

Trace element geochemistry in the upper Amazon drainage basin (Bolivia)

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Abstract

The distribution of trace elements (Sr, Mo, Ba, Rb, U, Mn, Ni, Cu, Zn, and Cd) was investigated in surface waters and associated particulates in two upper Amazonian basins (Mamore and Beni). Dissolved Sr, Ba, Mo, Rb, U and to a lesser extent Zn and Cd correlate with major ions and appear to be predominantly derived from soluble rocks (carbonates, evaporites or sulfides essentially contained in shales). These elements are conservative in waters except in highly alkaline or sulfate-rich waters where calcite and barite can precipitate. The concentrations of transition element are generally not correlated with major ion chemistry. Their behaviour can be largely explained by equilibrium reactions in solution and solid–liquid exchanges. Additionally, the distribution of Mn and Cu reflects also the lithological differences between the Mamore and Beni basins. The occurrence of mineralisation in the Beni basin explains the high Zn, Cd as well as the concentrations of Cu in some rivers of the Beni basin. The higher content of Mn in the Mamore basin may reflect the predominance of carbonate rocks. 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. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Elemental mass-balance of material carried by rivers to oceans can be better constrained by know-

ing the factors which determine the composition of the dissolved and particulate phases. 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,

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especially those of the transition elements, in rivers (e.g., Shiller and Boyle, 1985; Benoit, 1994).

Recent data on trace elements refer mainly to cratonic areas with the exception of the study of Louvat and Allegre (1997) on the Island of Reunion. According to Zhang and Huang (1993), weathering and erosion exert a major control on dissolved trace metal concentrations in the Huanghe river. Dupré et al. (1996) and Viers et al. (1997) 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 (e.g., Huang et al., 1992; 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 Sr, Mo, Ba, Rb, U, Mn, Ni, Cu, Zn, and Cd 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.

2. Studied area and sampling

The Mamore and Beni subbasins (Fig. 1) represent 74% of the Madeira basin, one of the 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-Jauregui, 1988; Guyot, 1993). These highly turbid rivers flowing out from the Andes correspond to white water rivers. The substrate lithology and the erosional regime of this basin has already been described by Stallard and Edmond (1983) who have outlined a clear relationship between geology, weathering regime and water chemistry.

Most of the samples analysed in the present study, have been collected in areas marked by pronounced topographic elevations (see Fig. 1 and Table 1) decreasing from 3000 m to 100 m above sea level. The Andean tributaries of the Beni river drain intrusive granitic rocks covered by thick sedimentary deposits from the Ordovician dominated by gray-green to dark shales and sandstones with ages ranging from the lower Paleozoic to Tertiary. Carbonate rocks and evaporite formations from abundant outcrops in the Mamore subbasin, especially in the Grande river catchment whereas intrusive granites, associated with sulfide mineralization exist in the Beni subbasin.

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 subboiled 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 preweighted and acid washed 0.22 μm teflon filters (Millipore) fitted on Sartorius polycarbonate filter holders for trace elements and 0.45 μm cellulose acetate filters for major components. For trace elements, the filtrate was transferred to acid-cleaned low density polyethylene Nalgene bottles and acidified to pH 2 using subboiled nitric acid 12 N 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.

For the Dissolved Organic Carbon (DOC) analyses, waters were filtered through a glass-fiber filter (GF/C, 0.7 μm) previously decontaminated by heating at 550°C. Samples were then stabilized with HgCl_2 and stored in glass tubes until analysis.

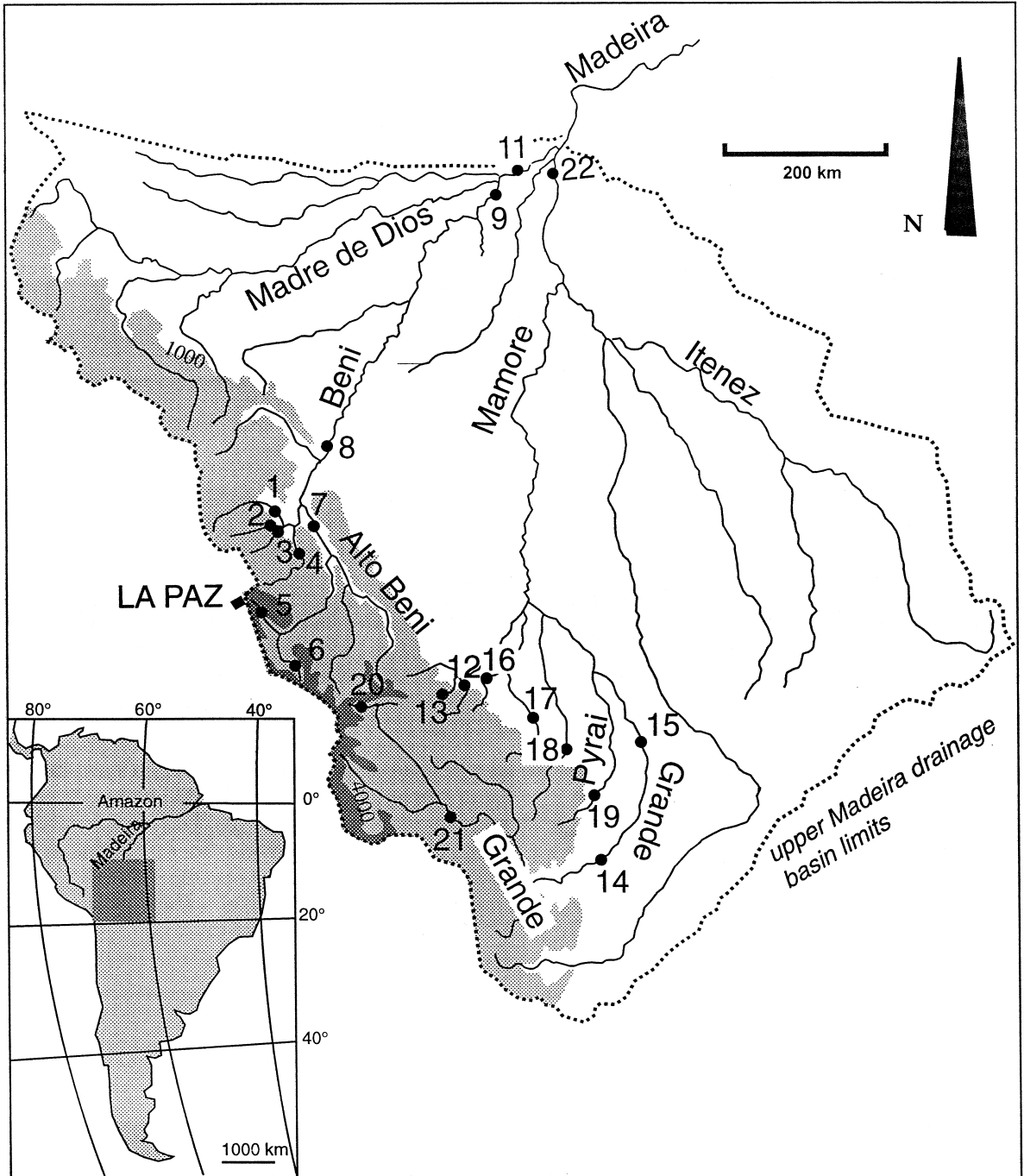


Fig. 1. Map of the Beni and Mamore subbasins showing sampling stations.

Table 1
Main characteristics of the studied basins

River at sampling station	Station number	Area of drainage basin at sampling station (km ²)	Minimum altitude (m)	Maximum altitude (m)	Altitude mean (m)	Mean slope (%)	Mean annual specific discharge (l s ⁻¹ km ⁻²)
Mapiri at Guanay	1	10 100	500	6400	3450	3.4	18
Tipuani at Guanay	2	1400	500	6000	3270	5.0	26
Challana at Guanay	3	1900	500	5900	3200	5.0	55
Coroico at Teoponte	4	5400	440	6100	3270	5.8	33
Unduavi at Puente Villa	5	360	1200	5100	3370	10.0	19
Taquesi at Puente villa	6	590	1200	6400	3780	6.5	19
Alto Beni at Puente Sapecho	7	29 100	380	6400	3400	1.6	21
Beni at Rurrenabaque	8	67 500	280	6400	3340	1.4	30
Beni at Riberalta	9	243 000	125	6400	3250	1.1	34
Beni at Cachuela Esperanza ^a	11	282 500	120	6400	2000	0.8	32
Espiritu Santos at V. Turnari	12	2700	300	2000	600	2.0	70
San Mateo at V. Turnary	13	2400	300	1800	550	2.1	70
Chimore at Bridge	16	1900	210	2900	1800	2.4	70
Ichilo at Bridge	17	2100	240	4200	2185	3.2	70
Yapacani at Bridge	18	6900	280	2400	1400	2.6	13
Piray at Guardia	19	4100	280	2400	1400	2.6	13
Challa at Guardia	20	1000	3100	4500	3750	8.0	5
Rio Grande at Abapo	14	59 800	450	5100	3340	0.8	5
Rio Grande at Santa Cruz	15	67 000	250	5100	3200	0.8	8
Grande at Puente Arce	21	23 700	1500	4800	3150	1.2	5
Mamore at Guayanamerin	22	599 400	110	5100	500	0.7	14

^aBolivian part of the basin.

3. Analytical procedures

3.1. Major elements and main physicochemical parameters

Particulate Organic Carbon (POC) was determined by a high-temperature catalytic oxidation method (HTCO), using a TOC-5000 Instrument (Shimadzu). More detailed information is given by Cauwet (1994).

pH was measured on the field using a glass electrode. Alkalinity was also measured on the field using acid titration.

For major components in the dissolved phase, analyses were performed in the ORSTOM laboratory at Bondy in France. SO_4^{2-} and Cl^- were determined by ion chromatography; Ca^{2+} , Mg^{2+} , Na^+ and K^+ by atomic absorption. Detection limits were 2 μM for SO_4^{2-} , Ca^{2+} , K^+ and Cl^- and 5 μM for Mg^{2+} and Na^+ . SiO_2 was measured by ICP-AES with a detection limit of 1 μM . DOC (Dissolved Organic Carbon) was measured by the same method as Particulate Organic Carbon.

3.2. Trace elements

For trace element determination, the SPM on the filters was dried at 60°C for 24 h. A HNO_3 – HF – HClO_4 digestion was carried out in sealed teflon

(FEP) beakers. The filters 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.

Analyses 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 (e.g., 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 latter are affected by Na argides. Therefore, the interference become noticeable only for $\text{Na} > 1 \text{ meq l}^{-1}$.

The accuracy and the precision of the analytical methods were tested using SLRS-2 (Riverine Water

Table 2
Analysis of International Standards

	SLRS2 (nM)		GBW07310-GSD 10 (ppm)	
	Measured value $\pm 1 \text{ SD}$	Recommended value $\pm 1 \text{ SD}$	Measured value $\pm 1 \text{ SD}$	Recommended value $\pm 1 \text{ SD}$
Mn	173 \pm 7	184 \pm 5	105 \pm 12	107 \pm 2
Co	1.68 \pm 0.12	1.07 \pm 0.20	960 \pm 21	1013 \pm 11
Ni	17.8 \pm 4.1	17.5 \pm 1.7	14.6 \pm 0.6	15.3 \pm 0.4
Cu	41.3 \pm 3.0	43.5 \pm 2.7	34.6 \pm 3.6	30.2 \pm 0.6
Zn	57.6 \pm 3.8	50.9 \pm 2.3	21.5 \pm 1.4	22.6 \pm 0.6
Rb			51 \pm 16	46 \pm 1
Sr	308 \pm 12	312 \pm 5	8.3 \pm 0.4	9.2 \pm 0.8
Mo	1.72 \pm 0.06	1.67 \pm 0.21	23.0 \pm 2.6	25.3 \pm 1.2
Cd	0.31 \pm 0.08	0.25 \pm 0.04	1.30 \pm 0.02	1.2 \pm 0.1
Ba	95 \pm 2	101 \pm 2	35 \pm 2	42 \pm 3
U	0.187 \pm 0.016	0.206 \pm 0.008	2.1 \pm 0.1	2.1 \pm 0.1

SLRS 2 (River Water, National Research Council Canada); GBW07310 (river sediment, National Research Center for Reference Materials, Beijing, People's Republic of China).

Table 3
Major and trace element concentrations in the dissolved phase

River	Mapiri	Tipuani	Challana	Coroico	Unduavi	Taquesi	Alto beni	Beni	Beni *	Beni	Beni *	Beni *	
Location	Guanay	Guanay	Guanay	Teoponte	Puente Villa	Puente Villa	Puente Sapecho	Rurenabaque	Rurenabaque	Riberalta	Riberalta	Cachuela Esperanza	
Station number	1	2	3	4	5	6	7	8	8	9	9	11	
pH	7.65	6.20	6.20	6.48	7.60	7.70	7.90	7.75	6.95	7.15	6.84	6.71	
DOC (ppm)	1.81	1.41	1.70		2.17	0.98	2.20	5.58	7.52	9.65	5.23	3.350	
TDS (ppm)	59	13	13	32	25	34	99	67	72	70	87	63.968	
Ca	0.392	0.039	0.031	0.104	0.119	0.194	0.532	0.393	0.437	0.396	0.448	0.246	
Mg	0.241	0.050	0.054	0.167	0.066	0.118	0.464	0.294	0.257	0.301	0.317	0.196	
K	0.018	0.004	0.002	0.007	0.000	0.000	0.037	0.025	0.031	0.034	0.062	0.040	
Na	0.080	0.015	0.012	0.057	0.056	0.062	0.249	0.114	0.113	0.107	0.106	0.101	
Alkalinity	0.250	0.020	0.025	0.165	0.180	0.245	0.570	0.450	0.550	0.620	0.660	0.500	
Cl ⁻	0.027	0.005	0.000	0.008	0.008	0.008	0.049	0.045	0.024	0.008	0.011	0.008	
SO ₄	0.478	0.082	0.072	0.166	0.056	0.124	0.664	0.327	0.229	0.202	0.333	0.124	
Σ ⁺	0.731	0.108	0.099	0.335	0.241	0.374	1.282	0.826	0.838	0.838	0.933	0.583	
Σ ⁻	0.755	0.107	0.097	0.339	0.244	0.369	1.283	0.822	0.803	0.830	1.004	0.632	
SiO ₂ (μM)	114	101	110	131	109	113	125	119	120	107	145	107	
Mn	375	849	323	373	50	264	143	43	75	179	709	285	
Ni	9.7	37.7	47.9	25.2	12.1	13.5	20.4	13.4		15.5	21.6	11.3	
Cu	5.4	4.6	12.9	6.7	3.6	17.5	10.7	11.1	13.7	23.7	31.6	27.4	
Zn	3.8	11.5	33.2	5.6	8.3	218.5	8.6	6.2	31.5	7.0	19.7	6.5	
Rb	13.0	20.2	15.8	5.7	3.3	7.1	14.3	10.4	13.0	11.6	14.2	12.3	
Sr	452	62	70	163	281	385	863	549	555	487	572	569	
Mo	1.33	0.61	0.30	0.43	0.95	3.09	4.05	2.27	3.83	3.96	2.95	2.56	
Cd	0.032	0.144	0.230	0.037	0.084	1.664	0.055	0.010	0.238	0.072	0.225	0.064	
Ba	37.6	5.5	8.0	12.5	3.5	7.0	83.7	164.5	144.9	217.4	280.7	205.5	
U	0.08	0.15	0.43	0.10	0.06	0.89	0.48	0.29	0.07	0.16	0.07	0.077	
K/Rb	636	91	58	560				1190	1099	1097	1344	2002	1494

Major anions and cations expressed in meq l⁻¹, trace elements in nM. (first 12 columns: Beni subbasin; succeeding 11 columns: Mamore and Grande river subbasins). All samples taken in April 1994 (high water stage) except (*) taken in November 1994 (low waters stage).

Abbreviations: DOC: Dissolved Organic Carbon; TDS: Total Dissolved Solids; Alkalinity: Carbonate Alkalinity.

River	Esp. Santos	San Mateo	Chimore	Ichillo	Yapacani	Piray	Challa	Rio Grande	Rio Grande	Rio Grande	Mamore
Location	V. Tunari	V. Tunari	Bridge	Bridge	Bridge	Guardia	Challa	Puente Arce	Abapo	Santa Cruz	
Station number	12	13	16	17	18	19	20	21	14	15	22
pH	7.70	7.90	6.60	6.20	7.80	8.50	8.18	8.65	8.40	8.10	6.50
DOC (ppm)	5.65	3.60	0.99	0.97	6.70	19.10		1.30	2.74	5.20	23.90
TDS (ppm)	103	91	38	50	136	275	101	673	317	332	58
Ca	0.525	0.541	0.200	0.291	0.928	1.342	0.490	2.577	1.405	1.749	0.266
Mg	0.323	0.344	0.143	0.163	0.354	1.156	0.563	5.152	1.835	1.669	0.211
K	0.026	0.019	0.015	0.024	0.047	0.094	0.058	0.172	0.092	0.108	0.047
Na	0.465	0.227	0.076	0.100	0.222	0.973	0.180	2.087	1.046	1.057	0.133
Alkalinity	0.670	0.740	0.120	0.190	1.300	2.220	1.010	3.490	1.820	1.780	0.470
Cl ⁻	0.338	0.104	0.008	0.008	0.002	0.002	0.056	0.835	0.279	0.327	0.028
SO ₄	0.345	0.305	0.307	0.384	0.330	1.258	0.233	5.246	2.229	2.496	0.153
Σ ⁺	1.339	1.131	0.434	0.578	1.551	3.565	2.344	9.988	4.378	4.583	0.657
Σ ⁻	1.353	1.149	0.435	0.582	1.630	3.478	1.308	9.571	4.328	4.603	0.651
SiO ₂ (μM)	124	105	119	138	178	207	44	159	182	136	133
Mn	815	143	3089	4291	80	55	1310	75	56	4	2064
Ni	7.0	20.4	46.5	48.9	8.7		1.6				18.8
Cu	6.0	10.7	4.1	4.1	13.8		5.5				31.2
Zn	3.9	8.6	28.5	10.8	1.3	6.7	2.3	14.4	9.1	7.6	4.2
Rb	13.1	14.3	9.6	13.1	12.9	17.6	7.6	72.0	18.4	20.4	16.5
Sr	895	863	426	470	1240	2342	430	3813	1943	1921	357
Mo	2.85	4.05	0.61	0.66	4.54	6.67	2.61	15.63	7.36	20.35	2.50
Cd	0.059	0.055	0.305	0.147	0.029	0.048	0.024	0.178	0.333	0.130	0.081
Ba	126.7	83.7	109.7	147.7	399.1	182.6	98.7	240.2	221.7	325.0	215.6
U	0.28	0.48	0.02	0.02	1.25	3.47	0.32	7.55	2.83	3.93	0.20
K/Rb	910	611	717	841	1669	2446	3492	1095	2297	2424	1305

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 (Table 2).

4. Speciation calculations

Calculations, necessary to assess dissolved trace element speciation in the different rivers and the saturation state of calcite and barite, were performed using the computer speciation program MINEQL + (version 3.01a) (Schecher and McAvoy, 1994). The equilibrium constant values are taken from the USEPA's MINTEQA2 model (Allison et al., 1991). The temperature was fixed at 25°C and ionic strength correction were made.

5. Results

5.1. Dissolved material

5.1.1. Major ions (Table 3)

The total dissolved solids (TDS) and the total cations (Σ^+) vary respectively from 13 to 673 ppm and from 99 to 10000 $\mu\text{eq l}^{-1}$. The pH values are between 6.2 and 8.85. These data are in agreement with the values given by Stallard and Edmond (1983) for the Andean subbasin of the Amazon river.

The generally low DOC values ($< 5 \text{ mg l}^{-1}$) indicate a small contribution of vegetation to water chemistry. An exception is the Mamore river at station 22 situated in the lowland region, where vegetation significantly increases the DOC (23.9 mg l^{-1}) load as indicated previously by Guyot and Watson (1994). The Mamore river crosses one of the most extensive floodplains of the Amazonian basin, characterized by an important production of phytoplankton.

Silica concentrations range from 47 to 207 μM and do not show systematic variations.

The major element concentrations vary according to the location of the rivers. In the Beni subbasin, the water chemistry evolves in a relatively small range

with TDS and alkalinity (alk) values comprised respectively between 13–86 ppm and 0.020–0.66 meq l^{-1} . In the Mamore subbasin, the values are generally higher and more variable (TDS = 49 to 673 ppm; alk values = 0.22 to 2.27 meq l^{-1}) reflecting their enrichment in bicarbonate and sulfate, especially in the Grande river.

5.1.2. Trace elements (Table 3)

The two groups recognized from major elements data are only partly reflected in the trace element distribution: Sr, Mo, U, Mn and Ba are higher whereas Zn and Cd are lower in the Mamore basin than in the Beni basin; otherwise Ni, Cu and to a lesser extent Rb have similar concentrations in the two basins. Compared to the already available data from the Amazon basin, (Gibbs, 1977; Furch, 1984; 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; differences may however be recognized for Sr, Ba, Mo and U, which have significantly higher content compared to rivers draining cratonic areas such as the Congo basin (Dupré et al., 1996).

5.2. Suspended particulate material (SPM) (Table 4)

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, chlorite and kaolinite are the main clay minerals in the Madeira basin. The average proportions of clay minerals are: illite (53%), kaolinite (20%), chlorite (18%), smectite (9%). No obvious difference has been detected between the Beni and Mamore subbasins. 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

Table 4
Major and trace element concentrations in suspended sediments

River	Mapiri	Tipuani	Challana	Coroico	Taqesi	Alto beni	Beni	Beni	San Mateo	Ichillo	Rio Grande	Mamore	Mean EF
Station number	1	2	3	4	6	7	8	9	13	17	14	22	
SPM	873	237	187	523	21	1670	832	937	644	357	788	409	
Al	11.3	11.7	10.9	9.2		12.3	7.7			9.0	8.3	9.2	
K	2.9	1.7	2.8	2.5		3.5	2.2			2.6	2.6	2.6	0.754
Ca	3.0	0.8	0.7	1.5		3.0	2.5			4.6	9.9	3.3	0.095
Si	21.3	8.1	21.6	16.3		17.6	18.6			28.0	25.0	26.7	
POC	0.58	0.82	0.95	0.51	2.06	0.56	0.54	0.44	0.60	0.76	0.61	0.79	
Mn	135	98	282	166	156	1094	336	358	651	312	204	269	0.424
Co	9.0	7.2	17.3	9.7	4.7	55.8	13.9	16.2	41.8	18.6	8.0	11.0	1.306
Ni	32	30	58	25	11	211	49	57	163	66	31	43	2.350
Cu	16	20	44	14	27	99	25	29	72	30	13	16	1.195
Zn	65	45	231	51	164	632	121	158	365	305	63	69	1.916
Rb	17	37	107	30	26	184	63	55	101	69	23	43	0.448
Sr	0.67	1.45	60	1.39	16.06	5.54	10.41	4.90	3.85	16.12	4.05	3.30	0.026
Mo	0.07	1.06	2.56	0.52	0.30	3.10	0.88	0.97	2.42	1.26	0.53	0.71	0.615
Cd	0.07	0.14	0.12	0.07	1.06	1.30	0.25	0.22	0.85	0.13	0.22	0.14	2.070
Ba	66	105	376	105	93	674	217	184	281	223	99	181	0.324
U	0.94	1.72	3.62	1.18	1.60	7.20	2.09	2.05	6.19	2.27	1.18	1.67	0.676

Al, K, Ca, Si and POC (Particulate Organic Carbon) in %, trace elements and SPM in ppm. The enrichment factor (EF) of the element in the suspended particulate matter (SPM) is defined by: $EF = (X_{SPM} / Al_{SPM}) \text{ ppm} / (X_{Crust} / Al_{Crust}) \text{ ppm}$ where X_{SPM} and X_{Crust} are, respectively, the concentrations of the element X in SPM and in the crust. Crust data are from Taylor and McLennan (1985).

Abbreviations: SPM: Suspended Particulate Matter; POC: Particulate Organic Carbon.

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 (Table 4) 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 varzea soils and sediments, which extend over the entire Amazon catchment, are composed of material derived from the Andes. The higher concentrations of Sr in the varzea is the result of a higher proportion of feldspars, (the main host mineral for Sr). This mineral, present only in minor quantity in SPM, may be sorted out from the water column during transport. The small relative decrease of Ba, which is partitioned between K-feldspars and mica, may also be predicated by a partial loss by sedimentation of K-minerals in the sampled area.

6. Discussion

6.1. Dissolved material

6.1.1. Major ion chemistry: influence of lithology

The atmospheric contribution from marine or terrestrial origin can be an important source of dissolved elements in waters. However the marine contribution decreases progressively in the Amazon basin with distance from the Atlantic ocean (Stallard and Edmond, 1981) and altitude (Meybeck, 1986). According to Stallard and Edmond (1981) this contribution is less than 3% for Ca^{2+} and K^+ in the Andes. Thus, our data were not corrected for marine contribution. The contribution of aerosols of terrestrial origin (wind-blown dust from deserts, forest fires, aerosols from the canopy) which is difficult to assess has also been ignored.

Two groups of river waters can be distinguished on the basis of pH and alkalinity (Fig. 2). The first type has a low pH (< 7.5) and low alkalinity (< 1

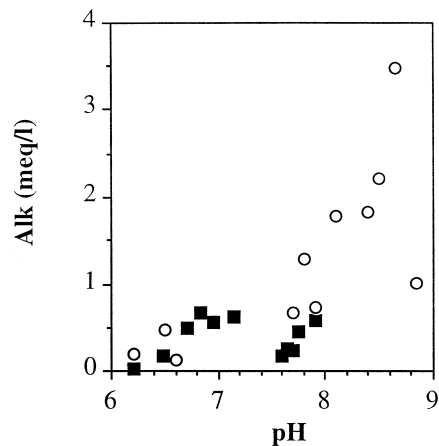


Fig. 2. Plot of Alkalinity vs. pH. Full squares: Beni subbasin; open circles: Mamore subbasin.

meq l^{-1}) and is represented by 6 rivers from the Beni basin and 3 rivers from the Mamore Basin. Sulfate, which probably results from pyrite weathering, is the major anion in the rivers having pH = 6.6. The other rivers are dominated by bicarbonate.

The second type of water with pH > 7.5 and with variable and often high alkalinity includes 8 rivers from the Mamore basin and 5 rivers from the Beni basin. In these rivers, pH increases regularly with alkalinity. SO_4^{2-} is the dominant anion in some of these waters and tends to increase with chloride and alkalinity. The weathering of sulfur contained in shales is probably a major source for sulfate, however some contribution from gypsum cannot be excluded.

The ratio $R = \text{Si}/\text{Na} + \text{K}-\text{Cl}$ (Fig. 3) for most of the analyzed waters is generally low (< 2) indicating either a low contribution from weathering of silicate phases or formation of cation rich clays, in agreement with Stallard (1985). The plot of R versus Alkalinity (Fig. 3) displays an asymptotic trend and suggests a predominant role of carbonate as a source for major dissolved cations. This interpretation is corroborated by the relationship between Alkalinity + SO_4 and Ca or Mg (Fig. 4) which plots along the dolomite dissolution line. On this figure, samples with the highest Ca content (Pyrai and Grande rivers) fall slightly below this line, suggesting calcite precipitation, in agreement with MINEQL calculations.

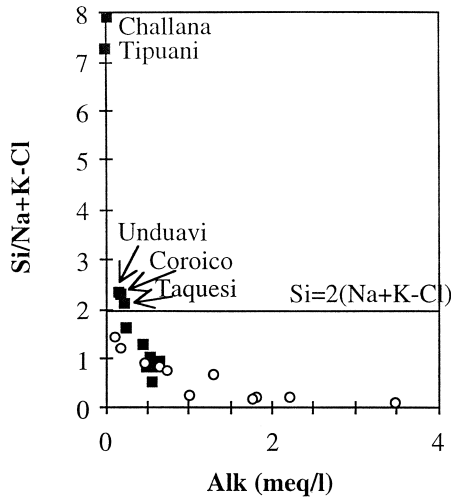


Fig. 3. Si/(Na + K–Cl) vs. Alkalinity. Symbols as in Fig. 2.

6.1.2. Trace elements: Rb, Sr, Ba, Mo, Cd, Zn, U

This group of trace elements correlates with major elements.

Rb, Sr, Ba and Mo and occur mainly as ionic species (Rb^+ , Sr^{2+} , Ba^{2+} , MoO_4^{2-} , $HMoO_4^-$) are

poorly adsorbed by particles (Martin and Whitfield, 1983). The positive Sr–Ca correlation and respectively Mo–Ca correlation (Fig. 5) indicate similar behaviour and probably the same carbonate source. Ba which is generally associated with K-minerals in rocks tends to increase with K in the Beni basin (Fig. 6). In the waters of the Pyrai, Grande and Mamore rivers, the correlation is rather poor. This could be due to precipitation of Ba in waters saturated with respect to barite.

Rb tends also to increase with K; the K/Rb ratio (Table 3) is high and varies over a large range, the highest ratios (> 2000) being encountered in the samples with highest K content. As shown from the K/Rb ratios in altered igneous rocks (e.g., Hart, 1971) such values cannot result from the fractionation of the main igneous rock types during weathering, and imply a source with a high K/Rb ratios. Such source may be evaporites, which have K/Rb ratios higher than 3000 ppm (Land et al., 1995). Alternatively, the observed enrichments of K over Ba and Rb could be due to emission of K-rich

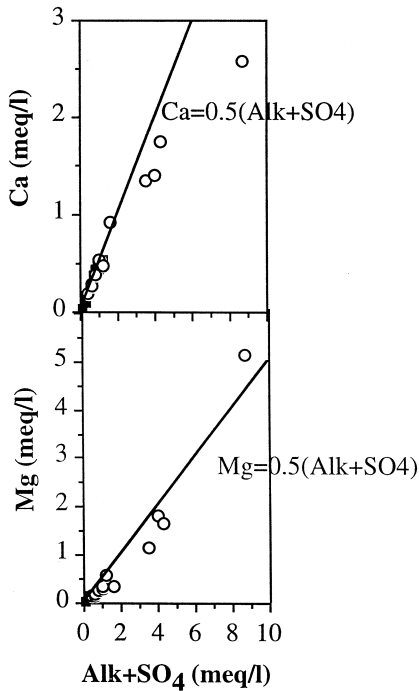


Fig. 4. Ca and Mg vs. Alkalinity + SO_4^{2-} . Symbols as in Fig. 2.

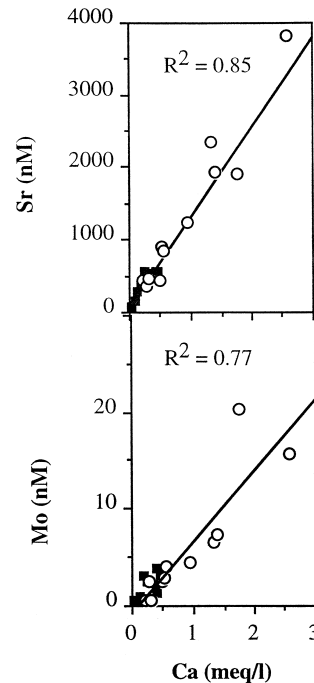


Fig. 5. Sr and Mo vs. Ca in the dissolved phase. Symbols as in Fig. 2.

biogenic aerosols by vegetation in the tropical forest (Croizat, 1979).

Zn and Cd do not show systematic relations with the main physicochemical parameters. In the Mamore basin, however, both elements increase when the $\text{SO}_4^{2-}/\text{Alkalinity}$ ratio increases (Fig. 7a and b). A maximum of Zn and Cd concentrations is observed in the Chimore river where the low pH, the low alkalinity and the dominant SO_4^{2-} ion probably reflects the oxydation of pyrite. The relation observed between Zn, Cd and $\text{SO}_4/\text{Alkalinity}$ indicates that Zn and Cd have the same origin as SO_4^{2-} (pyrite or gypsum weathering) and that their concentrations are diluted by carbonate derived waters.

In the Beni basin, a correlation is observed between Zn and Cd (Fig. 7c) with the highest concentrations encountered in the Taquesi, Challana and Tipuani rivers. This correlation may indicate the same origin for both elements, probably sulfide mineralization, where Zn and Cd are commonly associated. Mining is occurring in the Taquesi subbasin, where the highest concentrations are encountered and also in the Tipuani subbasin were intensive mining of alluvial placers for Au is taking place.

Uranium (Fig. 8) is strongly correlated with alkalinity (except in the Tipuani, Challana and Taquesi rivers) in agreement with U inorganic speciation which is dominated by carbonato-complexes. The exceptions correspond to rivers where pyrite drainage

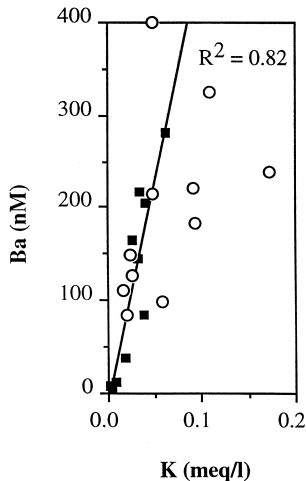


Fig. 6. Ba vs. K in the dissolved phase. Symbols as in Fig. 2.

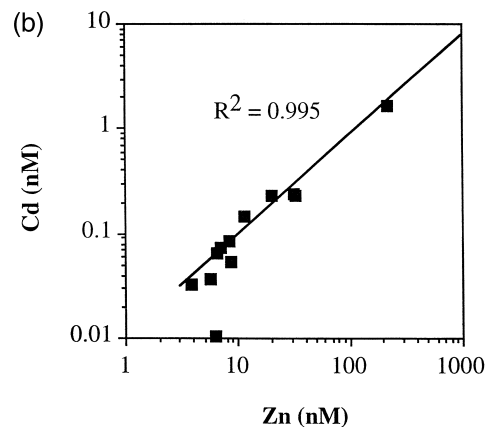
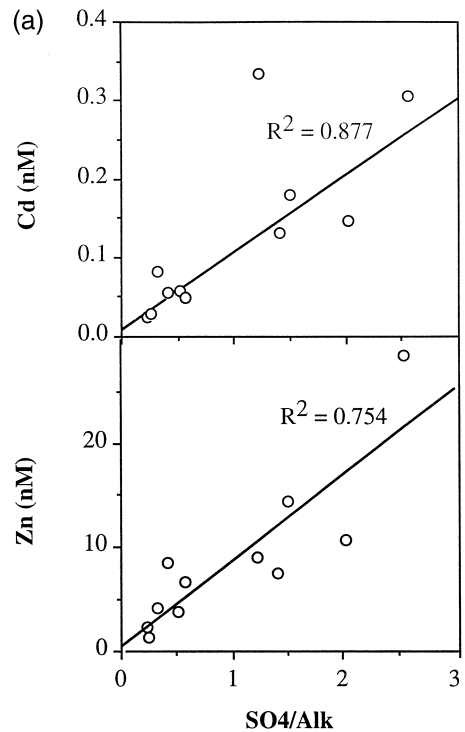


Fig. 7. (a) Zn, Cd vs. $\text{Alkalinity}/\text{SO}_4^{2-}$ in the Mamore subbasin. (b) Cd vs. Zn in the Beni subbasin.

is likely occurring and which have also Zn and Cd and Cu anomalies (see above).

6.1.3. Trace metals: Mn, Ni, Cu

This group of elements does not show systematic relations with major ions and pH. Their behaviour

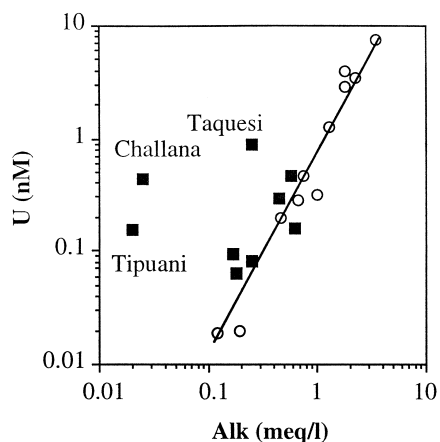


Fig. 8. U vs. Alkalinity. Symbols as in Fig. 2. U-carbonate complexes range from 32% (Challana, Tipuani) to 99.8% in the Beni basin and from 31.4 (Ichillo) to more than 94% in 8 rivers (out of 10) in the Mamore basin.

may, however, be described taking into account element speciation calculated using MINEQL.

Dissolved Mn concentrations reach 4290 nM in low pH (6.2) rivers where it appears as free cation; then it decreases with increasing pH (Fig. 9). A similar decrease with pH is observed for Ni in rivers having a pH = 7.15 (Fig. 9) where Ni^{2+} dominates dissolved Ni speciation. According to Shiller and Boyle (1985) such relationships with pH can result from variations in the amount of metal in the different source rocks or be chemical in nature. Alternatively, the decrease may result from an increased adsorption when pH increases according to the surface complexation theory (e.g., Schindler and Stumm, 1987). With regards to Mn, the two groups of content at low pH (Fig. 9) where Mn exists mainly as Mn^{2+} even in oxic waters, may reflect the relative abundance of Mn in source rocks.

In high pH rivers (pH > 7.15), the Mn concentration is generally low except in the San Mateo river and probably limited by precipitation of stable Mn oxides (Fig. 9).

Inorganic Cu speciation in low pH waters (pH < 7.5) is also dominated by Cu^{2+} ; however, Cu concentration does not show any relationship with pH. In the Beni and Mamore subbasins, dissolved Cu concentration tends to increase with DOC. If one excludes the Challana and the Taquesi rivers, which have rather elevated Cu concentrations compared to

DOC (Fig. 10). This may indicate a contribution of organic ligands which are known to complex Cu very efficiently (e.g., Xue and Sigg, 1993; Xue et al., 1995; Achterberg et al., 1997). In order to test this hypothesis, MINEQL calculations were redone with a fulvate concentration proportional to the DOC content of our waters (Fulvate = DOC/12.1). The proportion coefficient has been taken from the ratio DOC/natural Cu complexing ligand, given by Achterberg et al. (1997). The calculations indicate that at least 23% of Cu is organically complexed in 10 of the 21 rivers where DOC data are available. All Cu appear as organic complex in the Mamore river at Guyanamerin.

Contrary to the observation of Viers et al. (1997) in organic-dominated rivers of tropical basins (Coca-Cola rivers), organic matter appears to play a

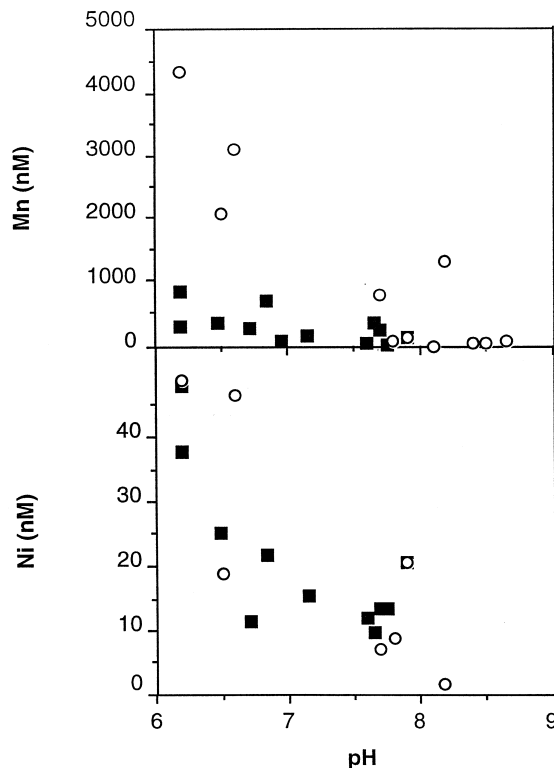


Fig. 9. Dissolved Mn, Ni, vs. pH. Symbols as in Fig. 2. Mn^{2+} and Ni^{2+} are the dominant species (> 96% and 75%, respectively) in the Tipuani, Challana, Coroico and Beni rivers (Beni basin) and in the San Mateo, Chimore, Ichillo, Mamore rivers (Mamore basin). In all other rivers, the main species are MnO_4^{2-} and NiCO_3 (around 100% and > 73%, respectively).

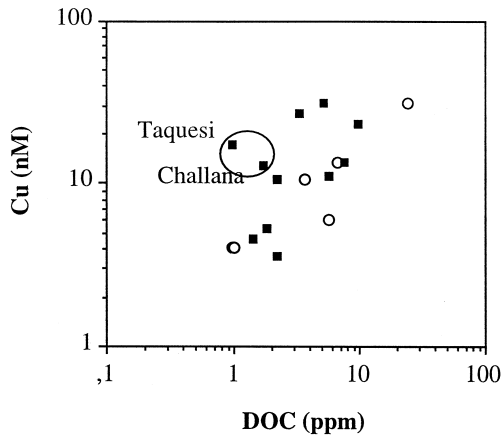


Fig. 10. Cu vs. DOC (Dissolved Organic Carbon). Symbols as in Fig. 2.

limited role in the Beni and Madeira basins, except for Cu. The contribution of the colloidal phase does not seem to be important since trace element varia-

tions can be interpreted by equilibrium processes in solution. Colloids may significantly contribute to metal transport in waters (Sholkovitz, 1995; Sanudo-Wilhemly et al., 1996; Eyrolle et al., 1996; Gaillardet et al., 1997; Viers et al., 1997). However, a comparison of the Ob, Yenesei and Rhone river shows that the contribution of the colloidal fraction tends to decrease when DOC decreases except for Fe and Cu (Martin et al., 1995; Dai and Martin, 1995). Further studies involving ultrafiltration experiments would be necessary to assess more precisely the importance of the colloidal phase in Beni and Mamore subbasins, however the generally low DOC at the time of sampling could explain the low contribution of organic complexation and colloidal phases to trace element transport.

6.2. Suspended particulate material

There is a high degree of correlation among the trace metals in the SPM, the only exception being Sr.

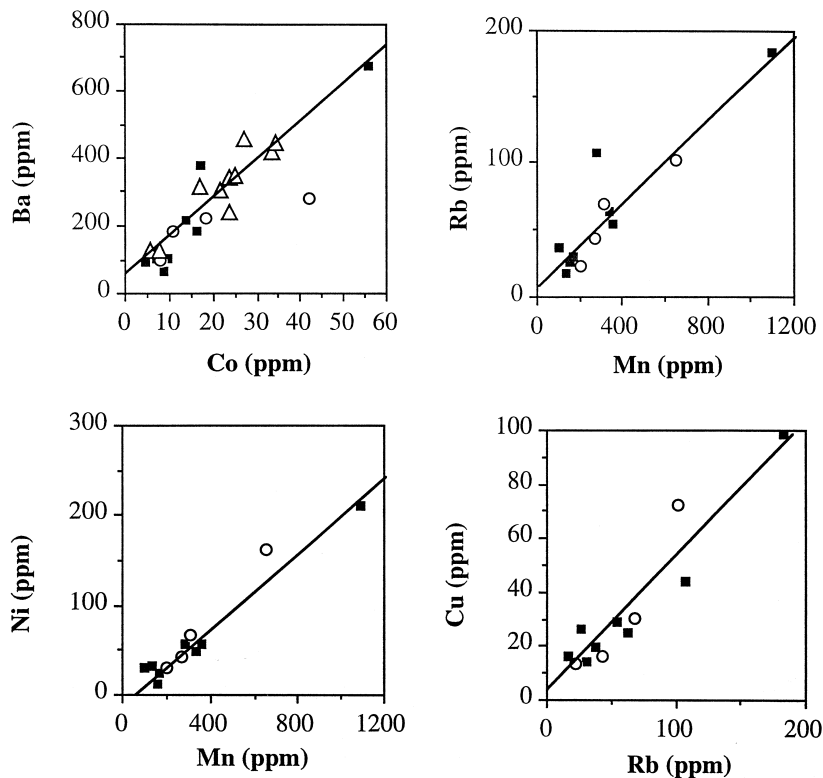


Fig. 11. Ba vs. Co, Rb vs. Mn, Ni vs. Mn and Cu vs. Rb in SPM (Suspended Particulate Matter). Full squares: Beni subbasin; open circles: Mamore subbasin; triangles: Congo basin (after Dupré et al., 1996).

Some of these correlations are illustrated in Fig. 11. The fractionation trend in SPM is unlike that encountered in igneous rocks where, for example, Co decreases while Ba increases. The trace element fractionation in SPM passes through the origin of the axes and reflects a dilution due to the variable abundance of quartz. This trend is a common feature in SPM from several rivers and lakes. For instance, the Congo river (Dupré et al., 1996), where the mineralogical assemblage of SPM is made up of kaolinite, illite and smectite with some quartz and feldspar (Jouanneau et al., 1990) displays a trend which is similar to that of Amazon (Fig. 11). In addition, the similarity of several trace element ratios in SPM of the Amazon and Congo rivers is striking in light of the different type of weathering in the two basins.

The mean enrichment factor (EF) values normalized to Al (Table 4) corroborate the recent findings of Dupré et al. (1996). Compared to the upper crust, the transition elements are enriched whereas Rb and Ba are depleted. To a first approximation, the lower content of Rb and Ba may reflect their more soluble character. On the other hand, the relative depletion of some elements ($EF < 1$) and the enrichment of others ($EF > 1$) may simply result from the sorting of feldspars, which concentrates alkali and alkaline-earth elements.

7. Summary and conclusion

Trace elements in the Bolivian Amazon drainage basin (Mamore and Beni subbasins) can be divided into two groups according to their relationships with major elements and pH: (1) 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; (2) those which are not correlated with major ions (Mn, Ni, Cu) are controlled by adsorption processes and/or complexation. This is illustrated by the decreasing solubility of Mn and Ni with increasing pH in the waters where they mainly exist as Mn^{2+} and Ni^{2+} . This behaviour can be explained by an adsorption process on particulate material which possesses

surface groups which may act as ligands and complex metals which are in cationic form. In addition, vegetation which produces organic material could control Cu solubility.

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.

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