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Origin of trace elements in the Bolivian Amazonian drainage basin

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Abstract The geochemistry of dissolved trace elements (V, Mn, Co, Ni, Cu, Zn, As, Rb, Sr, Mo, Cd, Sb, Cs, Ba, Pb and U) in the Upper Madeira basin, which constitutes the Bolivian part of the Amazon basin have been investigated. Using a statistical method (principal component analysis), the combined use of these geochemical data together with geological information on each watershed demonstrated the fundamental control of the substrate lithology on the trace chemistry of unpolluted surface waters within the catchment, at least in the Andean part of the basin. Three factors account for 87% of the variance. The first factor represents the influence of solution of evaporite and associated deposits occurring in the Andean Palaeozoic and Cretaceous sections; the second represents the influence of the mining activities being carried out in the Taquesi basin; and the third, the influence of black shale products and arenaceous-argillaceous rocks. In spite of the occurrence of evaporite rocks in the Upper Madeira watershed which tend to mask the trace-metal signatures of other lithological formations, it has been possible to discriminate the sources of trace metals present in the Andean and Amazonian Plain rivers.

Origen de los elementos en trazos en la cuenca Amazonica de Bolivia

Resumen La geoquímica de los elementos tracos (V, Mn, Co, Ni, Cu, Zn, As, Rb, Sr, Mo, Cd, Sb, Cs, Ba, Pb y U) de los rios de la alta cuenca del rio Madeira (Bolivia), un de los tributarios mas importantes del rio Amazonas que draina la cadena andina y el llano amazónico, fue estudiada utilizando una methoda estastística (análisis de las componentes principales). El estudio se basa sobre los datos geológicos de las cuencas y sobre los tenores de los elementos en trazos de las muestras obtenidas. Los trés primeros factores del análisis estatística representan: la influencia del drenaje de los sedimentos yesíferas y carbonatadas que se traduce por concentraciones elevadas Rb, Sr, Mo, Sb, Cs, U y Ba; la influencia de las actividades mineras encontradas en la cuenca del rio Taquesi (As, Zn, Cd); y la influencia de la erosíon de las series detríticas del Paleozoico de los Andes que se traduce por concentraciones elevadas en Co, Ni y Mn (rios Tipuani y Challana en la cuenca del Alto Beni). Un segundo análisis estatístico effectuado sobre las muestras de los rios que no estan drenando las formaciones evaporiticas como los rejectos de mina permite de discriminar el origen de los elementos en trazos encontrados en los rios de la llanura amazónica.

INTRODUCTION

Rivers are the major pathways for the transport of weathering materials from the land to the oceans. Geochemical studies on river water provide an insight into the weathering processes that control the distribution of elements and their fluxes. The upper drainage basins of the Amazon provide most of the dissolved and sediment yields leading to the Amazonian basin (Gibbs 1967a, b, 1972; Stallard & Edmond, 1983; Guyot *et al.*, 1988). Consequently, the geochemistry of the Bolivian rivers has been studied extensively during the last ten years, in the frame of the Project on Hydrology and Climatology and Bolivia (PHICAB) programme and the main results have been published (Guyot, 1993, 1994; Roche & Fernández-Jáuregui, 1988; Guyot *et al.*, 1988, 1989, 1990, 1993, 1994, 1995; Roche *et al.*, 1986, 1991). In spite of these numerous studies, the trace geochemistry of the Andean tributaries remains poorly known (Guyot, 1993), since prior geochemical studies were concerned essentially with the major element distribution. As a result, a detailed study of the trace element distribution of the Madeira basin was undertaken in 1993. In this paper, we present data on the dissolved trace elements in these river waters. The work focuses on the relationship between the chemistry of some trace dissolved species in rivers of the Bolivian Amazonian drainage system, and the lithology of their catchments. Using a factor analysis approach, a detailed examination of geological control and anthropogenic inputs of trace metals in the surface waters of the upper Madeira basin is reported. Discussion about the major dissolved species, the flow regimes and the chemical fluxes in the Madeira drainage basin are not included in this paper.

MAJOR HYDROLOGICAL FEATURES OF THE BASIN

The Bolivian Amazon region lies in the upper middle part of the Madeira River basin. The basin extends from the Eastern Cordillera of the Andes to the Amazon Floodplain and the Brazilian Shield. The Madeira basin is large (900 000 km^2 upstream the Brazilian boundary) and supplies annually on average 540×10^9 m^3 of waters, i.e. 10% of the discharge of the Amazon to the ocean (Roche & Fernández-Jáuregui, 1988). It is formed by the confluence of four rivers: the Madre de Dios and the Beni Rivers, which join to continue as the Beni River and represent 35% of the Madeira basin; and the Mamore and the Itenez which join to form the Madeira River and represent 65% of the whole basin. The Andean part of the Madeira basin extends from the Andean glaciers, 6500 m high, to the tropical humid forest of the piedmont at elevations below 25 m. Between these regions, the upper Beni watersheds traverse semiarid areas of high altitude. In the Amazonian plain (250 m to 100 m high), the forest progressively gives way to tropical savanna and forest gallery. The Madeira basin is not industrialized (with the notable exception of gold mines in the Taquesi River).

The hydrology of the Madeira River is well known owing to the large set of data acquired by the PHICAB programme. The mean annual volume flowing in the Madeira River has been estimated as 18 000 m^3 s^{-1}, 53.2% of which is contributed by the Beni River and 47.7% by the Mamore River. The Andes and the plain contribute equally to the water flowing into the Madeira River. The four large tributaries participate in different ways in supplying the Madeira River: 19% comes from the Beni, 29% from the Madre de Dios, 24% from the Mamore and 7% from the Itenez River. The remaining 20% comes from small tributaries discharging into the confluence of these rivers and the head of the Madeira. More complete information about hydrology of this region has been given by Roche & Fernandez (1988) and Guyot (1993).

The Andean rocks are mainly Palaeozoic, Mesozoic and Tertiary in age. The Rio Beni tributaries (Mapiri, Tipuani, Challana, Coroico, Unduavi and Taquesi rivers) drain the highest mountains of the Andes which are composed of intrusive granitoid rocks and of a thick mass of sedimentary rocks of Ordovician, constituted of grey-green to black shales mixed with sandstones. Carbonate rocks (mainly dolomites) are poorly represented in the studied zone. Locally the Silurian-Devonian series contain red, gypsiferous clays (Mapiri basin). A sodium chloride deposit can be found in the Rio Grande basin. In the Madeira floodplain, the sediments are essentially Quaternary in age. Such mineralization which might contribute to the delivery of trace metals in the waters are noted in Table 1.

SAMPLING AND ANALYSES

Surface water samples were collected along the Madeira River and its tributaries in March–April 1994 during the high water period (Fig. 1). For the mean tributaries Beni, Madre de Dios and Madeira, some samples were also collected during the low flow period in November 1995. Samples were taken using acid-washed polypropylene containers at the riverbanks in the turbulent Andean rivers and in the middle of the river, using a wooden boat, in the plain rivers. Each sample was filtered, on site, through 0.2 μm filters, either on acetate cellulose for major elements, or on precleaned Teflon® filters for trace elements. Samples for organic carbon determination were passed through glass fibre filters, previously heated at 550°C for 8 h, and poisoned with $HgCl_2$. Chemical analysis for major elements was performed at the ORSTOM Laboratory in France. Sulphate and nitrate were determined by ion chromatography; calcium, magnesium, sodium and potassium by atomic absorption. Detection limits were 2 $\mu mol\ l^{-1}$ for SO_4^{2-}, NO_3^-, Ca^{2+}, K^+, and Cl^-, and 5 $\mu mol\ l^{-1}$ for Mg^{2+} and Na^+. Trace element analyses were performed on the pH2 acidified samples using an inductively coupled plasma mass spectrometry technique, according to the method described in Seyler & Elbaz-Poulichet (1996). Dissolved Organic Carbon (DOC) was analysed using a non-dispersive infrared analyser (Shimadzu TOC500), described elsewhere (Seyler *et al.*, 1995).

RESULTS AND DISCUSSION

The physico-chemical parameters measured in the field (temperature, pH, conductivity), together with the concentrations of major species and dissolved organic carbon (DOC) are given in Table 2. The concentrations of trace elements (V, Mn, Co, Ni, Cu, Zn, As, Rb, Sr, Mo, Cd, Sb, Cs, Ba, Pb and U) are given in Table 3.

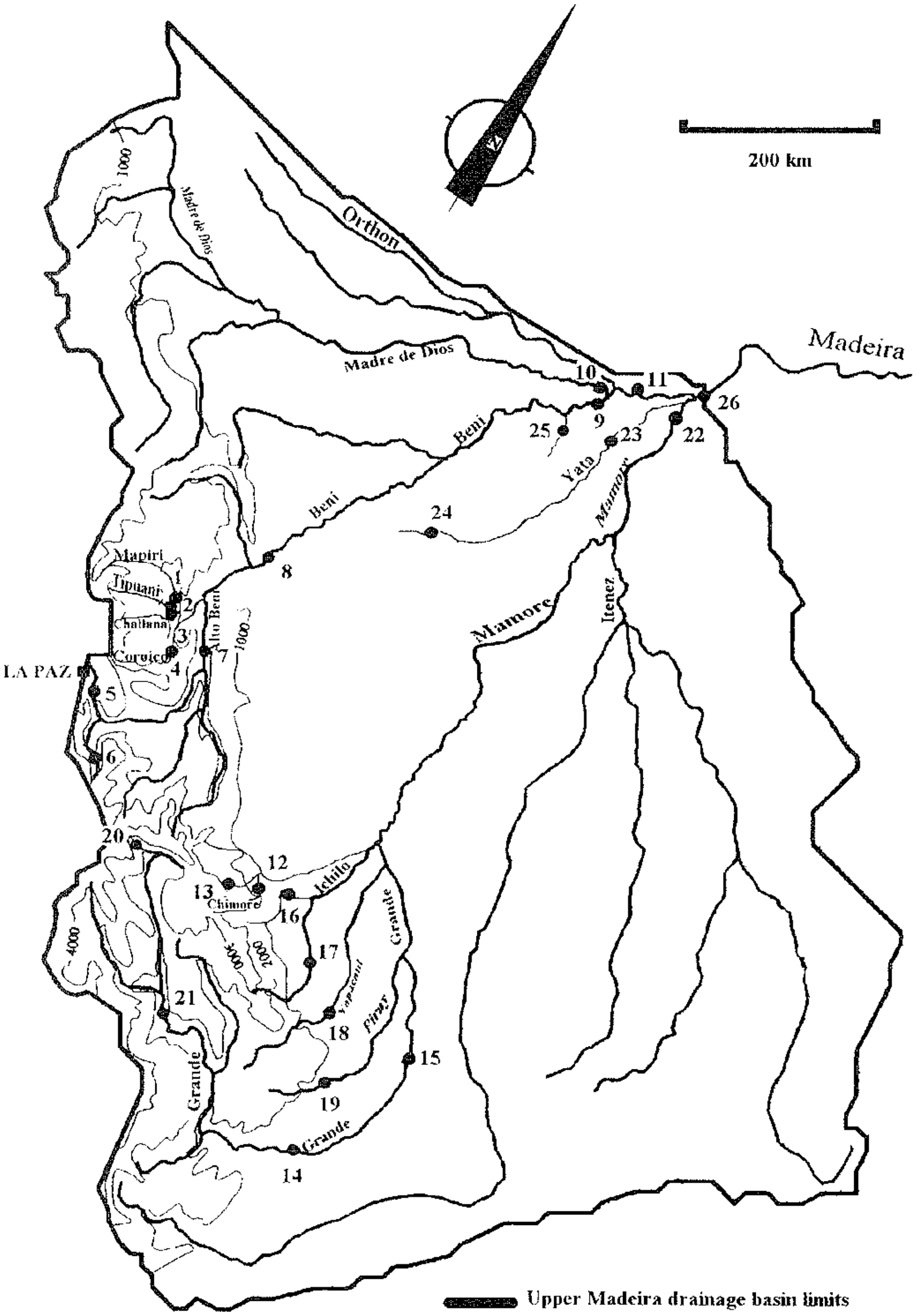

Fig. 1 Map of the Bolivian Amazon basin, showing the position of sample collection locations.

Table 1 Geomorphological characteristics and proportions of rock types in the drainage basins of the tributaries of the Madeira River.

River at sampling point	Station no.	Altitude (m)	Area (km^2)	Geology (%): Quaternary	Tertiary	Tertiary Intrusive	Secondary	Carboniferous-Permian	Silurian-Devonian	Ordovician
Mapiri	1	500	10 100	2	0	10	1	8	25	54
Tipuani	2	500	1 400	0	0	10	1	8	27	54
Challana	3	500	1 900	0	0	10	1	8	27	54
Coroico	4	500	5 400	0	0	8	1	8	29	54
Unduavi	5	1200	360	0	0	12	0	0	0	88
Taquesi	6	1200	590	0	0	13	0	0	17	70
Alto Beni	7	380	29 100	2	12	2	3	4	37	40
Beni at Rurrenabaque	8	280	67 500	1	16	2	4	6	30	41
Beni at Riberalta	9	125	243 000	10	20	0	5	6	29	30
Madre de Dios*	10	125	124 200	100	0	0	0	0	0	0
Beni at Cachuela Esperanza*	11	120	282 500	100	0	0	0	0	0	0
Espiritu Santos	12	300	2 700	0	0	0	0	0	33	67
San Mateo	13	300	2 400	28	25	0	7	25	15	0
Rio Grande at Abapo	14	450	59 800	2	10	0	9	9	42	28
Rio Grande at Santa Cruz	15	250	67 000	10	5	0	7	9	40	29
Chimore	16	210	1 900	27	13	0	6	6	40	8
Ichilo	17	240	2 100	27	13	0	5	6	39	10
Yapacani	18	280	6 900	28	26	0	7	23	16	0
Piray	19	280	4 100	29	20	0	12	24	15	0
Challa	20	3100	1 000	12	2	0	10	0	23	53
Grande at Puente Arce	21	1500	23 700	5	0	0	24	0	23	48
Mamore	22	110	599 400	99	1	0	0	0	0	0
Yata at Ferry-boat station	23	140	20 000	100	0	0	0	0	0	0
Yata at bridge	24	200	87 000	100	0	0	0	0	0	0
Yvon	25	140	10 000	100	0	0	0	0	0	0
Madeira	26	100	900 000	94	0	0	0	0	3	3

* Bolivian part of the basin.

Table 2 Physico-chemical parameters and major element concentrations (meq l^{-1}) of the surface waters of the Upper Madeira drainage basin in Bolivia.

River	Station	Station no.	No. of samples	Temp. (°C)	CND ($\mu S\ cm^{-1}$)	pH	Ca	Mg	K	Na	ALK.	Cl	NO_3	SO_4	DOC
Mapiri	Guanay	1	1	23.5	82	7.7	0.392	0.241	0.018	0.080	0.250	0.027	0.002	0.478	1.81
Tipuani	Guanay	2	1	22.9	19	6.2	0.039	0.050	0.004	0.015	0.020	0.005	0.002	0.082	1.41
Challana	Guanay	3	1	21.9	15	6.2	0.031	0.054	0.002	0.012	0.025	0.000	0.002	0.072	1.70
Coroico	Teoponte	4	1	22.8	37	7.0	0.104	0.167	0.007	0.057	0.165	0.008	0.002	0.166	ND
Unduavi	Puente Villa	5	1	17.3	26	7.6	0.119	0.066	0.002	0.056	0.180	0.008	0.002	0.056	2.17
Taquesi	Puente Villa	6	1	17.5	44	7.7	0.194	0.118	0.002	0.062	0.245	0.000	0.002	0.124	0.98
Alto Beni	Puente Sapecho	7	1	23.4	138	7.9	0.532	0.464	0.037	0.249	0.570	0.049	0.002	0.664	2.20
Beni	Rurrenabaque	8	2	25.2	93	7.3	0.415	0.276	0.028	0.114	0.500	0.035	0.002	0.278	6.55
Beni	Riberalta	9	2	27.5	98	7.1	0.422	0.309	0.048	0.107	0.640	0.010	0.002	0.268	7.44
Madre de Dios	Riberalta	10	2	27.0	52	7.1	0.272	0.100	0.026	0.076	0.353	0.016	0.009	0.091	6.22
Beni	Cachuela Esp.	11	1	27.4	71	6.7	0.246	0.196	0.040	0.101	0.500	0.008	0.029	0.124	3.35
Espiritu Santos	Villa Tunari	12	1	19.6	143	7.7	0.525	0.323	0.026	0.465	0.670	0.338	0.002	0.345	5.65
San Mateo	Villa Tunari	13	1	19.6	121	7.9	0.541	0.344	0.019	0.227	0.740	0.104	0.002	0.305	3.60
Grande	Abapo	14	1	23.3	416	8.4	1.405	1.835	0.092	1.046	1.820	0.279	0.002	2.229	2.74
Grande	Santa Cruz	15	1	26.5	441	8.1	1.749	1.669	0.108	1.057	1.780	0.327	0.002	2.496	5.20
Chimore	bridge	16	1	23.1	54	6.6	0.200	0.143	0.015	0.076	0.120	0.008	0.002	0.307	0.99
Ichilo	bridge	17	1	23.5	69	6.2	0.291	0.163	0.024	0.100	0.190	0.008	0.002	0.384	0.97
Yapacani	Yapacani	18	1	25.8	154	7.8	0.928	0.354	0.047	0.222	1.300	0.002	0.002	0.330	6.70
Piray	Guardia	19	1	19.7	353	8.5	1.342	1.156	0.094	0.973	2.220	0.002	0.002	1.258	19.10
Challa	Challa	20	1	17.7	105	8.9	0.490	0.563	0.058	0.180	1.010	0.056	0.009	0.233	ND
Grande	Puente Arce	21	1	20.5	882	8.7	2.577	5.152	0.172	2.087	3.490	0.835	0.002	5.246	1.30
Mamore	Guayanamerin	22	1	29.0	66	6.5	0.266	0.211	0.047	0.133	0.470	0.028	0.002	0.153	23.90
Yata	ferry-boat	23	1	28.5	9	6.6	0.019	0.028	0.005	0.002	0.055	0.002	0.002	0.002	8.60
Yata-1	bridge	24	1	28.5	48	6.6	0.125	0.196	0.039	0.182	0.520	0.002	0.002	0.002	13.70
Yvon	bridge	25	1	27.2	10	5.4	0.016	0.014	0.002	0.002	0.025	0.002	0.002	0.005	12.80
Madeira	Brazilian boundary	26	2	28.1	47	7.2	0.182	0.119	0.034	0.087	0.310	0.009	0.004	0.092	4.60

CND: conductivity; ALK.: alkalinity; DOC: dissolved organic carbon; ND: not determined.

Table 3 Trace element concentrations (nmol l^{-1}) in the surface waters of the Upper Madeira drainage basin in Bolivia.

River	Station	No.	V	Mn	Co	Ni	Cu	Zn	As	Rb	Sr	Mo	Cd	Sb	Cs	Ba	Pb	U
Mapiri	Guanay	1	18.92	375	2.85	9.7	5.4	3.78	4.8	12.98	452	1.33	0.03	1.24	0.35	37.6	0.07	0.08
Tipuani	Guanay	2	10.54	849	25.84	37.7	4.6	11.54	1.9	20.17	62	0.61	0.14	0.11	0.21	5.5	0.39	0.15
Challana	Guanay	3	10.06	323	22.39	47.9	12.9	33.17	2.2	15.84	70	0.30	0.23	0.10	0.18	8.0	0.19	0.43
Coroico	Teoponte	4	10.25	373	3.04	25.2	6.7	5.63	2.8	5.74	163	0.43	0.04	0.22	0.06	12.5	0.15	0.10
Unduavi	Puente Villa	5	1.75	50	2.21	12.1	3.6	8.31	20.8	3.32	281	0.95	0.08	0.21	0.12	3.5	0.04	0.06
Taquesi	Puente Villa	6	2.46	264	4.50	13.5	17.5	18.46	310.7	7.09	385	3.09	1.66	1.46	2.57	7.0	0.14	0.89
Alto Beni	Puente Sapecho	7	01.38	143	2.77	20.4	10.7	8.63	26.2	14.27	863	4.05	0.05	7.30	0.40	83.7	0.06	0.48
Beni	Rurrenabaque	8	38.73	59	1.58	13.4	12.4	6.20	12.5	11.70	552	3.05	0.12	10.51	0.17	154.7	0.22	0.18
Beni	Riberalta	9	43.45	179	1.59	18.5	27.6	7.04	9.1	12.91	529	3.46	0.15	6.61	0.15	249.0	0.58	0.11
Madre de Dios	Riberalta	10	28.58	122	0.95	8.6	23.0	3.15	6.0	11.43	499	3.47	0.07	0.72	0.04	138.1	0.18	0.10
Beni	Cachuela Esp.	11	11.74	285	16.66	11.3	27.4	6.53	3.5	12.28	569	2.56	0.06	4.37	0.11	205.5	0.44	0.08
Espiritu Santos	Villa Tunari	12	7.87	815	2.54	7.0	6.0	3.91	8.3	13.11	895	2.85	0.06	0.66	0.21	126.7	1.03	0.28
San Mateo	Villa Tunari	13	62.59	1113	4.49	13.1	3.2	4.01	7.4	14.57	946	2.51	0.04	0.77	0.23	266.4	0.08	0.27
Grande	Abapo	14	16.52	56	2.62	16.4	16.1	9.07	11.6	18.37	1943	7.36	0.33	8.72	0.68	221.7	1.57	2.83
Grande	Santa Cruz	15	7.60	4	2.84	15.9	14.1	7.60	9.1	20.44	1921	20.35	0.13	12.39	0.75	325.0	0.08	3.93
Chimore	bridge	16	0.84	3089	23.14	46.5	4.1	28.49	2.4	9.60	426	0.61	0.31	0.27	0.12	109.7	0.15	0.02
Ichilo	bridge	17	3.93	4291	27.33	48.9	4.1	10.75	3.0	13.10	470	0.66	0.15	0.20	0.12	147.7	0.22	0.02
Yapacani	Yapacani	18	16.04	80	1.94	8.7	13.8	1.27	8.8	12.92	1240	4.54	0.03	0.50	0.07	399.1	0.06	1.25
Piray	Guardia	19	9.41	55	5.14	21.3	20.3	6.67	17.4	17.63	2342	6.67	0.05	0.62	0.10	182.6	0.21	3.47
Challa	Challa	20	6.54	1310	1.84	1.6	5.5	2.27	8.6	7.62	430	2.61	0.02	1.27	0.05	98.7	0.01	0.32
Grande	Puente Arce	21	10.18	75	4.63	38.8	7.5	14.35	13.3	72.05	3813	15.63	0.18	31.22	3.74	240.2	0.24	7.55
Mamore	Guayanamerin	22	8.21	2064	4.40	18.8	31.2	4.15	8.1	16.53	357	2.50	0.08	1.06	0.04	215.6	0.44	0.20
Yata	ferry-boat	23	2.74	353	3.37	11.3	8.4	10.67	4.3	12.99	43	0.30	0.04	0.22	0.02	47.8	0.11	0.13
Yata-1	bridge	24	48.92	218	2.75	14.6	6.1	19.23	29.7	41.99	253	2.10	0.01	0.17	0.09	82.2	0.15	0.07
Yvon	bridge	25	24.03	257	4.06	7.2	3.9	13.08	4.9	11.76	24	0.12	0.03	0.18	0.08	32.6	0.15	0.05
Madeira	Brazilian boundary	26	9.08	120	7.83	1.9	13.3	18.63	9.2	22.32	614	4.04	0.02	4.48	0.07	236.0	0.02	0.05

V: vanadium; Mn: manganese; Co: cobalt; Ni: nickel; Cu: copper; Zn: zinc; As: arsenic; Rb: rubidium; Sr: strontium; Mo: molybdenum; Cd: cadmium; Sb: antimony; Cs: caesium: Ba: barium; Pb: lead; U: uranium.

Chemical load carried by river water originates in the weathering of the different lithologies occurring in the catchment. In addition to the weathering processes of the main rock types, silicates, carbonates and saltrocks, atmospheric input may also contribute to the riverine dissolved load. Following Stallard & Edmond (1981), the influence of the rainwater input on the river chemistry of the Madeira River is extremely low, and does not account for more than 3% for Cl, Ca and K, and less for other elements. Consequently, river concentrations for major ions were not corrected for atmospheric input.

Factor analysis was used to evaluate relationships among the chemical components and the physical environment. Since Reeder *et al.* (1972), who studied the hydrochemistry of the surface waters of Mackenzie basin, and Stallard & Edmond (1983), who studied the hydrochemistry of the rivers of the Amazon basin, the multispatial techniques proved to be a pertinent tool in the interpreting of geochemical data. Our use of the principal extraction technique, with varimax normalization are similar to those of these authors.

Initial examination of the data indicated that the NO_3 concentrations in most of the samples are equal to or lower than the detection limits, and accordingly this variable was not included in the factor study. Moreover, one variable (SiO_2) failed to exhibit a normal frequency distribution using either raw data or logarithmic transforms and it was discarded for factor analysis. The concentrations of Na, K, Ca, Mg, alkalinity, Cl, SO_4, DOC, V, Mn, Co, Ni, Cu, Zn, As, Rb, Sr, Mo, Cd, Sb, Cs, Ba, Pb and U were used to form the correlation matrix. A second factor analysis was carried out on a distinct group of samples using the factor scores from the varimax solution of the chemical data, together with physical properties. The application of this technique to the 26 river data points (Tables 2 and 3) shows that the spread of the data is mainly located in a three-dimensional space. The first principal direction explains 48% of the total variance, the second one 24% and the third one 15%. The loading of the ions on these factors is illustrated in Fig. 2, and the varimax factor scores in Fig. 3.

Almost half of the variance among the elements is explained by factor 1, which we interpret as representing the weathering of halite deposits and sulphate minerals (mainly gypsum). Essentially all variance of Ca, Mg, Na, K, alkalinity, Cl, SO_4 in the surface waters of the Madeira drainage basin is accounted for by this factor. With the few exceptions of the headwaters draining the intrusive series of the Cordillera, the river waters from the Andean part of the basins of Beni and Mamore present Ca and Mg concentrations comprising at least 70% of the total cations and SO_4 and HCO_3, and 80% of the total anions (Guyot, 1993 and references therein). The highest factor scores are associated with the Rio Grande River which drains the saline and gypsiferous Mesozoic deposit (Magat, 1981) and also the Silurian-Devonian black schists. This formation often presents sulphur-rich white exudations at the surface, which are leached in the rainy periods. According to Roche & Fernández-Jáuregui (1988), such efflorescences should arise in part from the oxidation of pyrite, which yields sulphate solutions. The first factor is also characterized by a high positive score for Rb, Sr, Mo, Sb, Cs and U (higher than 0.7), and medium positive scores for Ba (0.51). Cs, Rb, Sr, U and Ba are usually found in evaporite and carbonate rocks (Sarin *et al.*, 1990; Palmer & Edmond, 1993) and their presence in this factor is to be expected. Mo and Sb geochemistry is less documented and we may only

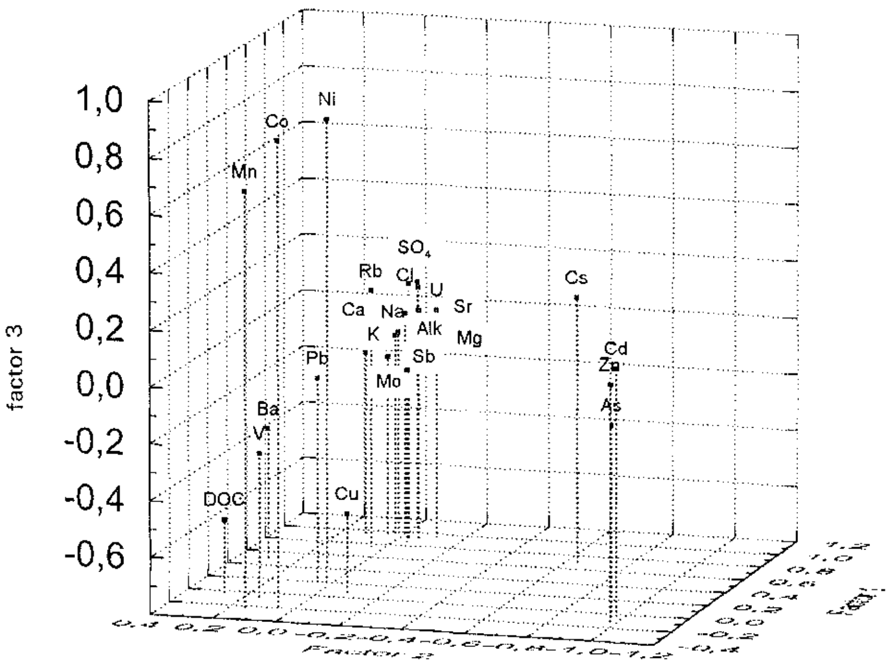

Fig. 2 Three-dimensional scatterplot of normalized varimax factor loadings of 26 chemical analyses from the rivers of the Madeira drainage basin (principal components extraction). Each chemical element is shown.

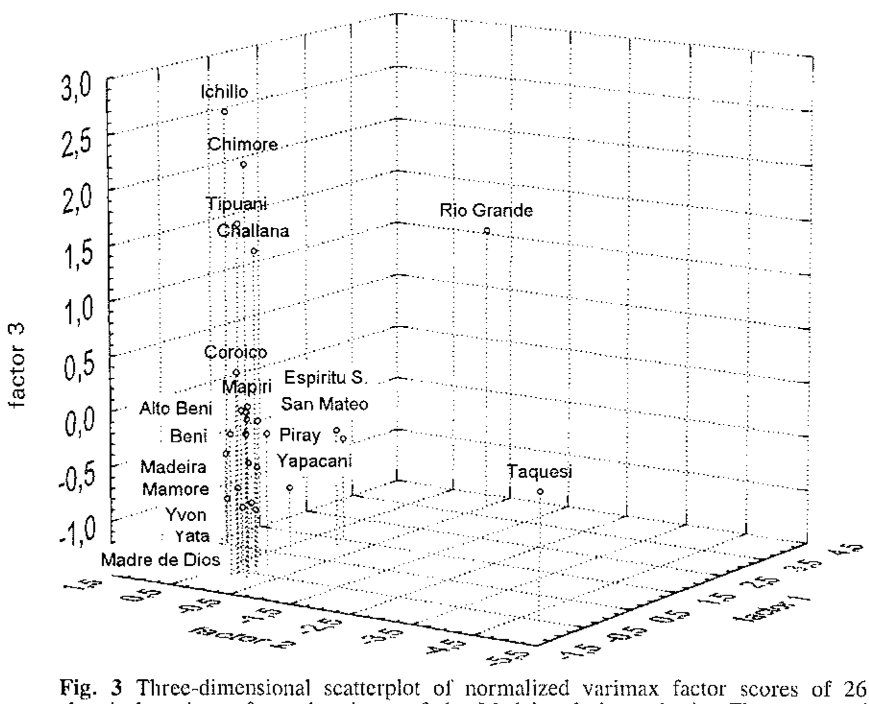

Fig. 3 Three-dimensional scatterplot of normalized varimax factor scores of 26 chemical analyses from the rivers of the Madeira drainage basin. The names of sampled rivers are shown.

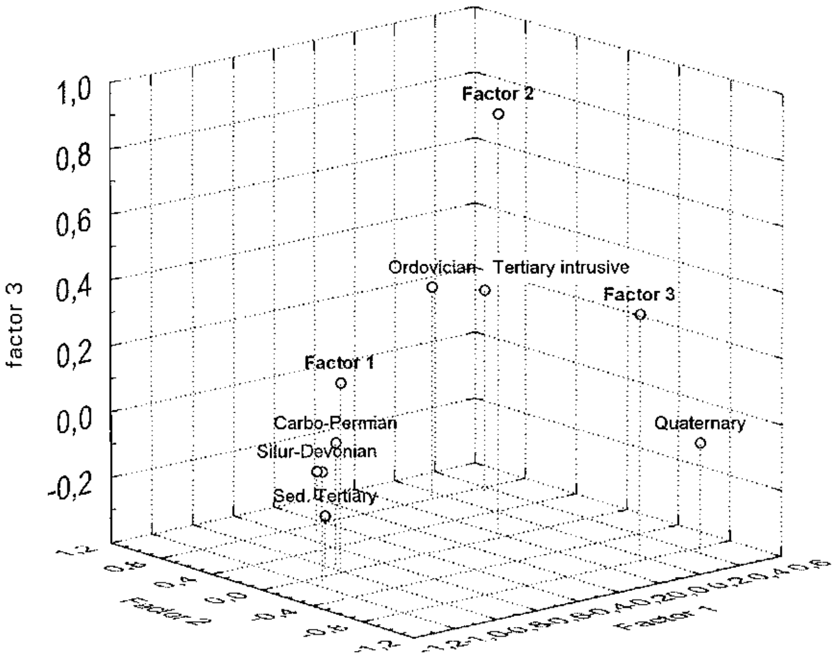

Fig. 4 Three-dimensional scatterplot of normalized varimax factor matrix of geological characteristics and factor scores for 21 surface waters from the Madeira drainage basin. The samples corresponding to the Mapiri River (contaminated) and the Rio Grande River (draining mainly evaporite rocks) have been discarded.

suppose a strong association of these elements with an evaporite weathering component.

The high negative score for As, Zn and Cd in the second factor suggest the influence of mining activities. No relationship between the geochemical characteristics and lithologies are discernible. The only sample showing a strong influence of factor 2 is from the Taquesi River, where active mining of lead (mainly as sulphides) and tin ore exploitation are located (Guyot, 1993). Acid waters from mine drainage flow directly into the Taquesi River, resulting in elevated concentrations of As (310 nM), Zn (218 nM) and Cd (1.66 nM). Conversely, a paucity of these elements, such as occurs in the rivers draining the same lithologies, results in low factor scores (Fig. 4). The third factor exhibits high positive scores for Co, Ni and Mn and medium negative scores for Cu, V and Dissolved Organic Carbon. The population represented by this factor is not homogeneous, with rivers flowing through different lithologies. The drainage basin of Ichillo and Chimore is mainly of Tertiary deposits, the Tipuani and Challana rivers flow through Ordovician arenaceous and argillaceous rocks and the Yata and Yvon rivers flow through Quaternary deposits.

Although the population sampled is not homogeneous and distinct groups are not obvious, it was decided to run a separate factor analysis on the sampled rivers which have components of factor 3. In this manner the individual effects of each of the new factors extracted could be emphasized to maximum advantage. Samples from the Rio Grande and Piray rivers were excluded owing to the presence of exposed evaporite and halite deposits, as were those from the Taquesi River because of the mining contamination. When the rock type data are combined with the three factors previously described, the trace metal signatures of rivers can be distinguished according to the lithology of the sub-basins (Table 1). Factor 1 (cations, anions and Rb, Sr, Mo, Sb, Cs, U) is associated with river samples flowing through Carbo-Permian, Siluro-Devonian and Tertiary sedimentary rocks (Tipuani, Challana and Alto Beni Rivers, Yapacani and Piray Rivers in the Mamore basin). Using our set of data, no further discrimination between these samples has been found. Factor 2 (As, Zn, Cd) appears to be associated with sampled rivers flowing through Ordovician terrain and Tertiary intrusive formations (Unduavi and Coroico Rivers). Factor 3 (Mn, Co, Ni, V and DOC) characterizes samples from rivers draining the Quaternary formations of the Amazon plain (Yvon and Yata Rivers). In these rivers, so-called "black rivers", the effects of vegetation and primary production may play important roles in the trace element dissolved concentrations. For instance, Co, Ni and V are known to have a nutrient-like behaviour with occurrence of cycles linked to the primary production of rivers (Edwards, 1973 and references therein), which is in agreement with our observations.

CONCLUSION

This study provides the first data on the geochemistry of trace elements in the Upper Madeira basin, which constitutes the Bolivian part of the Amazon basin. Using factor analysis to evaluate relationships among the dissolved trace element concentrations in river water and the environmental data, it appears that the substrate lithology exerts a fundamental control on the trace chemistry of surface waters within the catchment, at least in the Andean part of the basin. The most important source of trace elements is found in the weathering product of evaporite and associated deposits occurring in the Andean Palaeozoic and Cretaceous sections. Mining activity is clearly demonstrated by the high concentrations of Cd, Zn and As present in the Taquesi River. Secondary effects, such the influence of vegetation and/or biological uptake and release, probably play a role in the geochemistry of the lowland rivers.

This work must be considered as a preliminary study, and further investigations—in particular on the trace-element particulate load of these rivers—are needed to know more precisely the origin of some trace metals.

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