

## **Regional characteristics of the hydrochemistry in the humid tropics of Bolivian Amazonia**

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**Abstract** With an area of 872 000 km<sup>2</sup>, the Bolivian Amazon basin corresponds to the upper part of the basin of the River Madera, the principal southern tributary of the Amazon which has a mean discharge of 17 000 m<sup>3</sup> s<sup>-1</sup>. The Madera River receives 40 × 10<sup>6</sup> t year<sup>-1</sup> of dissolved material from its two principal tributaries (the Mamoré and the Beni) (1983–1989 average). The basins of these rivers include very contrasting biogeographical environments, from the glaciers of the eastern mountain chain of the Andes (6500 m a.m.s.l.), to the humid tropical rainforest of the Amazon plain (150 m a.m.s.l.). This work, based on the sampling of 395 rivers of the Amazonian basin of Bolivia, describes the major features of the regional distribution of the water chemistry (major elements of the dissolved phase) relative to the geology of the basin.

### **Caracterización regional de la hidroquímica en el tropico húmedo de la Amazonia de Bolivia**

**Resumen** Con una superficie de 872 000 km<sup>2</sup>, la cuenca amazónica de Bolivia corresponde a la parte alta de la cuenca del río Madera, principal afluente meridional del Amazonas, que tiene una descarga media de 17 000 m<sup>3</sup> s<sup>-1</sup>. El río Madera recibe de sus dos afluentes principales (ríos Mamoré y Beni) un flujo de materia disuelta de 40 × 10<sup>6</sup> ton año<sup>-1</sup> (en el período 1983–1989). Las cuencas de estos ríos corresponden a medios biogeográficos muy contrastados, desde los glaciares de la Cordillera Oriental de los Andes (6500 m.s.n.m.), hasta la selva tropical húmeda de la planicie amazónica (150 m.s.n.m.). Este trabajo, basado en el muestreo de 395 ríos de la cuenca amazónica de Bolivia, describe las tendencias mayores de la distribución regional de la química del agua (elementos mayores de la fase disuelta) en relación a los datos geológicos de la cuenca.

## **INTRODUCTION**

Since the work of Sioli (1968), who was the first to characterize the waters of the Amazon basin, there have been numerous studies in Brazil of the hydrochemistry of this vast basin, focussing on the large rivers and lakes of Varzea (Gibbs, 1967, 1972; Richey *et al.*, 1980, 1991; Stallard & Edmond, 1983; Furch, 1984; Forsberg *et al.*, 1988).

In Bolivia some observations of the chemistry of the waters of the Amazon basin have been conducted in the context of the biological populations (Pillari & Gihl, 1977; Corbin *et al.*, 1988), problems of irrigation in Andean valleys, and in a local hydrogeological study (Quintanilla *et al.*, 1989). However, comprehensive study of the physico-chemical behaviour of the rivers of the Amazon basin of Bolivia began with the projects of the PHICAB (Roche *et al.*, 1986, 1991; Roche & Fernandez, 1988; Guyot, 1993; Guyot *et al.*, 1987, 1991, 1993; Guyot & Wasson, 1994).

## SAMPLING AND ANALYSIS

This study was carried out on 395 rivers of various importance, from the glacier streams of the mountain chain of the Andes, to rivers of the Amazon plain, and including rivers in the semi-arid mountains (Fig. 1). Regular water sampling was conducted during different hydrological cycles at the most accessible sampling stations.

The number of samples obtained per station between 1983 and 1991 varied from 1–105, with an average value of two, and upper and lower quartiles (25% and 75%) of 1 and 5. For the stations of the PHICAB network, the number of samples varied from 35–105 depending on the commitment of the observers.

All the samples were analysed in La Paz at the laboratories of SENAMHI (conductivity; suspended matter by filtration and weight; colour and turbidity by spectrophotometry; bicarbonates by volumetry) and IIQ-UMSA (chloride, sulphate and dissolved silica by colorimetry; calcium, magnesium and iron by atomic absorption; sodium and potassium by flame spectroscopy).

## ATMOSPHERIC CONTRIBUTIONS

The atmosphere is an important source of dissolved materials in surface waters. The estimate of land surface contributions to the solutes in rivers is influenced by this atmospheric input. Generally the concentration of chlorides in rainfall, and so the atmospheric input to rivers, is inversely proportional to the distance from coasts (Meybeck, 1983). In the Amazon basin, there is a clear progressive decrease in the chloride concentration of rainwaters with distance from the Atlantic Ocean and this is evident over 3000 km from the ocean. These atmospheric contributions are not dominant except in the rivers of the coastal zone (Stallard & Edmond, 1981). Using the data and the calculation method of Stallard, the chloride concentration of oceanic origin in the rivers of the Madera basin in Villa Bella was calculated as between 4 and 6 mmol l<sup>-1</sup> (or 0.14–0.21 mg l<sup>-1</sup>), going from west to east in the basin. As these concentrations are equivalent to the precision of the analyses of chlorides carried out in La Paz, a correction factor for the atmospheric contributions has not been used in this study.

## THE RESULTS

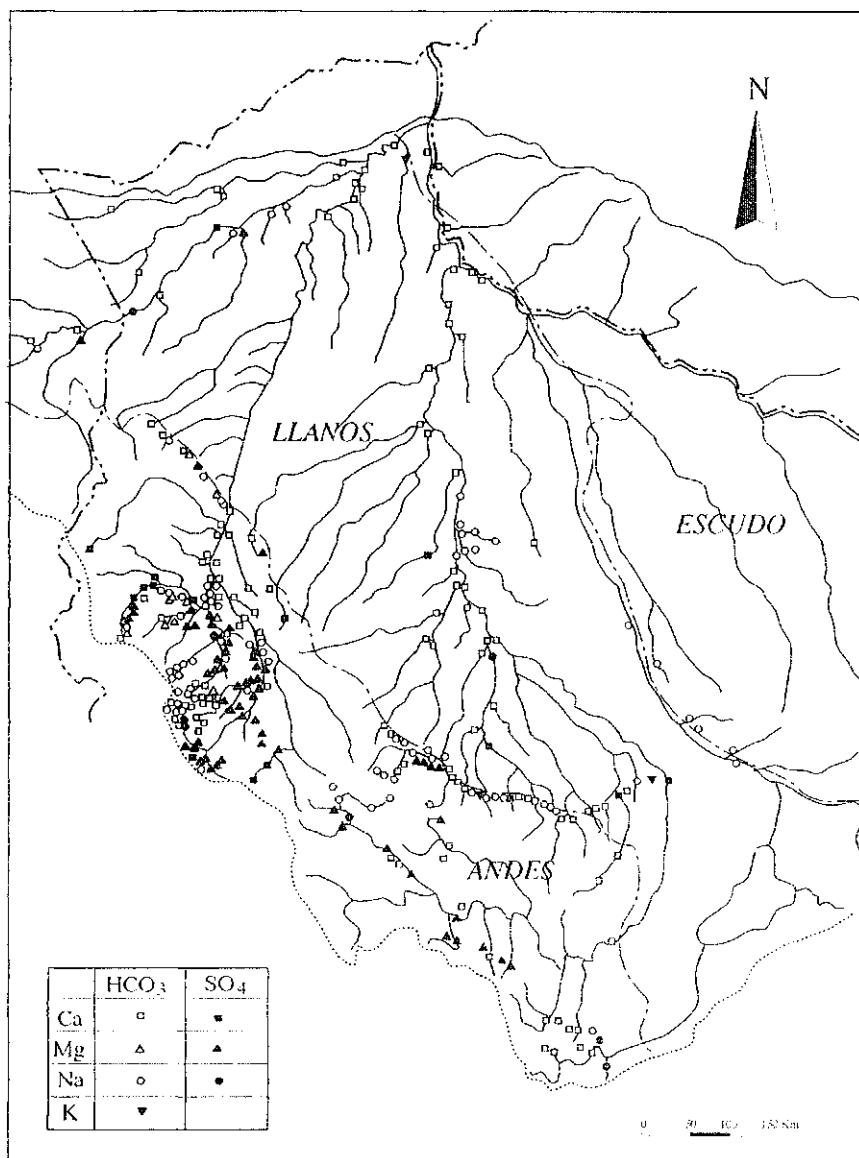


Fig. 1 Map of the dominant ions of the rivers of the Bolivian Amazon, 1983–1991.

Roche *et al.* (1986). The Andean basin of the River Beni (Alto Beni), includes the river drainage of the Kaka and Alto Beni, as well as that originating from the Andes (rivers Madidi, Tequeje and others) that join the River Beni on the plains.

The Andean basin of the Grande River includes the rivers draining into the Grande River and also the River Parapetí to the south and the rivers Pirai and Yapacaní to the north. The eastern Andean basins include the Andean tributaries of the Mamoré River located to the west of the Yapacaní River (rivers Ichilo, Ichoa, Sajta, Chimoré, Chaparé, Securé, Isiboro, Apere, Yacuma and others). The plains are classically subdivided in to two sub-basins, that of the Beni River and that of

Mamoré River. The shield was barely sampled because of the difficulty of access and remoteness from La Paz. The ten rivers sampled on the shield belong to the basin of the Mamoré River which is irrigated by the discharge from the Itenez River (Rivers Guaporé, Blanco-Baures, Itonomas, San Julián and others).

The altitude and the temperature of the water at the sampling points indicates the Andean dominance of each basin (Fig. 2). In the basin of the Alto Beni, the altitudinal range is greatest, but the average is less than 1000 m, while in the basin of the large river, the average is close to 2000 m.

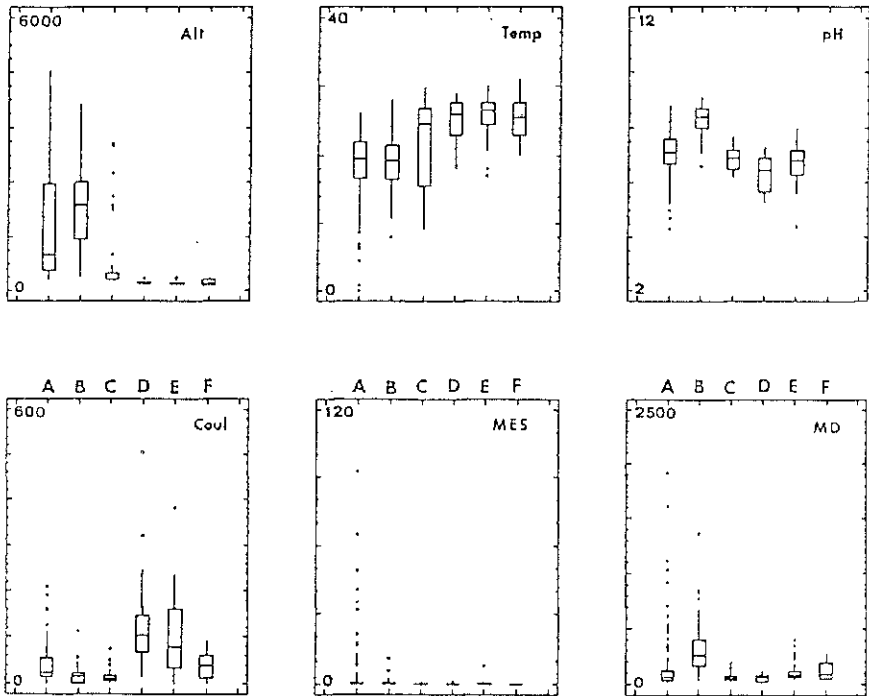


Fig. 2 Statistical distribution (median, quartile, deciles and extreme) of the physicochemical properties of the rivers of the Bolivian Amazon, 1983-1991. A = Alto Beni, B = Grande, C = Eastern basins, D = Beni, E = Mamoré, F = Shield.

In the eastern Andean basins, the altitudes are clearly less in spite of some extreme values that translate a sample essentially into a piedmont. The graph of the shield data should be interpreted with caution due to the smaller number of samples (12 stations).

Clearly higher values of pH were measured in the basin of the Grande River. The lowest pH averages were obtained in the plains, though the minimal values occurred in waters having low dissolved matter concentrations as a result of the oxidation of iron pyrites.

The most coloured waters are found on the plains due to the presence of organic matter. The suspended matter (MES) medians and quartiles are presented in Fig. 2. Extreme values can reach  $100 \text{ g l}^{-1}$  in the basin of the Alto Beni (region of La Paz).

The regional dispersion of the dissolved matter values is larger in the Andes than in the Amazon plain, with high values in the basin of the Grande River, and low values in the plains and the eastern Andean basins. The waters that drain the Brazilian shield have an intermediate mineralization and the Alto Beni presents a moderate value despite very large extreme values, indicating a heterogeneous basin. The distribution of the concentration of dissolved matter is a function of altitude. Figure 3 shows that the strongest concentrations are observed in the basins of the Rivers Alto Beni and Grande, but low concentrations are observed in all the basins studied.

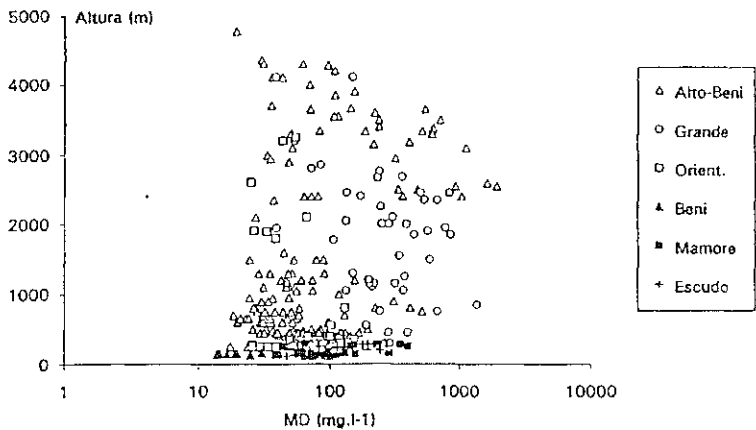


Fig. 3 Dissolved matter and altitude of rivers of the Bolivian Amazon. Average values for the period 1983-1991.

Figure 4 demonstrates that the sum of cations presents a distribution comparable to that of the dissolved matter. The variation within this distribution is seen in the graphs of the dominant major elements (bicarbonate, sulphate, calcium, magnesium and sodium). However the potassium concentrations are relatively higher in the plains and the shield, although strong concentration are observed in the Andean basins in association with drainage of evaporite deposits. The iron concentrations are

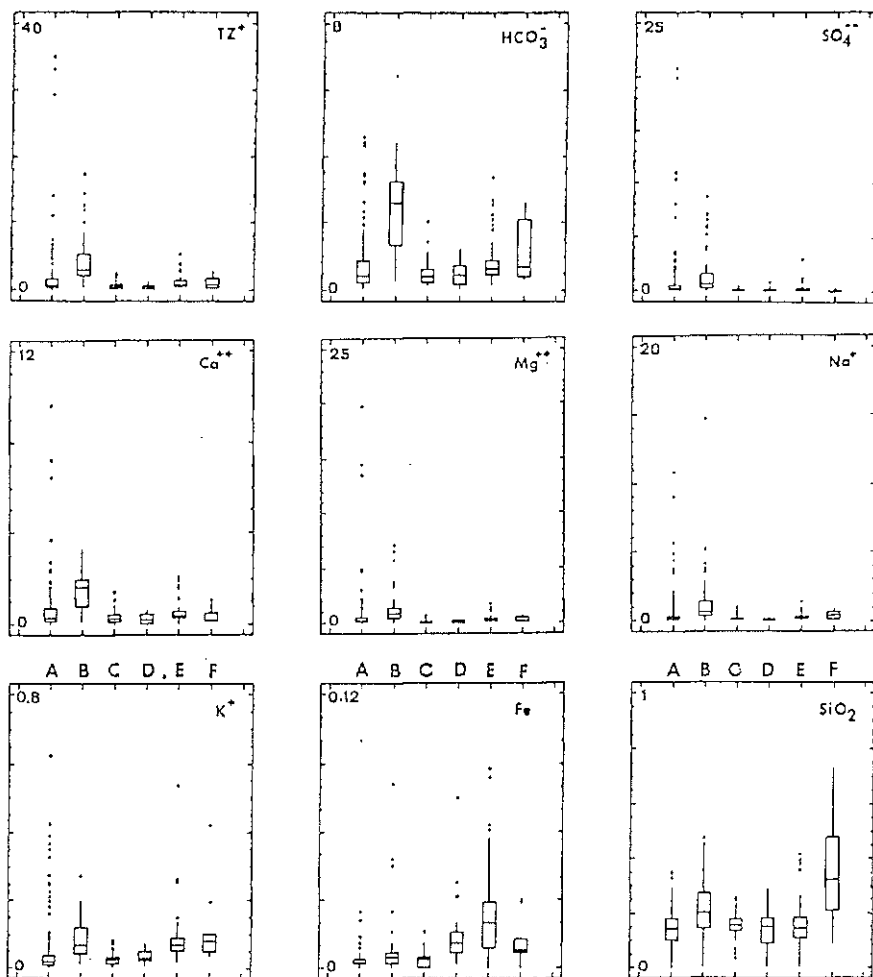


Fig. 4 Statistical distribution (median, quartile, deciles and extreme) of the major elements in solution in the rivers of the Bolivian Amazon, 1983-1991.  $\Sigma Z^+$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Fe}^{3+}$  in  $\text{meq l}^{-1}$ ,  $\text{SiO}_2$  in  $\text{mmol l}^{-1}$ .

The function of the dominant ions can be defined by different hydrochemical facies. Most of the rivers are of bicarbonate type, most frequently calcium or magnesium, but sometimes sodium, and rarely potassium (Fig. 1). In the Andes and in some rivers of the plains, the waters sampled were sulphated and correspond, as a rule, to stronger salinities.

#### THE HYDROCHEMICAL CHARACTERISTICS OF THE ANDEAN BASINS

About 300 rivers in the Andean basins were the subject of hydrochemical analysis; 66% of these were in the basin of the Alto Beni which is closer to La Paz and more accessible. The greatest concentrations ( $>1000 \text{ mg l}^{-1}$ ) occurred in the semi-arid

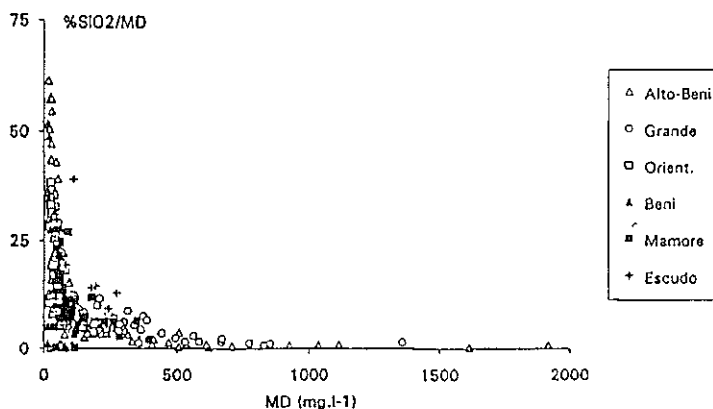


Fig. 5  $\text{SiO}_2/\text{MD}$  vs MD, rivers of the Bolivian Amazon. Mean values for the period 1983–1991.

zones of the region of La Paz–Luribay, as well as in the basins of the Grande and Parapeti Rivers. These are associated with sulphated-magnesium facies, or even sulphate-sodium. The lowest concentrations ( $< 50 \text{ mg l}^{-1}$ ) are found upstream of the hydrological systems of the Real mountain chain, or in the zones of the Chapare piedmont. They are substantially associated with bicarbonated-calcium or magnesium facies. The coefficients of variation ( $\text{CV} = \text{deviation type/average}$ ) of the parameters studied demonstrate that the regional variability is greatest for suspended materials and turbidity. Silica seems to be the most stable element of the dissolved materials.

### Alto Beni River basin

In the basin of the Alto Beni, the tributaries of the rivers Tipuani, Challana, Zongo, Coroico, Unduavi, Taquesi, Tamampaya and Miguillas, that drain the crests of the Real mountain chains and of Quimsa Cruz, as well as thick Ordovician sedimentary deposits, have concentrations of dissolved material of less than  $100 \text{ mg l}^{-1}$ . The silica concentrations frequently exceed 5% of the total mineralization. The waters are almost exclusively bicarbonated, with some rivers sulphate dominant due to the abundant presence of pyrites. In the valley of Sorata-Consata-Mapiri, upstream concentrations ( $< 100 \text{ mg l}^{-1}$ ) are comparable to those of the Rivers Tipuani and Challana. The marked increase in salinity, as well as suspended material, observed upstream in the River Consata, of  $300\text{--}500 \text{ mg l}^{-1}$ , are due to erosion of Silurian-Devonian sediments. The waters of this river are sulphated-calcium, due to the presence of gypsum series which are locally karstified. Therefore, the dissolved matter concentrations will not decrease downstream due to dilution by less mineralized waters.

In the basin of the La Paz, Sapahaqui and Luribay, the same phenomenon is observed with bicarbonated waters having low dissolved matter concentrations in the high basin of the Palca River, that drains the intrusive formations of the Illimani. In La Paz, the rivers originating from the Plio-Quaternary sedimentary series (rivers Huayllani, Quellumani, Achumani) have large suspended matter loads and dissolved

matter concentrations of between 100 and 300 mg l<sup>-1</sup>. Downstream, the salinity increases strongly as the rivers cross the Silurian-Devonian sediments and concentrations of 500–2000 mg l<sup>-1</sup> are frequently observed in the sulphated waters. The increase in the salinity in the basins of the Rivers Consata, Mapiri, La Paz, Sapahaqui and Luribay, as they cross the Silurian-Devonian sediments, is probably related to the presence of gypsum and also to alteration of black shales. This alteration produces white deposits which dissolve during rainy periods. At low water, similar saline deposits appear in the desiccated riverbeds. Geochemical analysis of these deposits showed that they have a substantial sulphate and magnesium content (Roche *et al.*, 1986). The two main elements (S and Mg) are highly soluble and cause the strong mineralization of waters crossing this region. Further downstream, as they cross the sub-Andean, the Rivers Kaka, Boopi and Alto Beni receive contributions from modest tributaries whose concentrations are between 100 and 200 mg l<sup>-1</sup>, and almost always bicarbonated calcium or magnesium. The increase in the salinity in the sub-Andean is probably related to the Tertiary sedimentary deposits that are widely represented in the region. The Andean tributaries of the Beni River that drain the northern edge of the Andes (of Rurrenabaque to Ixiamas) present the same characteristics.

### **Grande River basin**

In the basin of the Grande River, which has a very arid climate, the observed concentrations vary from 40 to 1000 mg l<sup>-1</sup>, and reach values of 1400 mg l<sup>-1</sup> in the basin of the Parapetí River located further south. The lowest concentrations are observed upstream, in the buttresses of the mountain chain of Tunari, near Cochabamba; the waters are bicarbonated-calcium type. The most strongly concentrated waters are also those that transport more suspended materials and originate from Silurian-Devonian deposits which are drained by the western tributaries of the Caine River (rivers Tapacarí and Arque). The facies of these waters is generally sulphated magnesium.

As the waters traverse the valley of Cochabamba, the salinity also increases due to erosion of saline and gypsum deposits of the Mesozoic (Ahlfield & Branisa, 1960). Downstream, in the region of Torotoro, the tributaries of the right bank are carbonated karstified by the Cretaceous rocks; the bicarbonated calcium waters have concentrations of between 200 and 400 mg l<sup>-1</sup>. The Andean tributaries of the Grande River in the plains (rivers Yapacaní and Pirafí) also have concentrations between 200 and 400 mg l<sup>-1</sup>, and one facies of bicarbonated calcium. Dissolved silica rarely represents more than 10% of the mineralization in these Andean basins.

### **Eastern Andean basins**

In the eastern Andean basins, the observed concentrations are clearly lower, never exceeding 150 mg l<sup>-1</sup>. In the Chapare the median concentrations are frequently less than 50 mg l<sup>-1</sup>. The waters are generally of type bicarbonate calcium, sometimes



magnesium. Greater concentrations are observed in the sub-Andean, in the Villa Tunari region where the tributaries of the Chapare River have concentrations slightly greater than  $100 \text{ mg l}^{-1}$ . The same occurs in the Andean tributaries of the Yacuma River, as well as with the tributaries of the Beni River. This slightly higher salinity seems to originate from the Tertiary sedimentary series of the sub-Andean.

## THE HYDROCHEMICAL CHARACTERISTICS OF THE PLAINS

In the plains of the basin of the Madeira River in Villa Bella, 88 rivers were sampled, regardless of their originating from the Brazilian shield; 35 belong to the basin of the Beni River and 53 to the basin of the Mamoré River. The concentrations found are generally lower than in the Andes due to the phenomenon of dilution by bank-side contributions to the rivers of the plains. The strong concentrations of the Grande River prevail quite far downstream. The coefficients of variation of each element show that the regional variability of the concentrations is lower in the plains than in the Andes, particularly for chloride, magnesium, sodium and iron. The Grande River causes this variability.

### Beni River basin

In the basin of the rivers Beni, Madre de Dios and Orthon, the rivers of the plain

## THE HYDROCHEMICAL CHARACTERISTICS OF THE BRAZILIAN SHIELD

A dozen rivers of the plain, originating from the Brazilian shield, were sampled. The small number of samples is due to access difficulties and the distance from La Paz. Despite the small sample, the coefficients of variation obtained indicate a regional variability in concentration.

The analytical results permit distinction of two types of rivers. The tributaries of the right bank of the Mamoré River (Rivers Negro and Ouro Preto), as well as the Guaporé-Itenez River, have low concentrations ( $<50 \text{ mg l}^{-1}$ ) and are of type bicarbonated calcium. These rivers mainly drain the acid plutonic Precambrian rocks of the socle (Pareja *et al.*, 1978). A second group is composed of more mineralized rivers ( $80\text{--}300 \text{ mg l}^{-1}$ ) which are generally bicarbonated sodium type. These rivers drain the southern edge of the socle and flow through rocks of the metamorphic Precambrian complex.

## REFERENCES

- Ahlfeld, F. & Branisa, L. (1960) *Geología de Bolivia*. Don Bosco, La Paz, Bolivia.
- Corbin, D., Guyot, J. L., Calle, H. & Quintanilla, J. (1988) Datos físico-químicos de los medios acuáticos de la zona del Mamoré central, región de Trinidad, Amazonia Boliviana. *ORSTOM, La Paz, Bolivia. Publ. no. 8*.
- Forberg, B. R., Devol, A. H., Richey, J. E., Martinelli, L. A. & Los Santos, H. (1988) Factors controlling nutrient concentrations in Amazon floodplain lakes. *Limnol. Oceanogr.* 33(1), 41–56.
- Furch, K. (1984) Water chemistry of the Amazon basin: The distribution of chemical elements among freshwaters. In: *The Amazon* (ed. by H. Sioli), 167–199. W. Junk, Dordrecht, The Netherlands.
- Gibbs, R. J. (1967) The geochemistry of the Amazon River system. Part 1: The factors that control the salinity and the composition and concentration of the suspended solids. *Geol. Soc. Amer. Bull.* 78, 1203–1232.
- Gibbs, R. J. (1972) Water chemistry of the Amazon River. *Geochim. Cosmochim. Acta* 36, 1061–1066.
- Guyot, J. L. Hydrogéochimie des fleuves de l'Amazonie Bolivienne. *Collection Etudes et Thèses, ORSTOM, Paris*.
- Guyot, J. L. & Wasson, J. G. (1994) Regional pattern of riverine Dissolved Organic Carbon in the Bolivian Amazonian drainage basin. *Limnol. Oceanogr.* 39(2), 452–458.
- Guyot, J. L., Calle, H., Quintanilla, J. & Calliconde, M. (1987) Resultados de una campaña de muestreo en período de aguas bajas en la Amazonia boliviana. *Revista Boliviana de Química* 7(1), 36–50.
- Guyot, J. L., Bourges, J., Cortes, J., Jouanneau, J. M., Quintanilla, J. & Roche, M. A. (1991) Regimes hidroquímicos e dos sedimentos dos rios da bacia amazônica da Bolívia. In: *Simpósio Brasileiro de Recursos Hídricos, Rio de Janeiro, Novembro 1991*, 149–158. Associação Brasileira de Recursos Hídricos.
- Guyot, J. L., Corbin, D., Quintanilla, J. & Calle, H. (1991) Hydrochimie des lacs dans la région de Trinidad (Amazonie Bolivienne). Influence d'un fleuve andin: le Rio Mamoré. *Revue d'Hydrobiol. Tropicale* 24(1), 3–12.
- Guyot, J. L., Jouanneau, J. M., Quintanilla, J. & Wasson, J. G. (1993) Les flux de matières dissoutes et particulaires exportés des Andes par le Rio Beni (Amazonie Bolivienne), en période de crue. *Geodinamica Acta* 6(4), 233–241.
- Magat, P. (1981) Première évaluation de la géochimie des eaux dans les vallées de la Cordillère orientale de Bolivie. *ORSTOM/UMSS, Cochabamba, Bolivia*.
- Meybeck, M. (1983) Atmospheric inputs and river transport of dissolved substances. In: *Dissolved Loads of Rivers and Surface Water Quantity/Quality Relationships* (ed. by B. W. B. Webb) (Proc. Hamburg Symp., August 1983), 173–192. IAHS Publ. no. 141.
- Meybeck, M. (1986) Composition chimique des ruisseaux non pollués de France. *Bull. des Sciences Géologiques* 39(1), 3–77.
- Pareja, J., Vargas, C., Suarez, R., Ballon, R., Carrasco, R. & Villarroel, C. (1978) *Mapa geológico de Bolivia, memoria explicativa*. Yacimientos Petrolíferos Fiscales Bolivianos y Servicio Geológico de Bolivia, La Paz, Bolivia.
- Pilleri, G. & Gühr, M. (1977) Observations on the Bolivian and the Amazonian Bufo with a description of a new subspecies. In: *Investigations on Cetacea* Vol. VII (ed. by G. Pilleri), 11–76.
- Quintanilla, J., Gemio, R., Calliconde, M., Martínez, J. & Wirmann, D. (1989) Estudio preliminar de la hidrología e hidroquímica de la laguna Santa Rosa. *Revista Boliviana de Química* 8(1), 49–56.
- Richey, J. E., Brock, J. T., Naiman, R. J., Wissmar, R. C. & Stallard, R. F. (1980) Organic carbon: oxidation and transport in the Amazon River. *Science* 207, 1348–1351.

- Richey, J. E., Vitoria, R. L., Salati, E. & Fosberg, B. R. (1991) The biogeochemistry of a major river system: the Amazon case study. In: *Biogeochemistry of Major World Rivers* (ed. by E. T. Degens, S. Y. Kempe & J. E. Richey), 57-74. Wiley, Chichester, UK.
- Roche, M. A., Fernandez, C., Apoteker, A., Abasto, N., Calle, H., Toleda, M., Cordier, J. P. & Pointillart, C. (1986) *Reconnaissance hydrochimique et première évaluation des exportations hydriques et salines des fleuves de l'Amazonie bolivienne*. PHICAB, La Paz, Bolivia.
- Roche, M. A. & Fernandez, C. (1988) Water resources, salinity and salt yields of the rivers of the Bolivian Amazon. *J. Hydrol.* **101**, 305-331.
- Roche, M. A., Fernandez-Jauregui, C., Aliaga, A., Bourges, J., Cortes, C., Guyot, J. L., Peña, J. & Rocha, N. (1991) Water and salt balances of the Bolivian Amazon. In: *Water Management of the Amazon Basin* (ed. by B. P. F. Braga & C. Fernandez-Jauregui), 83-94. UNESCO-Rostlac, Montevideo, Uruguay.
- Sioli, H. (1950) Das Wasser im Amazonasgebiet. *Forschungen und Fortschritte* **21/22**, 274-280.
- Sioli, H. (1968) Hydrochemistry and geology in the Brazilian Amazon Region. *Amazoniana* **1**(3), 267-277.
- Stallard, R. F. & Edmond, J. M. (1981) Geochemistry of the Amazon. 1. Precipitation chemistry and the marine contribution to the dissolved load at the time of peak discharge. *J. Geophys. Res.* **86**(10), 9844-9858.
- Stallard, R. F. & Edmond, J. M. (1983) Geochemistry of the Amazon. 2. The influence of geology and weathering environment on the dissolved load. *J. Geophys. Res.* **88**(14), 9671-9688.