



Controls on water chemistry of the Pilcomayo river (Bolivia, South-America)

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Abstract

In order to reveal the intra-annual variability of the major ion composition of the Pilcomayo river, a dryland river, and its relationship to discharge, water samples were taken at regular time intervals from May 1998 until February 1999 at the town of Villa Montes (Bolivia). Water chemistry of the Pilcomayo river was highly variable during the year and strongly influenced by differences in discharge between the wet and the dry season. Halite dissolution appeared to play an important role and both Cl and Na concentrations became very high ($\pm 10 \text{ mmol L}^{-1}$) during the dry season. Pyrite weathering and dissolution of gypsum, dolomite and calcite determined Ca, Mg, CO_3 and SO_4 chemistry. At the onset of the rainy season 'rinse out' effects occurred, resulting in marked concentration peaks especially for the least soluble ions. Possible effects on biota, such as consequences for trace metal toxicity, are discussed briefly.

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1. Introduction

The Pilcomayo river in Bolivia has been studied since the late 1960s (Bayley, 1973). As the Pilcomayo is populated by various migratory fish species which are important for the local (commercial) fishery much effort has been devoted to study the dynamics of fish populations in the river (Bayley, 1973; Payne and Harvey, 1989; Smolders et al., 2000, 2002). During the 1990s it became clear that the river was also progressively contaminated by mine tailings from the Potosí mining district, and studies were undertaken to reveal the possible effects of this contamination on the river system and its biota (Edwards, 1996; Garcia-Guinea and Huascar,

1997; Medina Hoyos, 1998; Smolders et al., 1999, 2002; Hudson-Edwards et al., 2001; Miller et al., 2002).

An important feature of dryland rivers, such as the Pilcomayo, is their extreme inter-annual and inter-seasonal variability in discharge (Davies et al., 1996). Inter-annual variation can be very large and seems to be affected by large scale climatic events such as ENSO (El Niño Southern Oscillation), which may have a strong influence on rainfall (Poveda and Mesa, 1997; Puckridge et al., 2000; Smolders et al., 2000, 2002). Such inter-annual variations may have a strong effect on river ecology. Smolders et al. (2000, 2002), for instance, found a strong effect of ENSO on the mean annual discharge of the Pilcomayo river (Bolivia) and established an effect of discharges in preceding years on the migratory Sábalo fish (*Prochilodus lineatus*) catches. Increased river discharge restores the connectivity with the river and increases the area of the floodplain that becomes

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inundated and thereby the surface area of the feeding grounds of migratory fish (Laë, 1992; Hamilton, 1999).

Inter-seasonal variation is also extreme in dryland rivers as, frequently, a clearly marked dry and rainy season can be distinguished. In the case of the Pilcomayo river, for instance, river discharge can become very low in the dry season ($<5 \text{ m}^3 \text{ s}^{-1}$) while in the rainy season river discharges can become very high ($>1000 \text{ m}^3 \text{ s}^{-1}$) (Bayley, 1973; Guyot et al., 1990; Smolders et al., 2002). These different hydrological regimes are likely associated with important variations in water chemistry and may have important effects on the functioning of aquatic ecosystems. In the case of the contaminated Pilcomayo river, such processes may also be highly important by altering the speciation and availability of potentially toxic metals (Playle, 1998).

Macro-ion composition of river water is determined by weathering processes. Weathering of evaporites (such as halite and carbonates) creates waters with relatively high concentrations of total dissolved solids (TDS), and weathering of silicates results in waters with low TDS (Stallard and Edmond, 1983, 1987). Because water chemistry may change as water passes from one geological environment to another, many hydrochemical studies regarding the processes involved in the evolution of major ion composition of river basins are based on spatial variation (Gibbs, 1970; Stallard and Edmond, 1983, 1987; Bartarya, 1993; Edmond et al., 1996; Elbaz-Poulichet et al., 1999; Négrel and Lachassagne, 2000; Dalai et al., 2002). In such studies water chemistry data collected in different parts of a river catchment are used to model the possible relationship between geology and the chemical composition of water samples. These models are based on equilibria among secondary minerals and salts formed by weathering and may predict the chemistry of the source rock involved.

In dryland rivers, however, fluctuations of discharge may have enormous effects on the hydrochemistry of the river (Allen, 1995; Davies et al., 1996). Equilibria of secondary minerals will be greatly affected by evaporation and dilution and may result in a highly dynamic water chemistry. In general, concentrations of major ions are negatively related to discharge, due to dilution and precipitation effects (Gibbs, 1970; Allen, 1995). However, because of differences in solubility not all ions are equally affected by these processes (Drever, 1997). 'Rinse-out effects', caused by the dissolution of precipitated salts at the onset of the rainy season, may cause temporary strong increases of major ion concentrations, despite dilution effects caused by increased discharge (House and Warwick, 1998; Keith et al., 2001). Application of geochemical modeling on time series of field data that include both data on chemical composition and data on river discharge would be highly desirable, especially in the case of highly dynamic river systems. Such data are scarce for most tropical dryland rivers. To

date, for instance, no thorough analysis of the water chemistry of the Pilcomayo river has been made, and therefore information on the relationship between discharge and major ion composition has been lacking.

In order to obtain information on the intra-annual variability of the major ion composition, water samples have to be collected at regular time intervals, preferably during an entire year. Detailed data on river discharge will also have to be available. Between May 1988 and February 1999, data on water chemistry and river discharge have been compiled for the Pilcomayo river. In this paper, seasonal variations of the macro-ion composition of the Pilcomayo river are described and discussed in terms of possible weathering reactions involved in water chemistry genesis and effects of discharge on intra-annual variations of ion concentrations. The possible effects on biota, including consequences for trace metal toxicity, will be discussed briefly.

2. Materials and methods

2.1. Pilcomayo catchment

The South-American Pilcomayo river (Fig. 1) is a tributary to the large 'La Plata' system and has a basin area of $\approx 98,000 \text{ km}^2$. The river arises in the Bolivian Andes (Cordillera Oriental, at $\approx 5000 \text{ m}$ above sea level) and cuts down through the Andes, through an inaccessible terrain with rapids and narrow canyons, until it reaches the Chaco plain near the town of Villa Montes ($\approx 400 \text{ m}$ above sea level). The Andean part of the river has a length of $\approx 500 \text{ km}$ and a mean slope of 10 per mill. The river then flows southward through the Chaco, where it forms the frontier between Argentina and Paraguay before it joins the Paraguay river just north of the town of Asunción (Fig. 1).

The upper parts of the Pilcomayo river have as yet not been regulated by dams or other hydro-technical works. The river is strongly influenced by the hydrological cycle, which is driven by the differences in rainfall between the dry (May–October; winter) and the wet seasons (November–April; summer). In the rainy season the susceptibility to erosion of the soils in the Andean region results in a very high load of suspended matter that consists of a very fine gray, quartz-rich sand (Guyot et al., 1990; Smolders et al., 2002). The fluvial deposits of the river have created a huge alluvial fan system (Iriondo, 1993; Wilkinson and Mohler, 1995). Alluvial sedimentation has interrupted the former direct connection between the upper reaches of the Pilcomayo river and the Paraguay river. In the Paraguay–Argentine territory large areas of land are inundated by the river during the rainy season; these floodplains serve as important feeding-grounds for many migratory fish species.

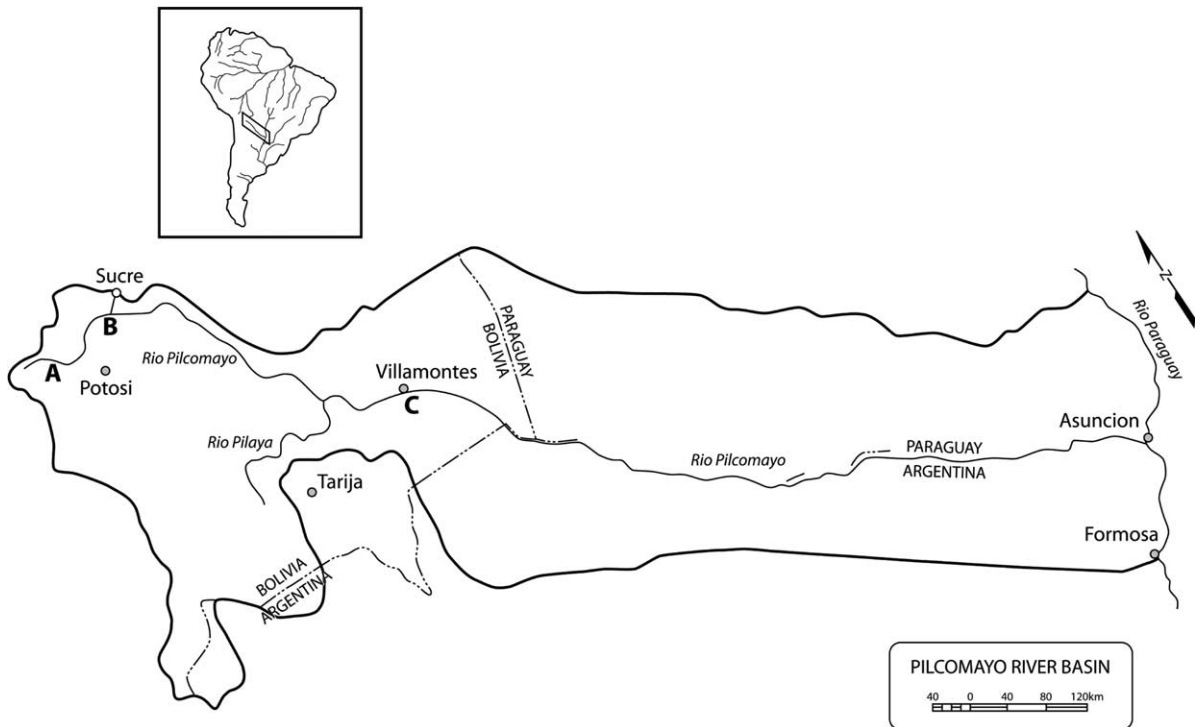


Fig. 1. Map of the Pilcomayo catchment. Sample locations: (A) Poituco, (B) Potosi and (C) Villa Montes.

2.2. Geology of the Pilcomayo catchment

The Pilcomayo catchment is underlain by Ordovician, Silurian, Cretaceous, Tertiary and Quaternary volcanic and sedimentary rocks that are intruded by dacites, quartz porphyries and adamellites. Deposits of halite, gypsum and carbonates are also present in the catchment (Rivas Valencuele, 2002). The Río Pilcomayo receives tailings effluent, which contains pyrite and other sulphide minerals, from the Cerro Rico mines at its headwaters at Potosí (Hudson-Edwards et al., 2001). Calcite, dolomite, albite, kaolinite, muscovite, chlorite and quartz are also present in Pilcomayo suspended sediments. Gypsum has been observed lining the banks of the upper Río Pilcomayo, and is interpreted to form as a consequence of the weathering of pyrite-bearing tailings and Ca-bearing minerals such as carbonates and feldspars (Hudson-Edwards et al., 2001).

2.3. Sample collection and analysis

From May 1998 until February 1999, water samples were collected in the Pilcomayo river near the town of Villa Montes (Bolivia) (Fig. 1). Samples were taken approximately 4 times a month. At Villa Montes the Pilcomayo river leaves the Andean zone and enters the Chaco plain. Water quality at Villa Montes can there-

fore be considered the overall result from the weathering, dilution, and precipitation processes in the Andean part of its catchment.

Immediately after collection temperature was measured and pH and HCO_3^- were determined using methods described in Roelofs (1983), after which samples were filtered ($0.45 \mu\text{m}$). One ml of conc. HNO_3 per 100 ml water was then added, and the samples were stored in pre-washed polyethylene containers at -20°C until analysis. For anion analyses samples were filtered ($0.45 \mu\text{m}$) and 60 mg citric acid per 100 ml water was added. Samples were stored in pre-washed polyethylene containers at -20°C until analysis.

In July 1999, sediment samples ($n = 5$) were collected at Poituco (A), Puente Sucre (B) and Villa Montes (C) (see Fig. 1 for exact locations) by means of a core sampler from the upper 10 cm of the sediment layer. Sediment samples were dried during 48 h at 70°C . After homogenization the sediment samples were digested with HNO_3 and H_2O_2 in sealed teflon vessels in a microwave oven (Milestone, type mls 1200 Mega). Samples were diluted after digestion.

Water samples and sediment digestates were analysed for Ca, Mg, Si, Sr, Fe and S on an inductively-coupled-plasma emission spectrophotometer (ICP) (Spectro Analytical Instruments, type Spectroflame, Kleve, Germany). In water samples (Cl^-) and SO_4^{2-} were analysed

colorimetrically; Cl^- according to O'Brien (1962) and SO_4^{2-} according to Technicon AutoAnalyzer Methodology (1981). Na and K were measured by flame photometry (FLM3 Flame Photometer, Radiometer, Copenhagen, Denmark). Blanks and standard samples were run to check accuracy.

Detailed river discharge data were obtained from an Argentinean monitoring station (La Paz hydrological station), located downstream of Villa Montes. These data were provided by EVARSA (Buenos Aires).

Saturation indices were calculated using Geochemist's Workbench[®] v. 4.0 (cf. Bethke, 1996).

3. Results and discussion

3.1. Discharge and overall water chemistry

The hydrochemistry of the Pilcomayo river is influenced strongly by the hydrological cycle (Figs. 2 and 3). During the dry winter season (May until October) river discharges show a gradual decline while concentrations of major anions and cations increase concomitantly. For most ions the increase gradually becomes weaker with decreasing river discharges and concentrations reach maximum values when river discharges become very low. Only Na and Cl show a distinct pattern, with increases becoming progressively more marked as river discharges further decrease. In the first week of October 1998, when water discharge was lowest ($2 \text{ m}^3 \text{ s}^{-1}$), Na and Cl concentrations reached levels as high as 11,200 and $9600 \mu\text{mol L}^{-1}$, respectively. Conversely, in January 1999, when discharge was highest (peak discharges $>1000 \text{ m}^3 \text{ s}^{-1}$), Na and Cl concentrations became as low as 680 and $370 \mu\text{mol L}^{-1}$, respectively. Sulphate, magnesium and calcium concentrations were also lowest in January 1999 ($1000\text{--}2000 \mu\text{mol L}^{-1}$ for SO_4 and $500\text{--}1000 \mu\text{mol L}^{-1}$ for Ca and Mg) and highest in the first week of October (3900 for SO_4 and 2200 for Ca and Mg, respectively). Compared with Na and Cl, differences between SO_4 , Ca and Mg concentrations at high river discharge and concentrations at low discharge were significantly less (Fig. 2).

Gibbs (1970, 1971) made an attempt to interpret the dominant processes involved in surface water chemistry. By plotting total dissolved salt concentrations against relative proportions of the principle anions for many surface waters in the world, he obtained a curve with two arms (Fig. 4). Proceeding along the lower arm to the right, waters become lower in salt concentration and achieve a composition resembling rain water (indicated by a high Cl to HCO_3 ratio). This arm indicates an increasing dominance of precipitation and thus dilution of dissolved solids. Proceeding to the right along the upper arm, waters with high salt concentrations are encountered, in which Cl (and Na) become dominant, due to

the high solubility of NaCl. This arm indicates a dominance of evaporation in determining water chemistry. On the left side (where the arms join) waters can be found in which rock and soil weathering is the dominant process (i.e. without much interference of dilution or evaporation). The plot, as applied to the Pilcomayo waters, shows that several obvious differences exist between the winter (April–September, months 5–9, Fig. 4) and summer water chemistry (October–March, months 10–2, Fig. 4). The winter waters are cooler and have higher concentrations of all of the major cations and anions than the summer waters. Discharges are considerably lower in the winter than in the summer (Fig. 2). During the winter months, low amounts of rainfall promote waters with higher ion concentrations that may then be subject to evaporation. This is clearly reflected in Fig. 4, which indicates a trend towards evaporation (and precipitation of the least soluble minerals) during the winter months (with gradually declining discharge values), and rock-dominated weathering during the summer months. Evaporation strongly increases between June and October (Fig. 5), while hardly any precipitation is recorded in this season. As a result, net water losses can be considerable, resulting in the observed strong decrease of water discharge and increased concentrations of dissolved ions. In the first months of the rainy season (points 11 and 12 in Fig. 4), the composition on the plots moves in the direction of precipitation dominance, indicating the initial dilution effect at the onset of the rainy season.

From a comparison of the mean composition of the Pilcomayo river as observed in this study (1998/1999) with the mean composition for the year 1968 (published in Bayley, 1971), it becomes clear that the bulk water chemistry has not changed importantly over the last 3 decades (Fig. 6). Overall SO_4 is the dominant anion in the Pilcomayo river while Na is the dominant cation. The 1998 Na and Cl concentrations are slightly higher than those from 1968. These somewhat higher values can be attributed to the fact that 1998, being an El Niño year, was characterised by very low amounts of rainfall during the dry season and thus very low river discharges of the Pilcomayo river (Smolders et al., 2002).

3.2. Calcium, magnesium, (bi)carbonate and sulphate chemistry

Although Ca and SO_4 exhibit a good correlation (Fig. 7), suggesting that simple gypsum dissolution may exert a control on the Ca chemistry (particularly during the summer months), there is too little Ca relative to SO_4 (particularly during the winter months) for gypsum alone to be responsible for Ca chemistry. The good correlations between Ca and HCO_3 and Ca + Mg and HCO_3^- (Fig. 7) suggest that calcite and dolomite weathering also contribute Ca ions to the river water.

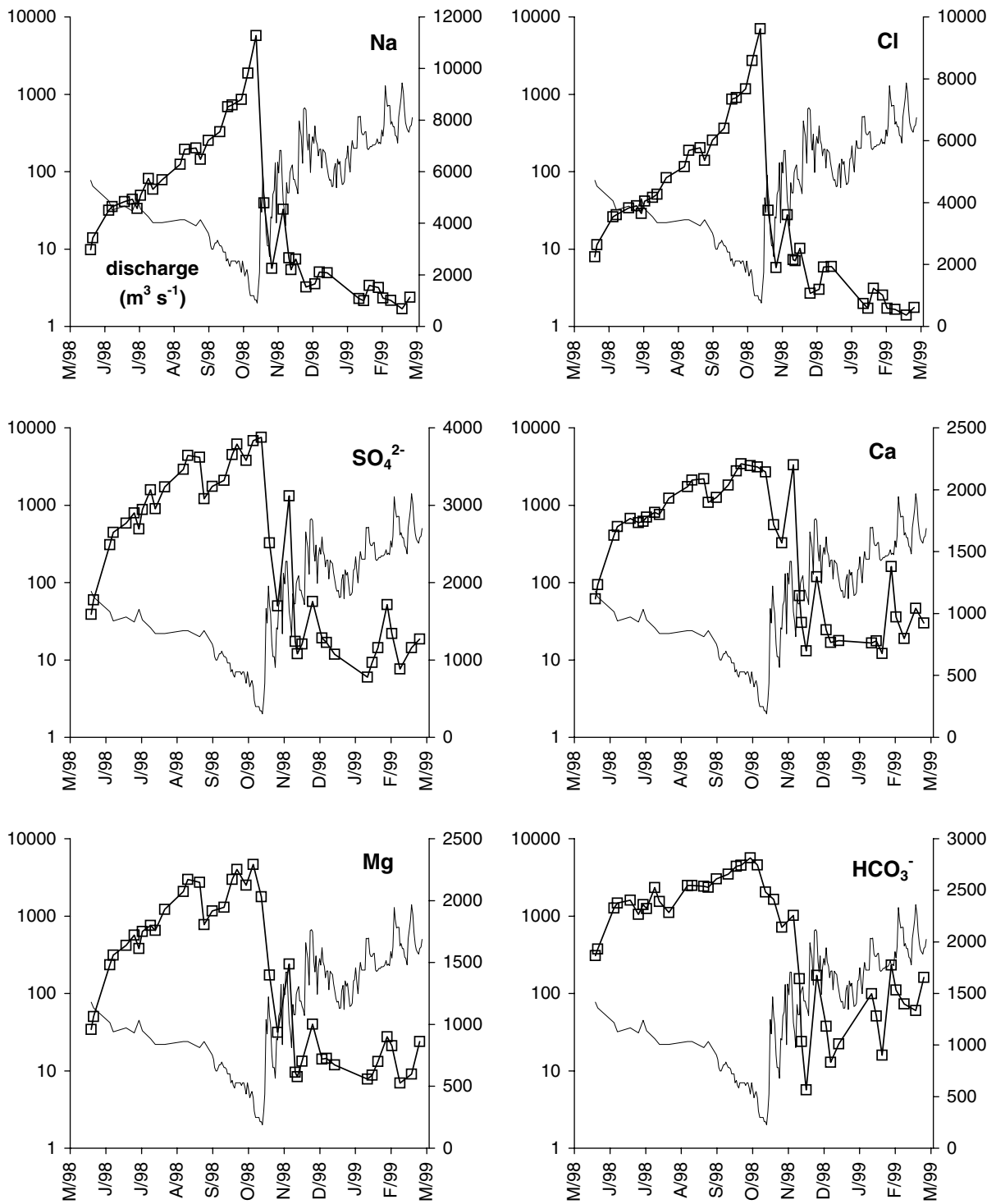


Fig. 2. Time of sampling versus Na, Cl, SO_4^{2-} , Ca, Mg and HCO_3^- concentrations (right y-axis) in Pilcomayo water samples collected at Villa Montes (Bolivia) between May 1998 (M-98) and March 1999 (M-99). All concentrations are given in $\mu\text{mol L}^{-1}$. The thin line indicates river discharge ($\text{m}^3 \text{s}^{-1}$) at La Paz (Argentina) (left y-axis, note the logarithmic scale).

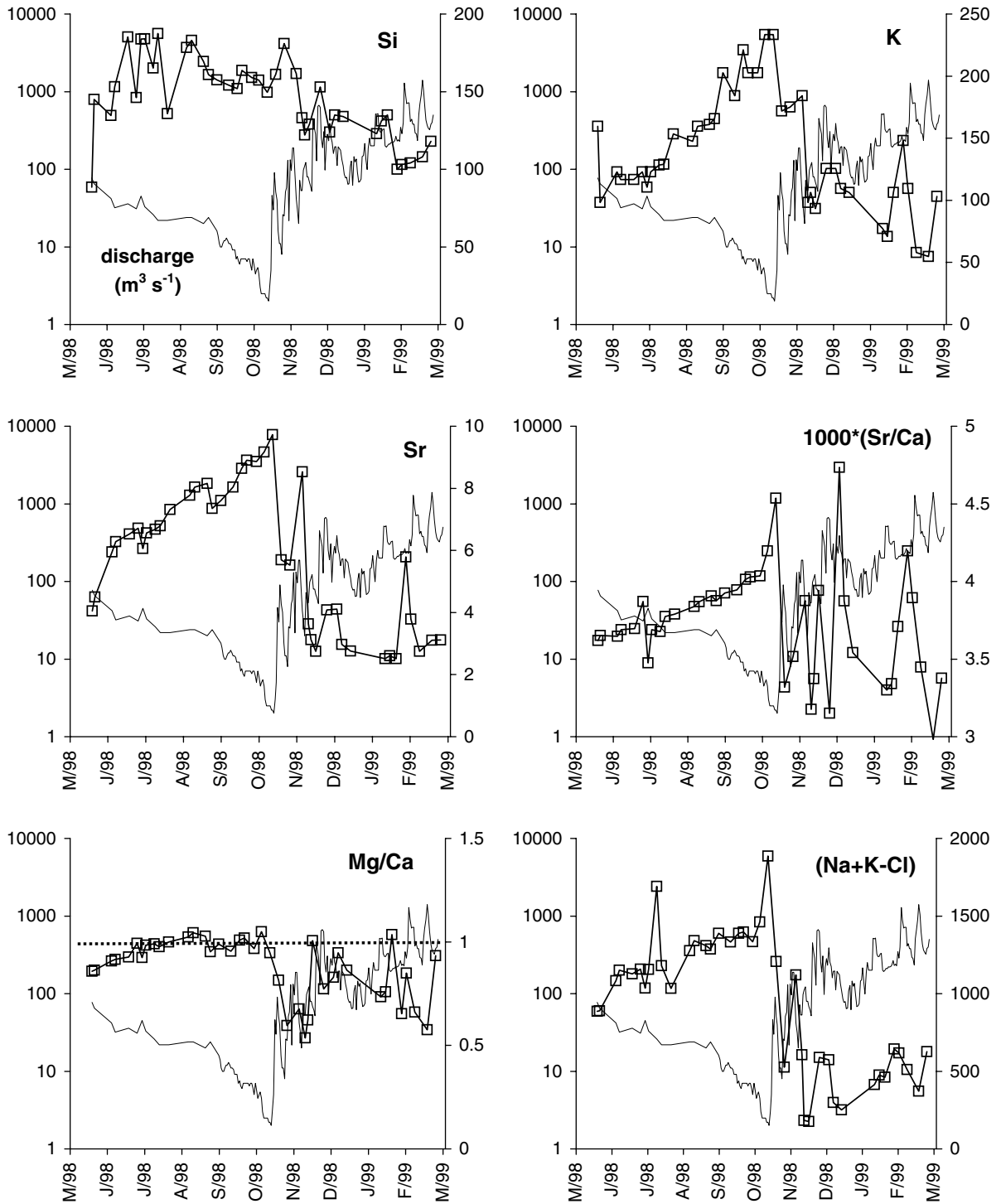


Fig. 3. Time of sampling versus Si, K, Sr and (Na + K - Cl) concentrations and $1000 \cdot (\text{Sr}/\text{Ca})$ and Mg/Ca ratios (right y-axis) in Pilcomayo water samples collected at Villa Montes (Bolivia) between May 1998 (M-98) and March 1999 (M-99). All concentrations are given in $\mu\text{mol L}^{-1}$. The thin line indicates river discharge ($\text{m}^3 \text{s}^{-1}$) at La Paz (Argentina) (left y-axis, note the logarithmic scale).

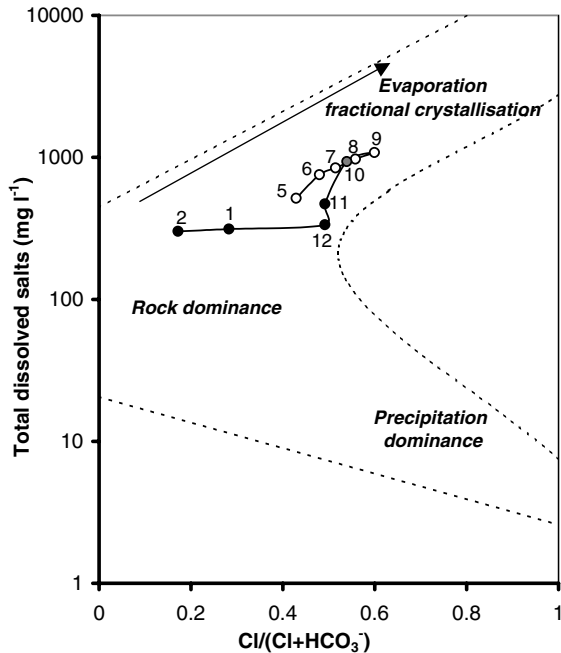
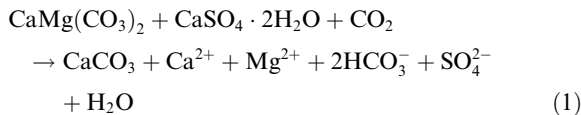


Fig. 4. $Cl/(Cl + HCO_3^-)$ versus total dissolved solids, after Gibbs (1970). The Río Pilcomayo water data trend toward the field of evaporation during the winter months (5–9; open symbols) and towards rock dominance during the summer months (10–12; filled symbols). Labels indicate months of the year.

The high Mg/Ca ratio strongly indicates that weathering of dolomite or carbonates containing high concentrations of Mg, may be important. The Mg/Ca ratio, which is near one during the winter months (Fig. 7), suggests that dolomite dissolution is favoured over calcite dissolution. The dissolution of both gypsum and dolomite will promote calcite supersaturation



This is supported by the generally positive saturation indices for calcite during the winter months (Fig. 8). The relatively high Mg/Ca and Sr/Ca ratios seen in winter water (Fig. 3) also tend to occur in solutions that have precipitated calcite. Strontium is derived from carbonates or sulphate salts (Vitousek et al., 1999; Fairchild et al., 2000). As precipitation of Sr-dominant minerals will not be important, because Sr is present in only minor amounts, Sr to Ca concentrations will gradually increase if calcium carbonates precipitate. The low discharge and relatively warm temperatures during the winter will promote precipitation of calcite, the least soluble mineral in the evaporation series (Fig. 8). Positive dolomite saturation indices (Fig. 8) also suggest

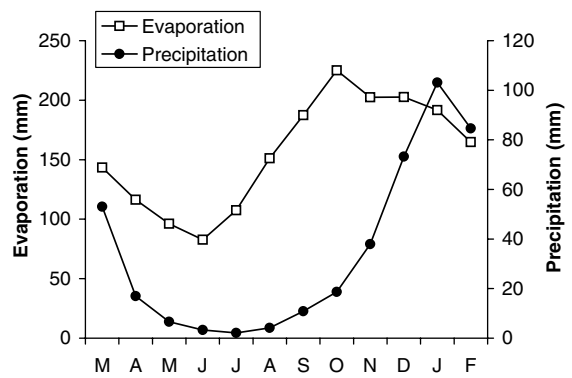


Fig. 5. Mean precipitation and evaporation at Villa Montes (Bolivia) in different months of the year (data from PROVISA, 1989).

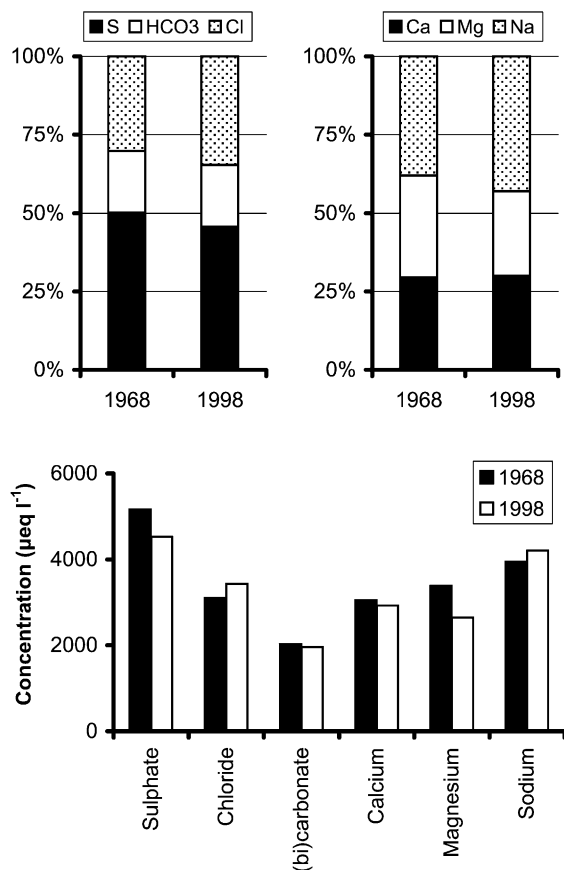


Fig. 6. Mean macro-ion concentrations in river Pilcomayo water in 1968 (data from Bayley, 1971) and 1998 (this study). All concentrations are expressed in $\mu\text{mol L}^{-1}$. The upper left and right figures give the relative macro-anion (left) and macro-cation (right) composition.

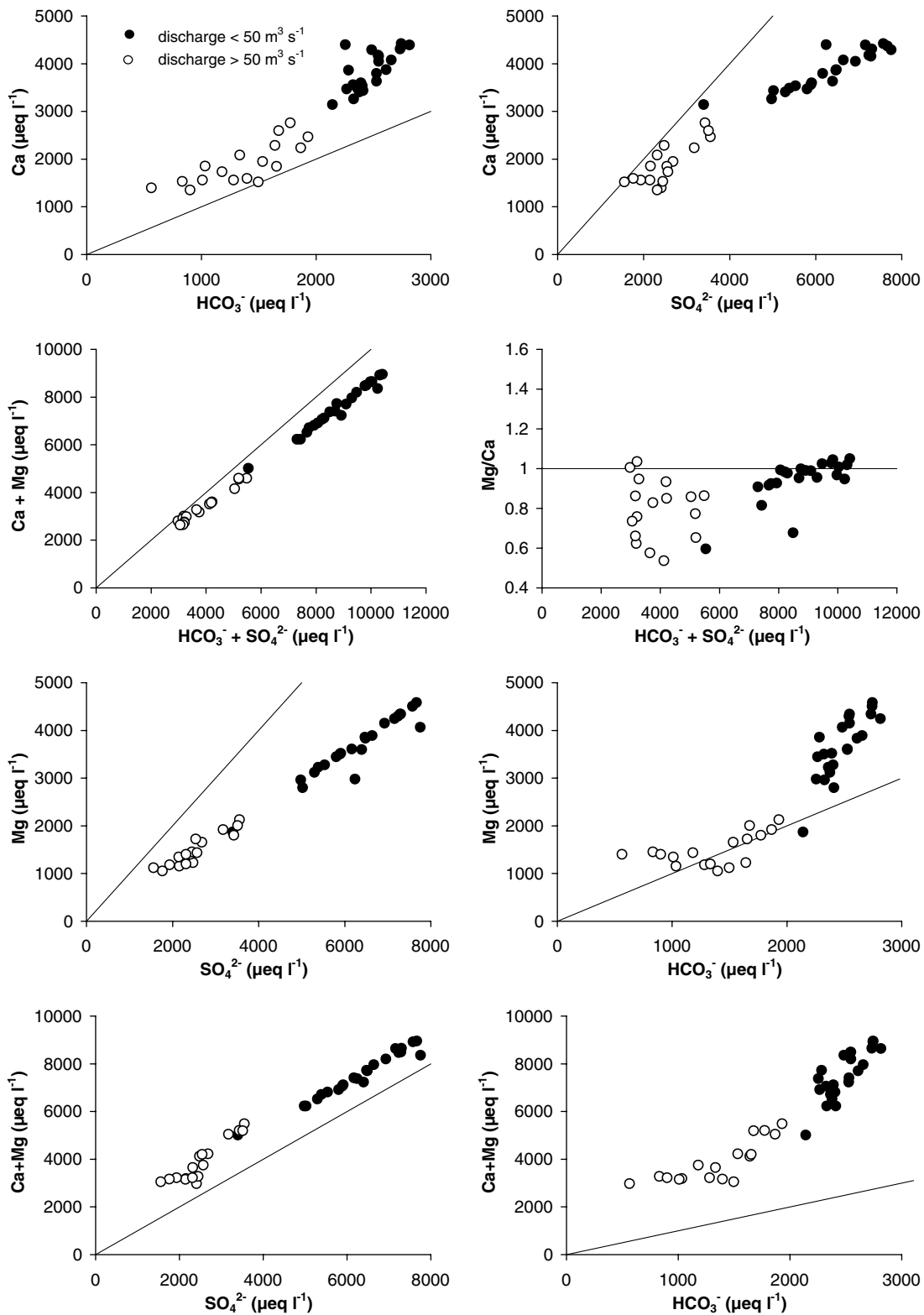


Fig. 7. Relationships between different ratios and ion concentrations for HCO_3^- , SO_4^{2-} , Ca and Mg. Open symbols indicate samples that were collected when discharge $> 50 \text{ m}^3 \text{ s}^{-1}$ and filled symbols indicate samples that were collected when discharge $< 50 \text{ m}^3 \text{ s}^{-1}$.

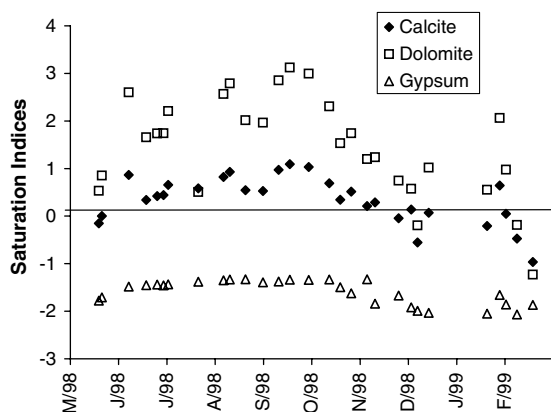
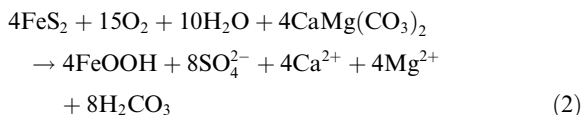


Fig. 8. Time versus saturation indices for calcite, dolomite and gypsum between May 1998 (M-98) and March 1999 (M-99).

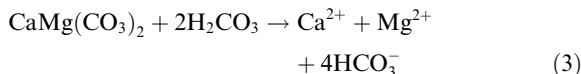
supersaturation of dolomite, but sluggish dolomite precipitation kinetics (Morse and Arvidson, 2002) will probably prevent its actual precipitation. This is reflected by the high Mg/Ca ratios in winter solutions (Fig. 2).

In the summer months (high discharge), the Mg/Ca ratio ranges from 0.5 to 1.0 (Fig. 2), calcite saturation indices range from slightly positive to negative (Fig. 8), gypsum saturation indices are negative and there is a trend towards 'rock dominance' on Fig. 4. These data suggest that during summer gypsum, dolomite and calcite dissolution control the Ca and Mg chemistry, and that calcite precipitation probably does not occur.

In addition to the combined dissolution of gypsum and dolomite, weathering of sulphide minerals (particularly pyrite) and the concomitant reaction of the produced acids with dolomite or calcite might produce the observed water chemistry



The H_2CO_3 produced may then react with dolomite (or calcite), producing an equivalent amount of Ca + Mg and HCO_3^- .



Indeed, pyrite weathering can explain the observed levels of Ca, Mg, HCO_3^- and SO_4^{2-} in the Pilcomayo river. Sulphate concentrations are high in the Pilcomayo river and SO_4 becomes the dominant anion during the rainy season. High SO_4 levels, in combination with high Ca and Mg concentrations, have frequently been explained by the weathering of reduced S (e.g. pyrite) from black shales (Stallard and Edmond, 1983; Elbaz-Poulichet

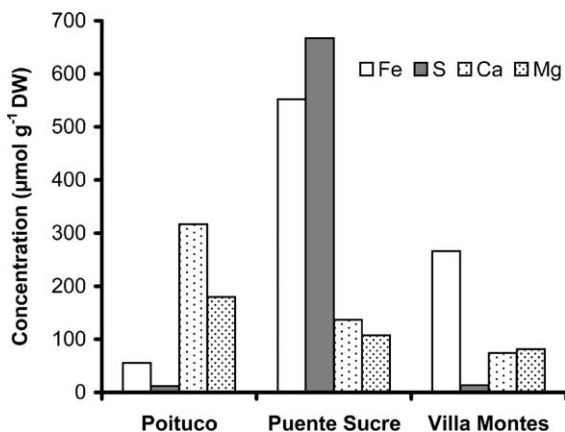


Fig. 9. Fe, S, Ca and Mg concentration of sediment samples collected from the Pilcomayo river in 1999. See Fig. 1 for the position of the sample locations.

et al., 1999; Dalai et al., 2002). In general, high SO_4 concentrations may be derived from either sulphide or SO_4 weathering (Stallard and Edmond, 1987; Drever, 1997). The region which feeds the Pilcomayo consists of Upper Cretaceous and Tertiary bed-rocks containing sulphide minerals, (dolomitic) limestones, gypsum and anhydrite (Cunningham et al., 1996; Camoin et al., 1997; Deconinck et al., 2000; Rivas Valencuele, 2002).

The Pilcomayo aqueous SO_4 is probably derived from gypsum weathering (Figs. 7 and 8) and sulphide weathering. In the Pilcomayo catchment, sulphides not only occur in bedrock and soils, but also in the river channel sediments (Hudson-Edwards et al., 2001). Large quantities of mine tailings are released in the river from the Potosí mining district. These mines have been operating since the 16th century to date. As a result, the channel sediments of the upstream parts of the river contain pyrite and other sulphide minerals (Hudson-Edwards et al., 2001; Miller et al., 2002; Smolders et al., 2003). The chemical composition of the channel sediment shows very high levels of S and Fe in the Potosí region compared with the uncontaminated parts further upstream (Poituco region) and further downstream (Villa Montes region) (Fig. 9). Oxidation of pyrite in the Potosí region may strongly increase SO_4 concentrations. The acids produced are consumed by carbonate buffering (Eq. (2)) and/or cation exchange reactions. Calcium and Mg are present in equivalent amounts in the channel sediments (Fig. 9), which is in accordance with the more or less equivalent amounts of these ions encountered in the water layer.

As discussed above, gypsum dissolution and pyrite weathering probably both contribute to the SO_4 load of the Pilcomayo river. Part of the aqueous SO_4 and Mg may also be derived by the weathering of a Mg sulphate mineral, given the good correlation between Mg and SO_4 (Fig. 7). However, the nearly equivalent amounts of

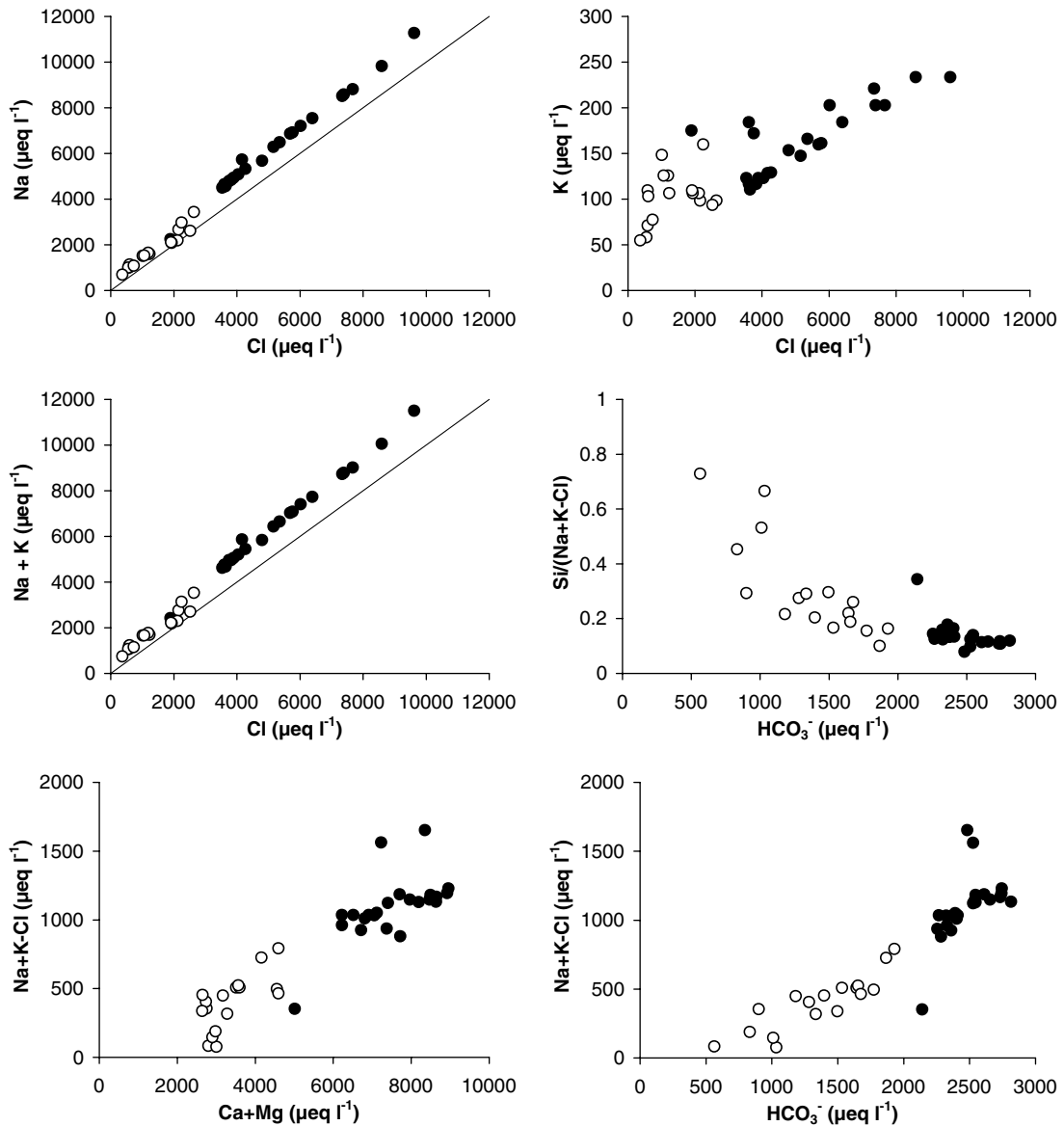


Fig. 10. Relationships between different ratios and ion concentrations for Na, Cl, K, Si, Ca, Mg and HCO_3^- . Open symbols indicate samples that were collected when discharge $>50 \text{ m}^3 \text{ s}^{-1}$ and filled symbols indicate samples that were collected when discharge $<50 \text{ m}^3 \text{ s}^{-1}$.

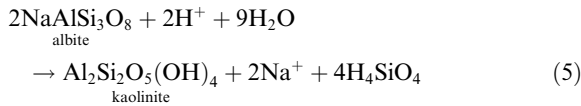
Ca and Mg in the river bed sediment and the water, as well as the evidence outlined above and in Figs. 2, 7 and 8, strongly suggest a role for dolomite dissolution. El-baz-Poulighet et al. (1999) also found nearly equivalent concentrations of Mg and Ca in the upper Beni and Mamore basins (Bolivia), which they ascribed to dolomite weathering. These basins are adjacent to the Pilcomayo basin and drain Andean uplands with comparable underlying geologies to the Pilcomayo.

3.3. Sodium, chloride, potassium and silicon chemistry

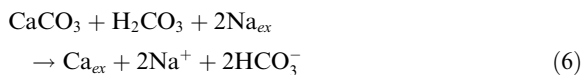
Although Na concentrations are somewhat higher than Cl concentrations, both are present in nearly equivalent amounts (Fig. 10). It can be concluded that Cl and, for the most part, Na, are derived from halite dissolution



Some of the Na, however, appears to be derived from other processes, as the Na/Cl ratio is greater than 1, especially in the more concentrated winter waters. Some may be derived from other Na-bearing silicate minerals such as albite (cf., Stallard and Edmond, 1983, 1987); this has been found in Pilcomayo suspended sediment, in addition to kaolinite (Hudson-Edwards et al., 2001). Weathering of albite produces kaolinite and Na ions

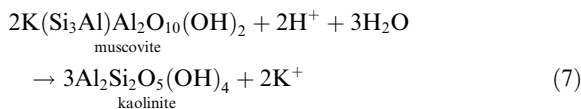


This reaction would result in a Si/(Na + K–Cl) of ± 2 . The Si/(Na+K–Cl) ratio encountered in the Pilcomayo is, however, much lower than 2 during the entire year and becomes even lower than 0.2 during the dry season (Fig. 10). As no silicate weathering reaction could explain such low ratios (Stallard and Edmond, 1987) the excess Na is probably not derived solely from silicate weathering. The (Na + K–Cl) values show a good correlation with both (Ca + Mg) and HCO_3^- (Fig. 10). Simple cation exchange between Ca or Mg and Na in saline bed-rocks might very well explain the excess Na concentration, especially in the winter samples (Varsányi and Kovács, 1997; Stimson et al., 2001). Thorstenson et al. (1979) noted that coupled calcite dissolution and ion exchange can be involved in the evolution of high alkalinity ground waters.



Alternatively, the dissolution of trona [$\text{NaHCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$] and nahcolite [NaHCO_3], which can both form part of halite deposits (Drever, 1997; Rivas Valencuele, 2002), may also be involved.

Potassium exhibits a good correlation with Cl (Fig. 10), suggesting that weathering of sylvite [KCl] controls the K chemistry. The higher K relative to Cl in the summer months suggests that other K-bearing minerals may be weathering during this time. One possibility is muscovite; it occurs in the Pilcomayo suspended sediment, and can weather to yield K ions and kaolinite:



The dissolution/weathering of evaporites clearly dominates the major element hydrochemistry of the Pilcomayo. The relatively low silicate concentrations compared to the high total dissolved ion concentrations indicate that, quantitatively, silicate weathering does not play an important role in the overall chemistry of the

river. The Si/(K + Na–Cl) ratio being well below 2 and the asymptotic trend showing the plot of this ratio against the HCO_3^- concentration (Fig. 10) both are consistent with a dominant role of carbonates as a source for major dissolved cations (Elbaz-Poulichet et al., 1999).

The role of silicate weathering seems to be relatively more important during the wet season, given the fact that Si concentrations are only moderately lower in summer (100–150 $\mu\text{mol L}^{-1}$) compared to winter (150–200 $\mu\text{mol L}^{-1}$) (Fig. 3). During the rainy season the river apparently receives considerable inputs from parts of the drainage basin that are dominated by silicate rocks. The higher Si/(Na + K–Cl) ratio also indicates that a larger part of the Na and K is derived from silicate weathering processes during this season (Fig. 10).

3.4. Rinse-out

At the onset of the rainy season concentrations of the major ions decrease with increasing river discharges, owing to the dilution of solutes in the base flow by surface run-off derived from rainfall. As discharge further increases during the following weeks, however, major ion concentrations suddenly show a sharp increase, resulting in marked peaks in the first week of November (Fig. 11). Such concentration peaks can be explained by the dissolution of salts that were formed during the dry season owing to evaporation processes, and the flushing of highly concentrated waters accumulating in the soil pores during the dry winter months (Caissie et al., 1996; Drever, 1997; House and Warwick, 1998; Keith et al., 2001). This is in accordance with the observed salt crusts on the dry parts of the river bed in the dry season (Hudson-Edwards et al., 2001). Interestingly, not all ions show the same response (Fig. 11); the heights of the peaks, for instance, differ considerably. This is also observed for the extent of the initial decrease of the concentrations, preceding the concentration peaks (Fig. 11). This decrease is much less for Ca and HCO_3^- , suggesting calcite dissolution from the channel bed upon decreasing concentrations in the water layer. The rinse out effects are most marked for the least soluble ions Ca and HCO_3^- and least marked for the highly soluble Na and Cl. Magnesium and SO_4 show an intermediate response. This is in accordance with the expectation that, due to precipitation processes in the dry season, higher amounts of the least soluble ions will accumulate in salt minerals, and these are the minerals that are dissolved during the rinse-out effects. In the last week of November a second peak is observed following a further increase of the discharge levels of the river. Again rinse out effects are largest for Ca and HCO_3^- and a dip is observed for Na and Cl. It is likely that the effects of dilution overwhelmed those of the rinse out for these highly soluble ions at this stage.

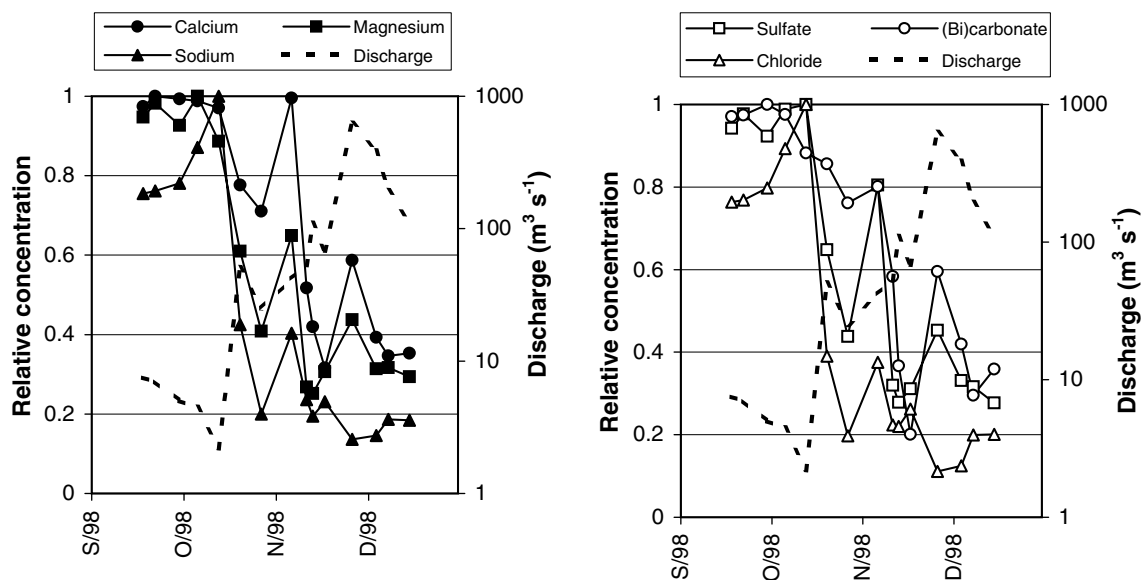


Fig. 11. Time versus Ca, Mg, Na, and discharge (a) and time versus SO_4^{2-} , HCO_3^- , Cl and discharge (b) for the transition period between winter (dry season) and summer (wet season) (S-98 = September 1998, etc.). Concentrations are all divided by the highest concentration observed during this period. Rinse out effects can be observed which differ between the different macro-ions.

3.5. Possible effects on biota

Many fish species from the Pilcomayo river show a migratory behaviour and start their upstream migration at the onset of the dry season, when river flows are relatively low. They spawn at the onset of the rainy season in the (Bolivian) upper reaches of the river, when river discharge strongly increases and fertilized eggs and larvae are transported with the rising water onto floodplains in Argentina and Paraguay (Bayley, 1973; Payne and Harvey, 1989; Smolders et al., 2002). Macro-ion concentrations might play an important role in the ecology of the river system, for instance, by serving as a trigger for processes related to the reproduction of fish. Many species from rivers that show a strong seasonal variation in discharge show synchronized reproduction at the onset of the rainy season (Bayley, 1973; Payne and Harvey, 1989; Winemiller, 1989; Paugy, 2002), for instance due to a strong drop of conductivity (Ramnarine, 1995; Kirschbaum, 1979). The present results show that the onset of the rainy season is also accompanied by a strong and sudden decline in dissolved solid concentrations, and thus conductivity, in the Pilcomayo river. Such a sudden and marked change of ion concentrations might well serve as a trigger for spawning behavior.

In the case of the contaminated Pilcomayo river concentration of dissolved solids may strongly affect the speciation of toxic metals and the toxicity of these metals. Complexation of metals by inorganic ligands such as CO_3^{2-} and Cl^- may strongly limit the bioavail-

ability and toxicity of metals (Playle, 1998; Bury et al., 1999; Bianchini and Bowles, 2002). Cations such as Ca and Mg reduce the toxic effects of metals for fish by competition for metal binding sites at negatively-charged fish gills (Pagenkopf, 1983; Playle, 1998). Both mechanisms may explain the generally observed protective effect of water hardness against metal toxicity. Given the relatively low dissolved metal concentrations observed in the lower reaches of the Pilcomayo river (Smolders et al., 2003), high dissolved solid concentrations at low river discharges may well prevent metal toxicity in the migratory fish that are present in the river during the dry season.

3.6. Conclusion

The authors have herein presented the first major set of baseline data for an unregulated, continental-scale South American river system. Water chemistry of the Pilcomayo river is highly variably during the year and is strongly influenced by the differences between the wet and the dry season. According to the classification of Stallard and Edmond (1983) for tributaries of the Amazon river, the Pilcomayo river can be characterised as a river draining marine deposits and major exposures of evaporites. As in other continental-scale catchments (Edmond et al., 1996; Sobieraj et al., 2002), lithology plays a significant role in determining the major element hydrochemistry of river waters at Villa Montes. For example, NaCl dissolution appears to control both Na

and Cl concentrations, with both of these becoming very high during the dry season. Pyrite weathering and dissolution of gypsum, dolomite and calcite determine Ca, Mg, SO₄ and HCO₃ chemistry. Comparison with data from 1968 reveals that water chemistry probably has not changed significantly in the last 30 a. At the onset of the rainy season rinse out effects result in temporary strong increases of major ions that are related to the dissolution of evaporite minerals.

Major ion river water composition may strongly affect river biota, especially regarding metal speciation and metal toxicity. Further research will be carried out to elucidate the importance of the hydrochemical dynamics for the functioning of the riverine ecosystem, also in relation to the metal contamination to which the river is subjected.

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