to the sorting of feldspars during transport in water, and to the mixing between clay minerals and quartz. These minerals, refractory to weathering and introduced in water rivers by mechanical erosion, have not contributed to the dissolved load and the contribution of silicate phases remains rather small.

CONCLUSION

Trace elements in the Bolivian Amazon drainage basin, Mamore and Beni sub-basins, can be divided into two groups according to their relationships with major elements : those which are correlated with major ions (Mo, Rb, Ba, U and to a lesser extent Zn and Cd) are controlled by their abundance in the most weatherable lithologies (carbonate rocks, evaporites and sulfides largely contained in shales) while silicate rocks have only a limited influence; those which are not correlated with major ions may be explained by their speciation (Mn, Ni, Cu). The weatherable rocks provide the major inorganic ligands (HCO_3^- , SO_4^{2-} , OH^- ..) which complex the reactive metals and increase their solubilities. This process is illustrated by the higher solubility of Ni in alkaline waters due to the formation of carbonato- or hydroxo-complexes. Surface groups of particulate material may act as ligands and adsorb metals which are in cationic form. This process is observed for Ni and Mn in the waters where they mainly exist as Mn^{2+} and Ni^{2+} . In addition to lithology, vegetation which produces organic material could control Cu solubility. The very high concentrations of Zn, As and Cd measured in the Taquesi R. reflects an anthropogenic influence on its geochemistry. The fractionation of trace elements in the solid load results mainly from a binary mixing between quartz and clay minerals. These minerals which are amongst the most resistant to chemical weathering, have been introduced in river waters by physical erosion.

Acknowledgments. In 1994, researchers from IRD (ex-ORSTOM), the French Scientific Research Institute for Development, in cooperation with Brazilian and Bolivian universities, initiated a global study of the hydrogeochemistry of the Amazonian basin (HiBAM Program). This study was financed by the PEGI-GBF Amazone Programme of INSU (Institut National des Sciences de l'Univers) and IRD. We acknowledge the Universidad Mayor de San Andres (La Paz) for their essential cooperation for the realisation of this program.

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