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Biogeochemical control on the temporal variability of trace element concentrations in the Oubangui river (Central African Republic)

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Abstract

Dissolved Ba, Cd, Co, Mn, Mo, Ni, Rb, Sb, Sr, U and V were measured in the Oubangui river (Central African Republic) during a complete flood period. The dissolved concentrations vary by factors ranging from 1.4 to 8.2 as a function of river discharge: Sr, Ba, Rb and Mo concentrations decrease with rising stage; Ni, U, Sb, Cd, V and Mn concentrations increase with rising stage. These distributions are explained by a mixing of quick flow, mostly surface runoff with delayed flow, mostly groundwater. The dual origin of stream waters is demonstrated by the major element ratios, which are close to a silicate end-member during the high-flow period and trend towards a carbonate end-member during the low-flow period. Moreover, geological heterogeneities in the Oubangui basin may play a role in the variation of concentrations observed at the basin outlet. The previously indicated presence of a subsurface carbonate sequence in the lower part of the basin is confirmed. Cd, V, Mn and Co show peak concentrations during decreasing stage. We suggest that biological processes such as release from phytoplanktonic material and dissolution of oxides or carbonate phases may explain this maximum.

1. Introduction

The biogeochemical processes that control trace element concentrations in natural waters are still poorly known. All the available time series for dissolved trace element concentrations concern human-affected systems in industrialized countries, such as the Mississippi (Shiller and Boyle, 1987a) or the Rhône (Elbaz-Poulichet et al., 1996).

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Until recently, the geochemistry of the rivers Congo and Oubangui—one of its main tributaries—was poorly documented. Most trace element investigations quoted by researchers are based on few measurements, which do not take into account seasonal variations, or they concern mainly the Congo estuary (Meybeck, 1978; Figuères et al., 1978; Van Bennekom et al., 1978). More recently, some Sr isotope and alkali-metal data have been published (Negrel, 1992; Negrel and Dupré, 1995).

The Oubangui basin is not industrialized and the river can be considered as a strictly natural system, ideally suited to the investigation of some of the natural processes that control trace element variations. The Oubangui river is the second largest tributary of the Congo river. Its restricted extent limits the variability of the system compared with larger basins such as the Congo (Negrel, 1992; Negrel and Dupré, 1995) or the Amazon (Konhauser et al., 1994).

In this paper, we report the results of an 8 month study on dissolved Ba, Cd, Co, Mn, Mo, Ni, Rb, Sb, Sr, U and V in the Oubangui river at Bangui (Fig. 1). The period of study extends over a complete flood period (Fig. 2).

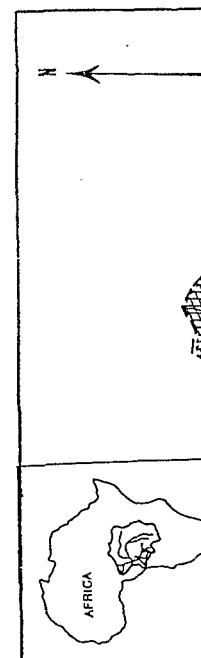
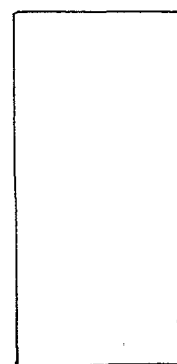
2. Major environmental features of the Oubangui basin

The Oubangui river is 1170 km long and drains a large river basin of 644 000 km² in the centre of the African continent (Fig. 1). The mean discharge of the Oubangui river from 1951 to 1990 at the Bangui station was 3750 m³ s⁻¹ and average precipitation for the same period was 1539 mm year⁻¹ (Olivry et al., 1995).

The stream regime of the Oubangui river is characterized by high discharge from October to November during the rainy season, followed by a decline until low flow which is reached in March. This mainly pluvial regime is typical of many tropical rivers. Some major features of the 1989–1990 hydrological year (from April to March) are shown in Fig. 2. During this hydrological year, the rainfall maximum in Bangui was observed in August, whereas the peak discharge occurred in October and the maximum suspended load in September.

The morphology of the Oubangui basin consists of plateaux resulting from the slow peneplanation of the old African plate and of weakly inclined slopes cut out by valleys. Crystalline and metamorphic rocks (mainly amphibolite and pyroxenite) dominate in the Oubangui catchment, and have been weathered in a surface ferricrete layer. Typical soils of the Oubangui basin have been characterized by Boulvert (1990) and Beauvais (1991). Furthermore, the presence of a hidden carbonated sequence, a 'palaeocryptokarst' in the Precambrian carbonate formation has been pointed out by Boulvert and Salomon (1988). The vegetation consists mainly of savanna type, dry or forested. More complete information about morphology, lithology and vegetation of the region has been given by Boulvert (1990).

Compared with other large rivers, such as the Amazon tributaries (Stallard and Edmond, 1983), the conductivity and total dissolved solids concentration (TDS) in the Oubangui river are low. From January 1989 to December 1992 conductivity ranged from 30.6 to 70.2 $\mu\text{S cm}^{-1}$ (mean of 47 values is 46.6 $\mu\text{S cm}^{-1}$) and TDS (defined as the sum of cations plus anions plus dissolved silica) from 33.3 to 70.6 mg l⁻¹.



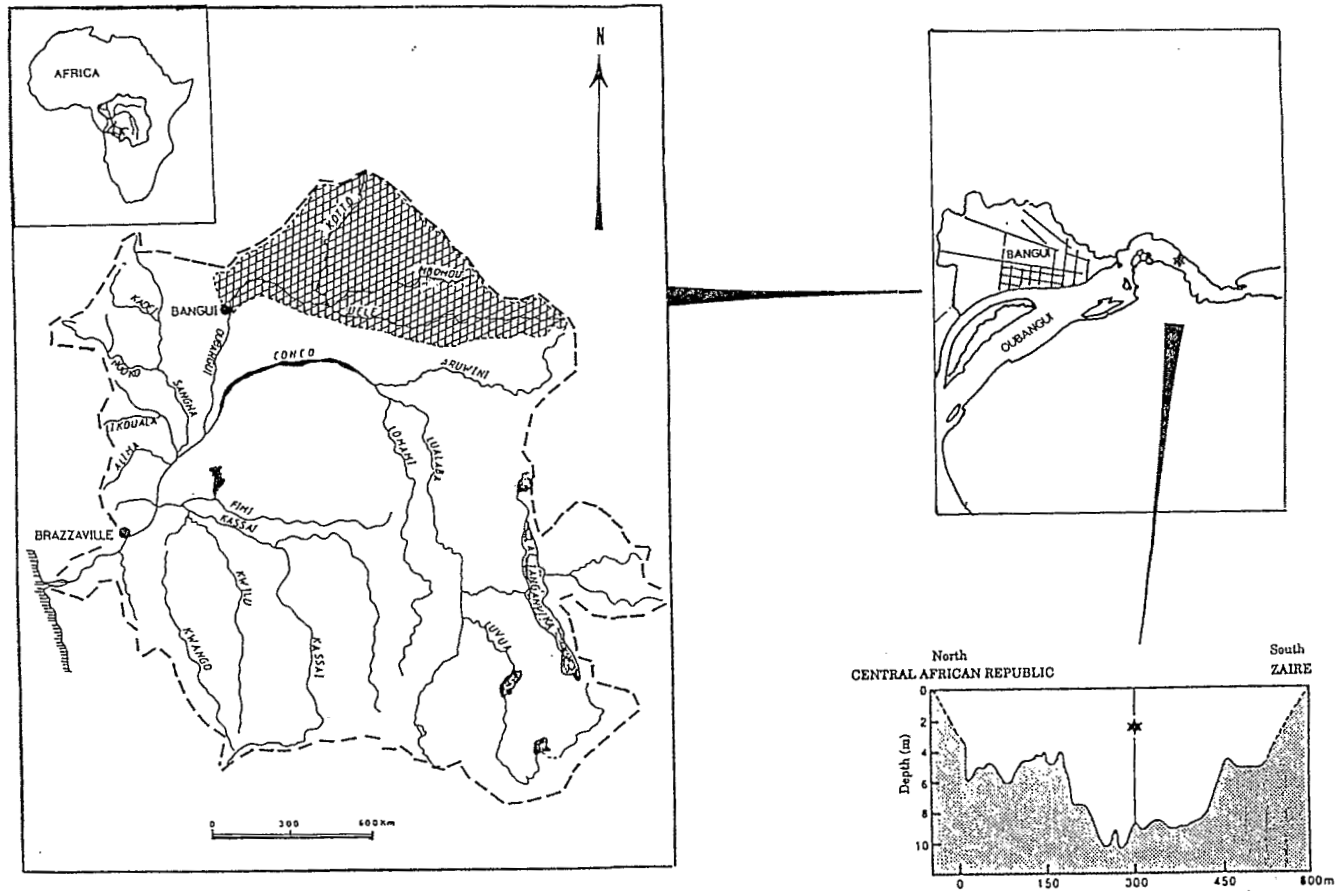


Fig. 1. Sketch map of the Oubangui basin and sampling location.

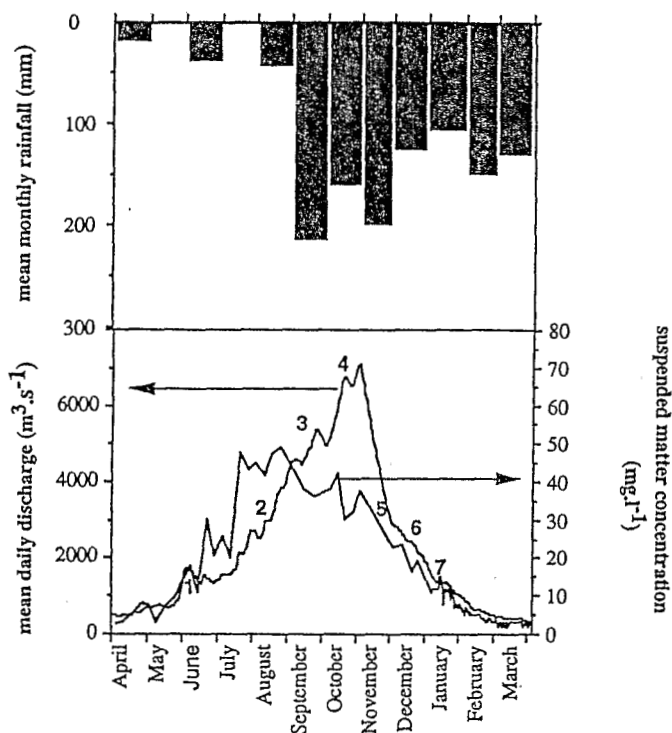


Fig. 2. Hydrograph, hietograph and suspended matter concentrations of the Oubangui river at Bangui during 1989–1990 hydrologic year. Numbers on the graph are sample numbers (see Table 1).

Major features of the major ion chemistry have been reported by Probst et al. (1992) and Sontag et al. (1995).

Suspended matter in the Oubangui river is organic rich. The mean POC (particulate organic carbon) content is 14%. A maximum of 32% POC is observed during the low-water stage. During the high-water stage, the POC content is lower and is mainly of detrital origin, whereas during low-water stage, the water transparency favours the growth of phytoplankton and the organic matter is mainly of autochthonous origin (Seyler et al., 1995).

3. Sampling and methods

River samples were collected, once a month, 2 km upstream of the city of Bangui (Fig. 1) from June 1989 to January 1990. For major elements the samples were filtered using $0.45 \mu\text{m}$ filters. Chemical analysis was performed in the ORSTOM laboratory in France. Sulphate and nitrate were determined by ion chromatography; calcium, magnesium, sodium and potassium by atomic absorption. Detection limits were $2 \mu\text{mol l}^{-1}$ for SO_4^{2-} , NO_3^- , Ca^{2+} , K^+ and Cl^- , and $5 \mu\text{mol l}^{-1}$ for Mg^{2+} and Na^+ .

Fig. 3. Analysis of . analyses ± 1 S.D., f

Dissolved silica $1 \mu\text{mol l}^{-1}$.

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4. Results and d

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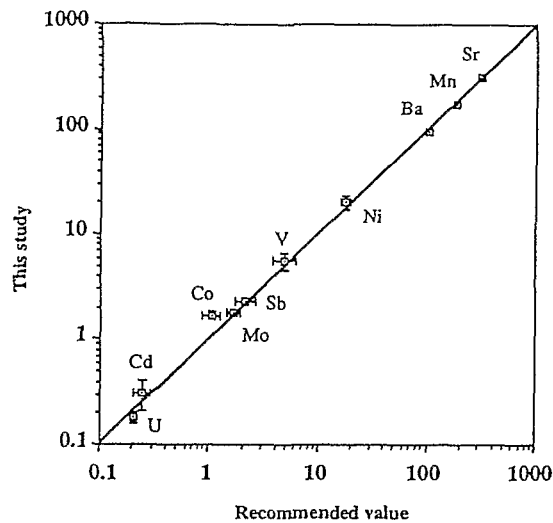


Fig. 3. Analysis of SLRS-2 river water standard. Reported points correspond to the mean of five replicate analyses ± 1 S.D., for the certified and experimental concentrations (nmol l^{-1}).

Dissolved silica was measured by plasma spectrophotometry, with a detection limit of $1 \mu\text{mol l}^{-1}$.

For trace elements, acid-washed polyethylene containers were used. The samples were taken using a wooden boat and filtered on site using $0.2 \mu\text{m}$ precleaned polycarbonate filters, and acidified to pH 2. The trace elements were analysed by inductively coupled-plasma mass spectrometry using a VG-Elemental model PQ2 instrument. Concentrations were determined by calibrating peak intensity acquired in scan mode with standard solutions. An indium internal standard was added to each sample to correct for changes in peak intensities owing to instrumental drifts. Vanadium concentrations were corrected for interferences from ClO.

The accuracy and the precision of the analytical method have been tested using the SLRS-2 trace element standard (Riverine Water Reference Material for Trace Metals, National Research Council of Canada). Except for Co, our results reported (Fig. 3) show a generally good agreement with the certified values to within 1 S.D. This discrepancy might be due to interferences with Ca species such as CaOH (Beauchemin et al., 1987).

4. Results and discussion

The data obtained for major elements, trace elements and nutrients are listed in Table 1. The discharge weighted mean dissolved concentrations of the Oubangui are reported in Table 2. The concentrations vary by factors ranging from 1.4 for Ba to 8.2 for Cd. Except for Ni and Cd, the range of trace metal concentrations in the Oubangui river are close to those found in similar weathering systems such as the Amazon or

Table 1
Trace element concentrations (nmol l^{-1}), major element concentrations (mmol l^{-1}) and nutrient concentrations ($\mu\text{mol l}^{-1}$) in the Oubangui river at Bangui

Sample no.	Date	Discharge ($\text{m}^3 \text{s}^{-1}$)	V	Mn	Co	Ni	Mo	Cd	Sb	Ba	U	Rb	Sr
1	Jun. 89	1420	7.09	10.3	0.815	19.3	0.799	0.220	0.127	170	0.085	62.2	314
2	Aug. 89	3100	10.36	8.2	0.805	21.2	0.546	0.230	0.149	126	0.166	39.6	197
3	Sept. 89	5280	11.91	16.1	0.886	26.4	0.615	0.519	0.173	124	0.211	35.0	189
4	Oct. 89	6760	11.31	8.0	0.864	18.7	0.516	0.270	0.08	121	0.155	36.5	170
5	Nov. 89	2910	9.94	9.3	0.728	20.2	0.538	0.181	0.096	127	0.144	32.5	222
6	Dec. 89	2510	12.27	38.7 *	1.267	19.7	0.613	1.483	0.096	121	0.142	33.7	230
7	Jan. 90	1360	7.50	6.6	0.582	16.5	0.664	0.324	0.128	127	0.098	41.6	255

Sample no.	pH	Ca^{2+}	Na^+	Mg^{2+}	K^+	SiO_2	Cl^-	NO_3^-	HCO_3^-
1	7.70	84	87	95	56	239	27	<2	450
2	7.60	47	62	43	31	261	20	<2	250
3	7.56	43	59	38	26	258	17	<2	220
4	7.28	39	56	35	29	242	16	<2	210
5	7.46	48	73	45	21	274	20	<2	250
6	7.30	81	73	60	27	367	20	15	305
7	7.39	95	81	70	32	265	25	8.06	366

Table 2
Dissolved trace
Element

Ni
U
Sb
Cd
Co
V
Mn
Sr
Ba
Rb
Mo

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Table 2
Dissolved trace element concentrations in the Oubangui river, Amazon river and world averages (nmol l^{-1})

Element	Oubangui		Amazon	World average
	Mean	Range		
Ni	21	16.5–26.4	5	8.5
U	0.16	0.08–0.21	0.17	0.78
Sb	0.11	0.08–0.17		1
Cd	0.44	0.18–1.48	0.06	0.09
Co	0.64	0.56–1.25		1.7
V	11	7.1–12.3	13.2	15
Mn	13	6.6–38.7	300	149
Sr	205	170–314		913
Ba	126	121–170		438
Rb	38	32–62		17.6
Mo	0.6	0.52–0.80	1.5	8.3

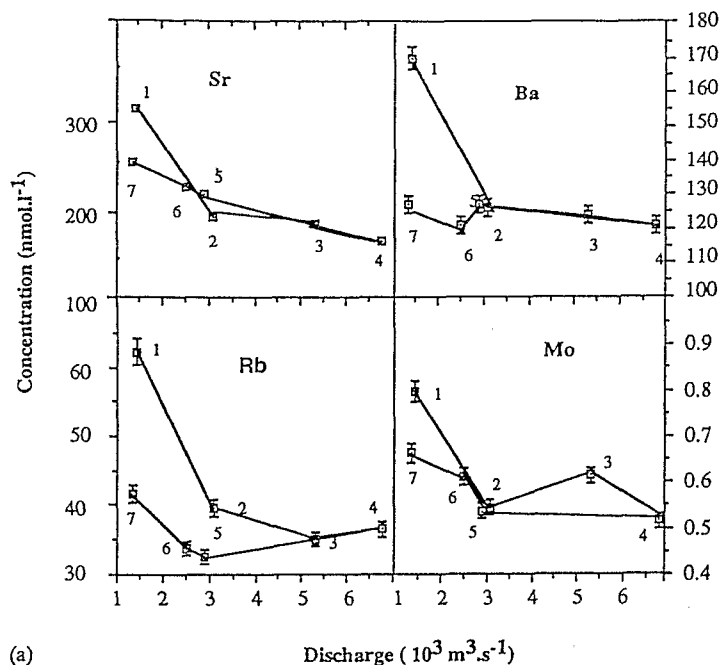
World averages are from Martin and Meybeck (1979), Shiller and Boyle (1987a), Martin and Windom (1991) and Palmer and Edmond (1993). Amazon data are from Gibbs (1977), Boyle et al. (1982), Shiller and Boyle (1987a) and Palmer and Edmond (1993).

Orinoco (Gibbs, 1977; Boyle et al., 1982; Shiller et Boyle, 1987a,b; Palmer and Edmond, 1993) and comparable with world average values (Table 2). Origins of trace metals are discussed below, but as transition metals are concentrated in iron crusts in the Oubangui basin (Beauvais, 1991; Beauvais and Colin, 1993) relatively high Ni concentrations are not surprising. As compared with the world average and Amazon value, the mean Cd concentration in the Oubangui is high. Unfortunately, owing to the lack of literature data, this value cannot be compared with data for a river draining a climatologically and lithologically comparable watershed. Because of the low level of human activity in the region, and the consistency in the variations of concentrations of Cd, Vn and Mn, we suppose that the enrichment of dissolved Cd in the Oubangui river is due to the lithology of the drainage basin.

Dissolved concentration–discharge plots are reported in Figs. 4 and 5. The relationships between dissolved concentrations and water discharge are extremely variable, and depend on the sources and behaviour of the elements (Livingstone, 1963, and references therein; Whitfield, 1981; Meybeck, 1985; Shiller and Boyle, 1987a).

During the rising stage, the trace elements show contrasting behaviours: Sr, Ba, Rb and Mo generally decrease (Fig. 4(a)), as do major cations such as Ca, Na, Mg and K (Fig. 5); Ni, U, Sb, Cd, V and Mn generally increase, and Co can be considered as almost constant (or slightly increasing) (Fig. 4(b)). During the decreasing stage, peak concentrations are observed for Cd, Mn and Co and to a lesser extent for V, if the analytical error is taken into account.

These different geochemical pathways suggest the occurrence of two different end-members for Oubangui waters, as demonstrated by the major cation ratios (Figs. 6(a) and 6(b)). To consider only weathering processes in determining the mobilisation of major cations, the concentrations of Na, Ca, K and Mg are corrected for atmospheric input, according to Negrel and Dupré (1995). These workers have estimated the



(a)

Fig. 4(a).

contribution of rain to the river water by reference to the river chloride concentrations and the X/Cl ratios in the rainwaters (X being Na, K or Mg). During the high-flow period the major cation ratios are close to the average ratios given for waters draining mainly siliceous rocks (Meybeck, 1986, 1988; Negrel and Dupré, 1995). During the low-flow period the ratios trend towards those reported by the same workers for waters draining carbonate rocks. Bicarbonate concentrations (Table 1) are in good agreement with the trends of major cation ratios, being higher during the low-water stage, probably owing to the increased influence of carbonate dissolution under the low-flow conditions. Although dissolved silica and pH do not show trends consistent with the hypothesis of silicate-dominated reaction during high flow and carbonate-dominated reaction during low flow (both are highest at high river stage), it is considered that their variations are controlled by other processes (photosynthetic activity, Edwards, 1973; Meybeck, 1985).

Considering the global geomorphological distribution of soils in the Oubangui basin (Beauvais and Colin, 1993), two main weathering domains of hydrological interest are (1) the forested slope system where the saprolite is characterized by relatively high concentrations of transition metals such as Mn, V, Ni, Co, Cr and Cu as compared with (2) the low flat system where the saprolite layer (most of the time below the water table) is characterized by a depletion of transition metals and conversely a relative enrichment of alkaline earths such as Sr, Ba and rare earth elements. Moreover, in the last area, occurrence of a highly karstified carbonate sequence was recently reported (Boulvert and Salomon, 1988). This series is 100 m thick and does

Concentration (nmol.l⁻¹)

Concentration (nmol.l⁻¹)

(b)

Fig. 4. Concentration during increase

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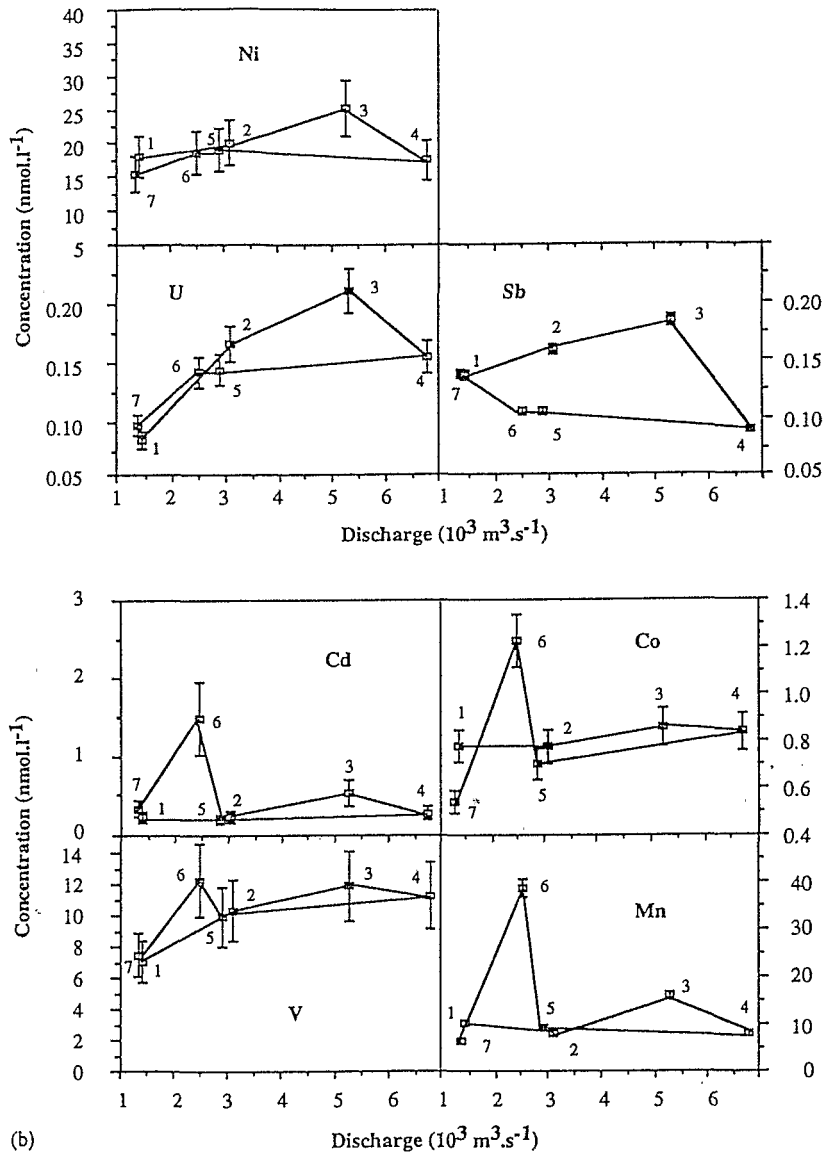


Fig. 4. Concentration–discharge plots for trace elements: (a) trace elements having a decreasing trend during increasing flood; (b) trace elements constant or having an increasing trend during increasing flood.

not crop out. Following the functional model proposed by Negrel (1992) and Negrel and Dupré (1995) on the basis of Sr-isotope signatures, we considered the low flat area with carbonate as the major source during the low-flow period, and the forested slope area as a significant source of water during the high-flow period. On this basis, we can attribute the two different patterns observed to a mixing of a baseflow

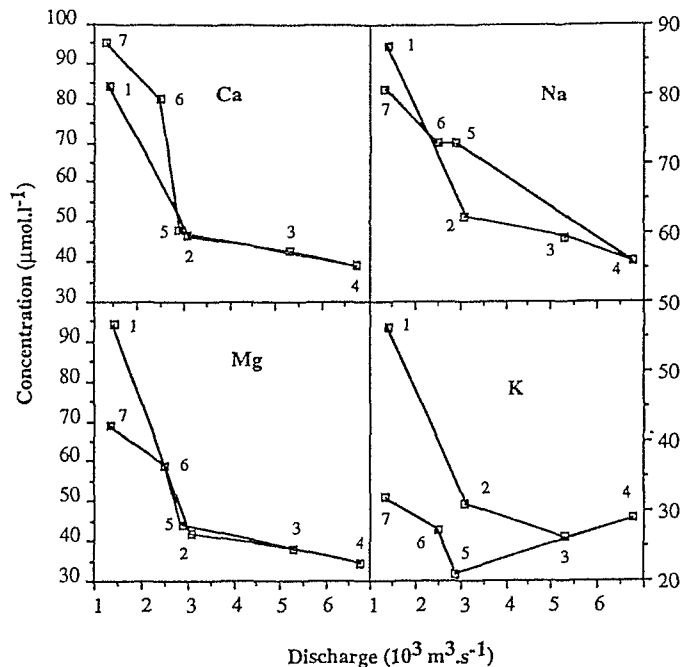


Fig. 5. Concentration–discharge plots for major elements.

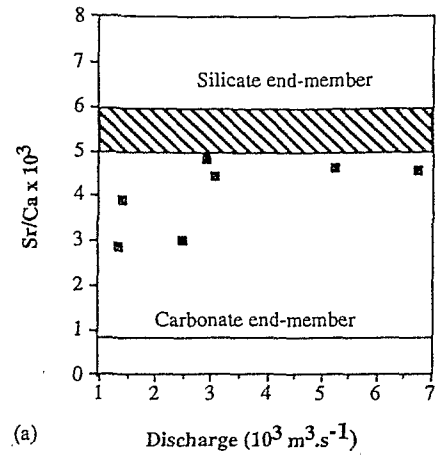
permanently draining the low flat area with waters (surface and subsurface flow) draining temporarily the forested slope domain.

For the elements whose concentrations increase with discharge, there is a striking correlation between their concentration maximum (with the exception of V) and the maximum of suspended matter concentrations (Fig. 2). As this maximum is strongly linked with the soil surface erosion, an increase of dissolved concentrations with increasing discharge can be also attributed to soil weathering. This behaviour, previously described by Cleaves *et al.* (1970) and Meybeck (1985) for elements whose concentrations are higher in soil leachates than in groundwaters, is confirmed by the higher depletion of these elements observed in the top of soils (iron crust) than in the base layers (clay layer and saprolite; Beauvais and Colin, 1993).

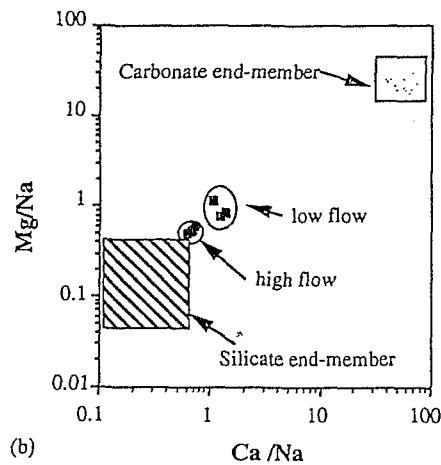
Some trace-elements—Cd, Mn, Co and, to a lesser extent, V—show a maximum concentration during decreasing stage, 2 months after the peak discharge. This maximum is accompanied by a decrease of pH and an increase in nutrient (nitrate and silica) concentrations (see Table 1). The variations of these parameters reflect changes related either to sources or to processes occurring in the riverbed itself. In the first case, the ratios of major cations (Ca/Na, Mg/Ca) should be modified but this is not observed. Therefore, the second hypothesis seems more likely, because variations in nutrient concentrations are found that are often associated with in situ biological activity. Occurrence of cycles showing high concentrations of nutrients when production is low and low concentrations when primary production is high

Fig. 6. (a) M. from Negrel Ca and Na c. (1995).

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(a)



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Fig. 6. (a) Molar Sr/Ca vs. discharge in the Oubangui river. Carbonate and silicate end-member ratios are from Negrel and Dupré (1995) and Meybeck (1988). (b) Molar Mg/Na vs. Ca/Na in Oubangui river. Mg, Ca and Na concentrations are corrected from atmospheric contribution determined by Negrel and Dupré (1995).

(through uptake and release by living organisms) are well known in river waters (Edwards (1973) and references therein). In the Oubangui river, the primary production is mainly due to phytoplankton population (Barreau, 1992), and the sudden increase observed for nitrate and dissolved silica may be due to a breakdown of primary production, followed bacterial degradation of organic material.

Cd and V, whose nutrient-like behaviour has been demonstrated in environments such as estuary and ocean (Bruland, 1983; Collier, 1984; Jeandel et al., 1987; Shiller and Boyle, 1987b) may be taken up by phytoplankton and released into solution during phytoplankton decay. To confirm our hypothesis we computed, from the fluxes, the molar ratios of Cd and V to nutrients. The molar ratios of the released

Cd and V to the released P during this regeneration process (assuming that the N:P molar ratio is 16 in phytoplankton) are 1.4×10^{-3} and 0.8×10^{-3} for Cd and V, respectively. Similar ratios have been found in estuarine and marine waters and attributed to regeneration of organic material from phytoplankton species (Collier and Edmond, 1984; Windom et al., 1991). Ni (also a nutrient-like element; Bruland, 1983) is expected to show an identical behaviour. Assuming a molar ratio close to the values of Collier and Edmond (1984) ($(1.4-2.6) \times 10^{-3}$), we can calculate that a release in solution of all the Ni taken up by phytoplankton would not give a detectable increase in Ni concentration in the Oubangui river, which is in agreement with our observations.

Mn and Co peaks suggest that dissolution of Co and Mn phases (oxides or carbonates) takes place. This dissolution may be due to a slight decrease of pH or to a shift of Eh towards lower values in response to O₂ consumption during the degradation of the organic load. Indeed, dissolved oxygen concentrations in the Oubangui river are generally low, at around 5 mg l⁻¹, and are associated with high water temperatures which may reach 34°C (Thiébaux, 1987).

The mobilization processes described above are linked to photosynthesis–respiration processes and hence should not be permanent features in the Oubangui river. Further study on diurnal cycles of trace elements during the low-flow period with a constant water discharge and a limited variation of source material is needed.

5. Conclusion

This study provides the first data on biogeochemistry of trace element in a tropical and as yet pristine river system. Trace metal concentrations in river water are controlled by the lateritic weathering system and lithological heterogeneity in the Oubangui basin. Trace element concentrations of waters reflect the geochemical features of the soil layers and/or parent rocks which are drained in a permanent or temporal way. In addition, the strong erosion of the surface iron crust leads to leaching of Ni, U, Sb, V and Mn. Besides geochemical processes, additional mechanisms are needed to explain fully the pattern of some elements, such as the nutrient-like (Cd and V) and the redox (Mn and Co) elements. These mechanisms could be linked to biological uptake and release and to dissolution of carbonate or oxide phases and subsequent remobilization of associated trace metals.

This work must be considered a preliminary study, and further investigations are needed to understand the origin of trace elements in tropical river system and, in particular, the respective role of the soil transformation in weathering profiles and riverine transport processes.

Acknowledgements

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