

Major and trace element geochemistry in the upper Niger river (Mali): physical and chemical weathering rates and CO₂ consumption

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Abstract

This study describes the chemistry of the upper Niger river system upstream of the inland delta in Mali. It constitutes the first geochemical investigation of suspended and dissolved loads of this region of the world. The Niger, on its way between Banankoro and Ké-Macina and its tributary, the Bani river at Douna, were sampled during eight hydrological years (from 1991/1992 to 1997/1998). Major elements were determined for all 8 years and trace elements during 2 years (1996/1997 and 1997/1998). The total period of investigation is representative of the hydrological fluctuations over the last 25 years. Dissolved concentrations show that in comparison with other rivers, the upper Niger rivers are among the least mineralised and are strongly influenced by silicate rocks, which underlie almost the totality of the basin. The contribution of atmospheric precipitation to the rivers' chemistry (using the technique of marine contribution) appears very low. Normalised to the upper crust, the chemical composition of the different phases shows that in each tributary, suspended sediment and dissolved load are chemically complementary for the most soluble elements (Ca, Na, Sr, K, Ba, Rb and U). The depletion of these elements in the suspended phase (and the corresponding enrichment in the dissolved phase) is related to their high chemical mobility during silicate weathering. The variability over the hydrological year of trace elements in suspended matter has been attributed to the mixing between inputs of clay minerals and quartz. The distribution of the dissolved particulate ratio in the upper Niger basin leads to the conclusion that for the majority of elements, the sediment content controls the quantity of elements in the dissolved phase. As carbonate outcrops are insignificant in the upper Niger basin, it is possible to calculate chemical denudation rates by correcting water quality for atmospheric inputs. For the studied period, the denudation rates found range from 0.2 to 1.9×10^6 tons/year, corresponding to 26×10^3 to 100×10^3 mol CO₂/km²/year. Physical denudation rates were also estimated and range from 3.9 to 8.2 tons/km²/year. It appears that the low values of these chemical and physical denudation rates are related to a number of factors such as the lithology (silicate rocks), the lack of tectonism (permitting thick soil formation that limits bedrock weathering) and low precipitation (limiting runoff). Finally, a simple steady state model has been applied to the chemical composition of dissolved and solid products of silicate weathering. This model shows a good agreement between the modelled and the measured values of the suspended sediment concentrations, thus confirming the existence of steady state conditions in this tropical area. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Geochemistry; Chemical and physical denudation rates; Steady state; River Niger

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1. Introduction

Large rivers are the major pathways for the transport of erosion products from the continents to the oceans. They are studied by geochemists to estimate the fluxes of continental material supplied to the oceans, to investigate the erosion processes on a global scale and to calculate chemical and physical denudation rates. They also provide important information on CO₂ consumption through the acid degradation of continental rocks (e.g., Stallard and Edmond, 1983; Milliman and Meade, 1983; Meybeck, 1987; Négrel et al., 1993; Probst et al., 1992; Summerfield and Hulton, 1994; Boeglin and Probst, 1998; Gaillardet et al., 1995, 1997, 1999a; Roy et al., 1999). Such studies also enable important information concerning the average chemical and isotopic characteristics of the earth's continental crust to be deduced (Taylor and McLennan, 1985; Gaillardet et al., 1995; Dupré et al., 1996, Ramesh et al., 2000) and the processes which govern elemental distribution between particulate and solution phases in rivers (e.g., Goldstein and Jacobsen, 1988, Zhang et al., 1994; Dupré et al., 1996; Gaillardet et al., 1997; Elbaz-Poulichet et al., 1999; Tricca et al., 1999).

This paper presents the results of a major research programme on the Niger basin upstream of the inland delta (upper Niger) to determine the presence of trace and major elements in the dissolved and solid phases. The study was carried out by IRD (Institut de Recherche pour le Développement, France) during the period 1991/1992 to 1997/1998 (e.g., Olivry et al., 1995b; Bricquet et al., 1997a; Olivry, 1998) and only from 1996/1997 to 1997/1998 for trace elements (Picouet, 1999). The purpose of this paper is to elucidate the origin and behaviour of major and trace elements in these rivers and to determine their distribution patterns. Additionally, it estimates the present rock weathering rate and the flux of atmospheric/soil CO₂ consumption in the upper Niger basin.

2. Main features of the Niger basin upstream of the inland delta

The Niger river basin upstream of the inland delta (upstream from Ké-Macina on the Niger and Douna on the Bani, Fig. 1) in West Africa covers an area of about 250,000 km² and includes parts of four coun-

tries: most of the basin is found in Guinea and Mali, but smaller parts are in Ivory Coast and Burkina Faso. The basin is bordered by the Guinean ridge to the south, by the Fouta-Djalou and the Mandingue Mountains to the west and northwest. The main rivers are the Niger and the Bani that is coming from the south. The drainage basin area of the Bani at Douna is around 102,000 km². The mean elevation is around 500 m for the upper Niger river basin and around 300 m for the Bani river basin.

The upper Niger flows from the humid tropical zone at the southwest (annual precipitation more than 1500 mm) to the savanna zone at the northeast (annual precipitation close to 500 mm). For the period 1951–1990, the mean annual rainfall was around 1450 mm for the Niger and around 1110 mm for the Bani. These differences explain why, for the same period, annual depth of runoff was much greater for the Niger at Koulikoro (358 mm/year) than for the Bani at Douna (220 mm/year). Due to the type of climate with two seasons, a rainy season between July and September and a wet season between October and June, approximately 80% of the annual runoff is discharged during the warmest months (August to October). The annual flood begins in May. The rising limb of the hydrograph usually lasts until September. The recession is rapid, corresponding to an increased proportion of base flow. For an average year, peak discharge reaches 5600 m³/s at Koulikoro and 2450 m³/s at Douna (Olivry et al., 1995a).

The Niger river exhibits prolonged large changes in its flow characteristics before and after the early 1970s. This phenomena has been documented and analysed in a number of studies (e.g., Olivry et al., 1993, 1995a; Bricquet et al., 1997b) and took the form of marked decreases in Niger river flow. The changes in runoff and in rainfall between these two periods (changes are much larger, in percentage terms, for the runoff than for the rainfall) are accompanied by substantial changes in the runoff coefficients (rainfall/runoff depth × 100) which are associated with changes in groundwater resources within the upper Niger basin and possibly changes in land use/cover (e.g., Bricquet et al., 1996; Olivry et al., 1998). In view of this situation, it is thus important to note that the period of chemical investigations (1991/1992 to 1997/1998) is representative for the hydrological fluctuations over the last 25 years of drought (Fig. 2). In these 8 years,

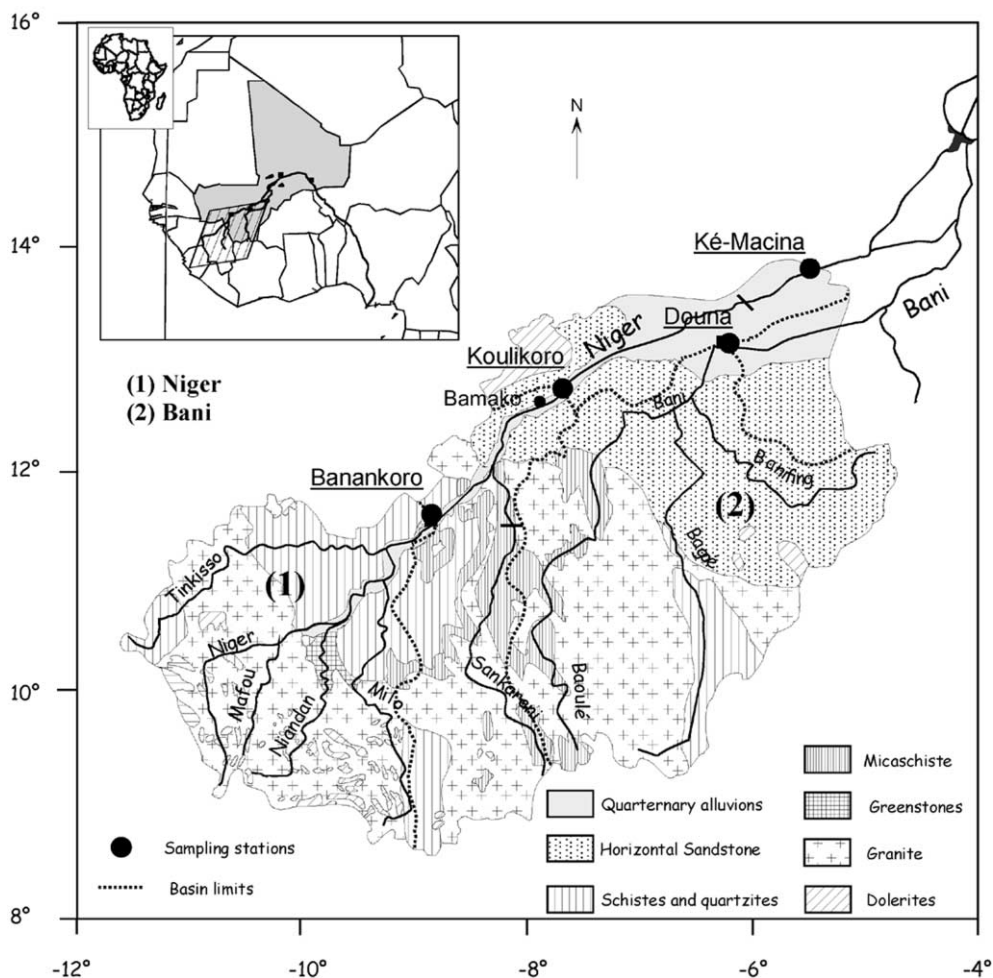


Fig. 1. The upper Niger basin. Simplified geological map and sampling locations.

the average discharges at Banankoro, Koulikoro, Ké-Macina and Douna were, respectively, around 740, 1020, 900 and 220 m³/s.

Geologically (Fig. 1), the Precambrian basement that underlies the southern part of the upper Niger basin and belongs to the West African Craton, is formed mainly by gneiss and granite complexes (Bessoles, 1977). The main metamorphic rocks here are schist, micaschist, quartzite and basic rocks transformed into greenstones. More recent dolerite intrusions are observed in all these formations. Birrimian rocks underlie the other half of the catchment. These Cambrian and Ordovician formations are mainly represented by sandstone. Quaternary fluvio-lacustrine

sediments underlie the lowland part of the Niger basin. The pedological cover, resulting from the weathering of these lithological formations, consists of ferralitic soils (upstream of Siguiri) and tropical ferruginous soils (in northern Guinea and southern Mali). Ferricrete layers often appear at the top of lateritic profiles. The vegetation consists mainly of savanna, dry or forested according to the climatic zone.

3. Sample sites, collection and analytical methods

River samples for the analysis of major and trace elements were collected at four different flow mon-

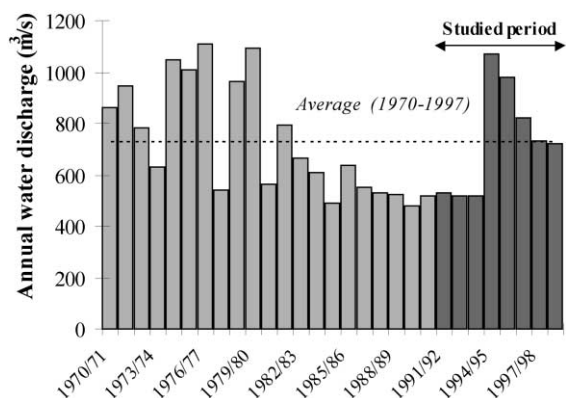


Fig. 2. Annual water discharge at the Koulikoro gauging station (Niger River) from 1970 to 1999. Average discharge for the period 1970–1997.

iting stations: Banankoro, Koulikoro and Ké-Macina are located on the Niger and Douna on the Bani (Fig. 1). Discharge, concentration of suspended sediment and major dissolved elements were analysed during eight hydrological years (1991/1992 to 1997/1998). Trace elements in the dissolved and suspended phases were only monitored for two hydrological years (1996/1997 and 1997/1998).

3.1. Major elements

Samples from the subsurface (at 40 cm depth and in the middle of the river) were collected twice a month. After collection, the samples were stored in the dark at each sampling location. Every 2 months, these samples of 1 l each were brought back to the Bamako laboratory where they were filtered with 0.2 μm cellulosic nitrate filters. Suspended sediments were isolated. Further chemical analysis was performed at the IRD laboratory in France. Between 1991 and 1996, the concentrations of SO_4^{2-} , NO_3^- and Cl^- were determined by ionic chromatography with a detection limit of 0.5 mg/l. The cations Ca^{2+} , Mg^{2+} , Na^+ and K^+ were analysed by atomic absorption with a detection limit of 0.001 mg/l. Dissolved silica was measured by plasma spectrophotometry, with a detection limit of 1 $\mu\text{mol/l}$. From 1997, both cations and anions were measured by ionic chromatography. The detection limits for the cations were: Ca: 0.1 mg/l; Mg: 0.05 mg/l; K: 0.025 mg/l; Na: 0.05 mg/l; NH_4^+ : 0.05 mg/l; for the anions: 0.05 mg/l. Sampling methods and analytical methods were

described in more detail in Gourcy (1994) and Picouet (1999).

3.2. Trace elements

3.2.1. Sampling and filtration

For the determination of trace elements, eight or nine samples were collected at each gauging station at different river stages. Acid-washed polyethylene containers were used (250 ml). Samples were collected by hand from the subsurface water (40 cm depth and in the middle of the river). The acid-washed polyethylene containers were closed into the stream. Two groups of samples were collected: bulk samples (for total phase analyses) and filtration samples (for the dissolved phase analyses). Immediately after collection, the second group of samples was filtered on-site through a 0.2- μm cellulose acetate filter. The filtration was performed with a pressurised Sartorius[®] teflon unit enclosed in a plastic chamber (homemade in Mali) to minimize the potential for introducing airborne contaminants. Filtered stream samples were then stored in polypropylene acid-washed bottles. Filtration blanks were run on the field before the stream sample filtrations. During the field trip, all the equipment used to prepare and preserve the stream samples for laboratory analyses is placed in clean plastic bags and then in a plastic box. All working procedures (sampling, filtration, storing) were carried out within standard guidelines in order to minimise contamination.

3.2.2. Analyses

Trace elements were analysed in the dissolved phase obtained after filtration (see above) and in the total phase (bulk sample) obtained after evaporation and attack with HF/HNO_3 . The choice of using the total phase is based on the fact that the concentration of suspended sediment is very low. The concentration of trace elements in the particulate phase can be then obtained with the following equation:

$$C_P = \frac{C_T - C_D}{SSM} \quad (1)$$

where C_P is the concentration in ppm of trace element in the particulate phase; C_T , the concentration in ppb of trace element in the total phase; C_D , the concen-

tration in ppb of trace element in the dissolved phases; and SSM, the suspended sediment matter in mg/l.

A procedure similar to the one used by Freydier et al. (1998) was applied to the bulk sample before the analyses. An aliquot of the sample (10 ml) was evaporated in a Teflon beaker at 40–50 °C. The residue was treated with 1:1 HF/HNO₃ and evaporated during 12 h at 80 °C. The HF/HNO₃ solution was then evaporated (40–50 °C) and diluted in 10 ml distilled water with 2% HNO₃. These operations were performed under a laminar airflow bench. Blanks with deionised water were submitted to the same treatment as the sample. Concentrations observed in the blanks were negligible compared to river sample concentrations.

The concentrations of trace elements in the dissolved and total phases were measured by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). Samples were analysed in a Perkin–Elmer ELAN 5000 ICP-MS equipped with a standard pneumatic nebulizer and an automatic sampler (AS-80) and using the internal standard method with Indium (Dupré et al., 1996). The samples, reference samples for the internal standard method and blanks were treated with 2% HNO₃ solutions. The accuracy and precision of the analytical method were tested using the SLRS-3 standard (National Research Council Canada), which has certified concentrations for certain elements (Mg, V, Cr, Mn, Co, Ni, Zn, Rb, Sr, Ba, Pb, U, Al, Fe). The estimated uncertainties for trace elements are two standard deviations of the concentrations. For Mg, Mn, Rb, Sr, Ba, U, Al and Fe, concentrations were found to be in agreement with the certified values at approximately 10%. Greater uncertainties were estimated for Ni (11%), V (12%), Cu (14%), Pb (14%), Co (20%), Cr (24%) and above all Zn (42%). Detection limits (Table 2a) were calculated according to normal conventions (Vandecasteele and Block, 1993) with 12 HNO₃ blanks.

Concentrations in the blanks were not significant for any of the elements when compared to the concentration of the river samples. Potential contamination during filtration due to containers or environmental features was also tested using filtration blanks, both in the laboratory and in the field. The comparison between these two filtration blanks showed that the differences in concentration are not significant for any of the elements except for Zn which was therefore excluded from further analysis. Mg, Al and Mn presented very

low concentrations in the blanks probably due to the filter and/or the environment of the filtration in the field.

4. Results

4.1. Dissolved load

4.1.1. Major elements

The mean chemical composition (volume weighted mean concentrations) for the different gauging stations is shown in Table 1. The total cation charge (Σ^+), the total anion charge (Σ^-), the charge balance defined in percentage as $\Sigma^+ - \Sigma^- \% = 200 \times (\Sigma^+ - \Sigma^-) / (\Sigma^+ + \Sigma^-)$, the total dissolved load (TDS) and the suspended sediment concentration (SSM) are also given. The Niger and its tributary, the Bani, have very low mineralisation ($300 < \Sigma^+ < 430 \mu\text{eq/l}$). The least mineralised site is on the Niger at Banankoro, while the Bani at Douna is the most mineralised. These values are very low compared to the mean total cation charge of other unpolluted rivers of the world ($800 \mu\text{eq/l}$, Meybeck et al., 1996). TDS values, ranging from 38 to 49 mg/l, are in agreement with data on the Niger presented by Gourcy (1994) and Boeglin and Probst (1996). They are also similar to the values obtained in other West African rivers: 36.4 mg/l for the Congo at Brazzaville (Laraque et al., 1995), 48 mg/l for the Oubangui at Bangui (Orange et al., 1995), 42 mg/l for the Senegal at Bakel (Gac, 1986), 44 mg/l for the Gambia (Meybeck et al., 1987) and about 33.0 mg/l for tributaries of the upper Niger river in the Fouta Djallon (Orange, 1992).

Table 1 shows some other characteristics of the Niger.

(1) The concentration of anions follows the order $\text{HCO}_3 > \text{Cl} > \text{NO}_3 > \text{SO}_4$. HCO_3 is the most abundant anion in each river; it accounts for 90% of the dissolved ions (in $\mu\text{eq/l}$). Among the cations, Na is slightly dominant for the Niger at Banankoro, accounting for about 30% of the total cations (in $\mu\text{eq/l}$). Concentrations of cations vary in the order $\text{Na} > \text{Ca} > \text{Mg} = \text{K}$ in this river. For the Bani at Douna, Ca is dominant (in $\mu\text{eq/l}$). Here, the concentration of cations follows the order $\text{Ca} > \text{Na} > \text{Mg} > \text{K}$. Variations in bedrock composition lead to the differences in stream water chemistry observed between the Niger and the Bani rivers. This

Table 1
Major mean concentrations weighted by discharge for upper Niger rivers for the period 1991–1997

	Niger River										
	Banankoro (71000 km ²)							Koulikoro (120000 km ²)			
	1991– 1992	1992– 1993	1993– 1994	1994– 1995	1995– 1996	1996– 1997	Mean	1991– 1992	1995– 1996	1996– 1997	Mean
<i>N</i>	31	8	12	24	19	18		23	24	16	
Ca	48.4	56.6	36.7	62.2	57.4	47.5	51.5	50.4	62.5	58.2	57.0
Mg	44.3	30.1	51.4	54.9	55.5	47.4	47.2	37.8	47.7	43.7	43.0
K	46.0	29.2	35.0	36.7	32.3	22.7	33.7	64.7	38.1	32.8	45.2
Na	95.5	154.9	129.3	92.6	93.8	90.7	109.5	120.3	120.5	132.5	124.4
Alc	324	356	344	341	334	318	336	328	381	370	360
Cl	17.7	15.9	12.9	19.7	15.6	10.1	15.3	30.8	20.6	18.4	23.3
SiO ₂	219	276	236	194	209	209	224	139	227	241	203
Σ ⁺	327	357	341	363	352	303	341	361	370	369	367
Σ ⁻	345	383	358	379	351	333	358	375	384	390	383
Σ ⁺ –Σ ⁻	–5%	–7%	–5%	–4%	0.2%	–9%	–5%	–4%	–4%	–6%	–4%
TDS	40.7	47.1	42.7	41.6	40.5	38.6	41.9	38.4	45.6	45.6	43.2
SSM	20.1	25.1	28.4	23.7	27.9	22.0	24.5	25.1	24.5	29.0	26.2
<i>Q</i>	531	521	521	1070	977	858	746	767	1310	1050	1039

N is the number of samples. The major element concentrations are in μmol/l. The total cation charge (Σ⁺) and the total anion charge (Σ⁻) are in eq/l. Total Dissolved Solid (TDS) and Suspended Sediment Matter concentration (SSM) are in mg/l. The mean annual discharge *Q* is in m³/s.

slight difference corresponds to the fact that there are more sandstone formations in the Bani catchment than in the Niger catchment where granitic formations dominate. Indeed, it has been known for a long time that lithology is a key factor for most major dissolved elements in streamwater: for example, the abundance of Na (in μeq/l) is greater for the monolithologic catchments characterized by granite rock type than for the monolithologic catchments characterized by sandstone rock type and conversely for Ca (Meybeck, 1987; Meybeck, 1994). However, weathering is only one of several geochemical processes that release Ca to soil solution and then to stream water: displacement of Ca from soil exchange sites and mineralization of Ca associated with soil organic matter may also contribute to solution Ca fluxes (Likens et al., 1998).

(2) The difference between total cations and anions, that is, Σ⁺–Σ⁻% (Σ⁺–Σ⁻% = 200 × (Σ⁺–Σ⁻)/(Σ⁺+Σ⁻)), is generally less than 5% and nowhere exceeds 10%. This result indicates that organic anions (not measured in this study) are not abundant in the Niger when compared, e.g., to the rich organic water of the Congo (Probst et al., 1992; Dupré et al., 1996; Orange, 1996) and Amazon (Guyot, 1993; Gaillardet et al., 1997). The dissolved organic carbon concentration was determined by Picouet (1999) and ranged from 0.9 to 7

mg/l in all gauging stations. These values are in agreement with the world average of 4.2 mg/l estimated by Meybeck et al. (1996) and are significantly lower than the values measured in humid tropical sites: e.g., 10 to 20 mg/l on the Mengong in Cameroon (Viers et al., 1997) and 10.5 mg/l on the Congo at Brazzaville (Seyler et al., 1995). The upper Niger rivers are therefore non-organic rivers.

(3) A major feature of the Niger rivers is that the dissolved load is dominated by SiO₂ and HCO₃ which represent 78% to 81% of the total dissolved load (26% to 32% of TDS for SiO₂ and 49% to 53% for HCO₃). The concentrations of dissolved SiO₂, of which the interannual mean ranges from 203 to 224 μmol/l (11.9 to 13.5 mg/l), are explained by the quantity of silicate rocks that underlie the catchment. These values are close to the world average concentration, which is equal to 10.8 mg/l (Meybeck et al., 1996).

The concentrations of major elements in the upper Niger stream water show a large variability during the year in relation with the hydrological cycle (Fig. 3). For the upper Niger rivers, the total dissolved solids (TDS) decline in concentration with increased discharge and vice versa. Such variability, common to most of the rivers, has been reported by numerous authors (e.g., Walling and Foster, 1975; Walling and Webb, 1980;

Ké-Macina (141000 km ²)							Bani River						
							Douna (102000 km ²)						
1991– 1992	1992– 1993	1993– 1994	1994– 1995	1995– 1996	1996– 1997	Mean	1991– 1992	1992– 1993	1993– 1994	1994– 1995	1995– 1996	1996– 1997	Mean
24	12	15	22	26	14		36	12	17	21	19	7	
50.6	48.4	54.4	65.5	68.6	66.9	59.1	60.4	69.9	64.8	81.4	70.1	68.1	69.1
36.6	27.2	55.8	47.1	47.8	45.7	43.4	48.8	38.5	57.4	57.0	53.0	51.5	51.0
30.0	44.4	42.1	38.1	37.8	37.3	38.3	55.7	56.6	55.7	57.5	48.9	47.6	53.7
122.7	150.3	156.9	106.4	117.1	124.2	129.6	104.2	156.9	104.9	92.7	110.5	105.5	112.5
314	319	372	369	398	401	362	359	389	400	424	390	375	389
9.4	37.7	31.3	14.4	15.2	14.7	20.4	23.5	22.0	11.8	16.2	13.0	12.8	16.6
226	243	246	154	230	232	222	192	255	210	151	–	223	206
327	346	419	370	388	387	373	378	430	405	427	406	392	406
332	366	403	384	413	421	386	398	449	414	446	406	411	421
–2%	–5%	4%	–4%	–6%	–8%	–4%	–5%	–4%	–2%	–4%	0%	–5%	–3%
40.4	43.6	47.8	40.5	47.7	47.3	44.5	43.2	46.1	46.1	45.7	–	46.8	45.6
–	32.9	33.3	50.6	45.9	54.2	43.4	42.8	52.3	74.1	50.3	55.1	66.9	56.9
686	681	647	1320	1180	929	907	190	139	135	459	224	200	225

Davis and Keller, 1983; Kattan and Probst, 1986; Probst et al., 1992; Meybeck et al., 1996). It can be explained by a conservative mixing relationship between a high-solute-concentration component, base flow (groundwater input) and a low-solute-concentration component, runoff (rainwater input). The relationships between dissolved concentration and discharge, which take the form of a linear equation or a power function, express a dilution of the river waters by rain and surface waters. The high evaporation occurring at the end of the rainy season also leads to increasing concentrations. Hysteresis in the relationship between discharge and concentration can be recognised for some elements, hydrological years and gauging stations: the concentration at a given discharge on the rising limb of the hydrograph differs from that at the same discharge on the falling limb. Anticlockwise hysteresis loops are observed for elements such as Na, Ca, Mg and HCO₃, whereas clockwise hysteresis loops are observed for K. The clockwise hysteresis loops for K is due to the fact that K is leached from organic material and is therefore more concentrated in surface water than in groundwater, contrary to the other elements (e.g., Pierson and Taylor, 1994). These kinds of cycles are well illustrated for the Bani river, where the minimum dissolved concentration appears distinctly

earlier than the peak of water discharge (see examples of hysteresis loops in Fig. 4 for Banankoro and Douna gauging stations). This hysteresis in the episode concentration/discharge has been observed by many authors and is commonly explained by a difference in the relative timing or form of solute and discharge responses (e.g., Walling and Foster, 1975; Walling and Webb, 1980; Davis and Keller, 1983; Ewans and Davies, 1998). Assuming that dissolved elements and water are transported at the same speed, these hysteresis loops could be explained by three main factors: early episode flushing of soluble material, variable seasonal contribution of different reservoirs (rainwater, subsurface runoff water, runoff water, groundwater, soil water...) and different spatial contributions of different tributaries. However, additional works and modelling would be required to use solutes as hydrologic tracers in the upper Niger basin.

Finally, the specific dissolved loads are calculated from the total dissolved loads (TDS) and expressed in tons/km²/year (Picouet, 1999). The upper Niger rivers are then characterised by low chemical denudation rates: values vary from 9.6 to 19.8 tons/km²/year for the Niger at Banankoro, from 7.7 to 17.5 tons/km²/year at Koulikoro, from 6.7 to 17.7 tons/km²/year at Ké-Macina and from 2.0 to 7.7 tons/km²/year for the

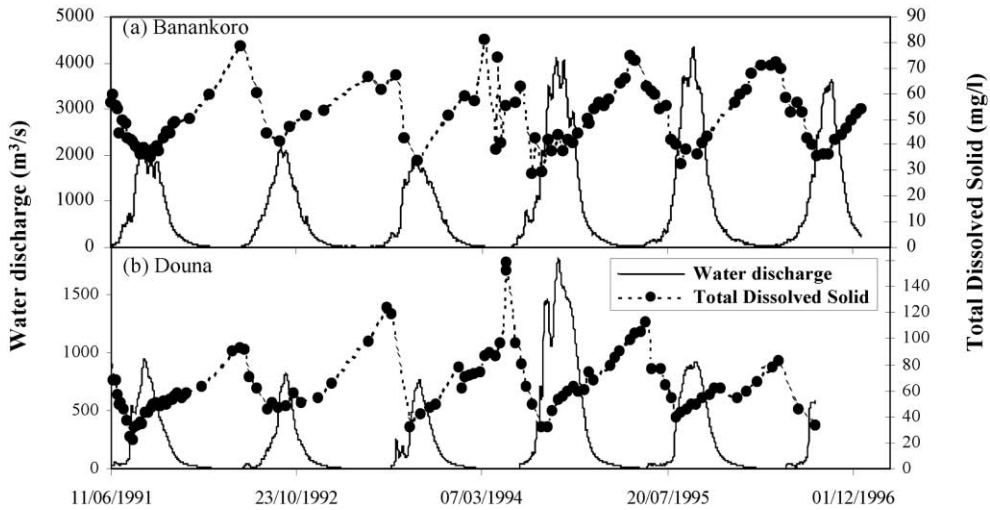


Fig. 3. Time evolution of discharge (Q) and Total Dissolved Solid concentration (TDS—Dashed line) at Banankoro and Douna gauging stations (for the period 1991 to 1996). The discharge data are recorded daily whereas the concentrations are usually recorded at 1-month intervals. The period from May to April represents one hydrological year.

Bani at Douna. Low annual runoff is the main factor explaining the lack of dissolved loads observed on the Bani catchment. Because of a large number of reasons (atmospheric inputs, differences in rock solubility,

non-conservative behaviour of elements, contribution of human activities, etc.), these specific dissolved loads should not be considered as weathering rates. These will be estimated in Section 6.

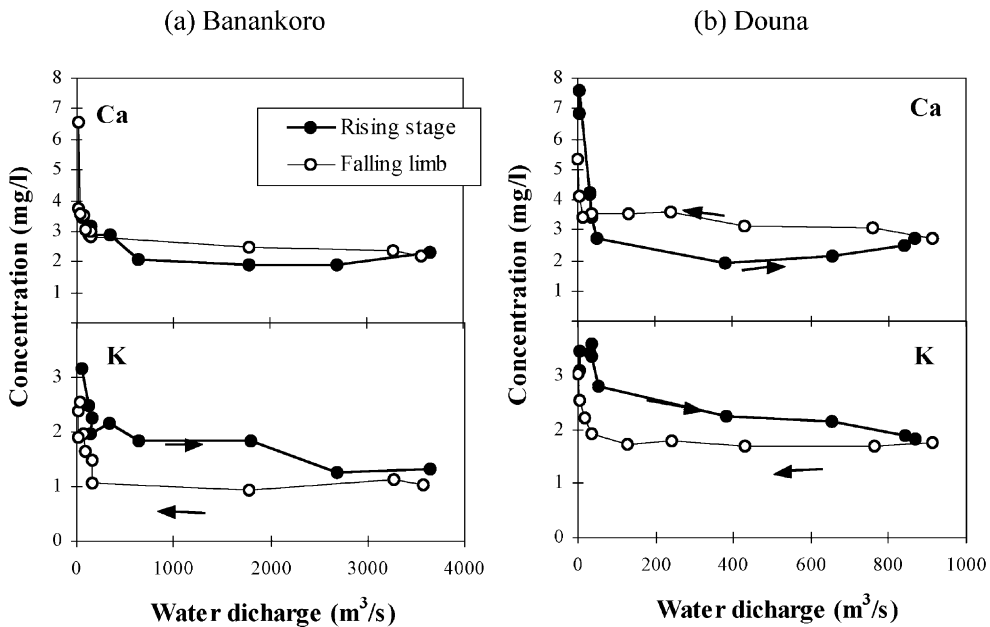


Fig. 4. Typical relationships between dissolved concentrations and discharge for the Niger at Banankoro (a) and for the Bani at Douna (b). Examples for Ca and K elements and for the hydrological year 1995–1996.

4.1.2. Trace elements

No data exist for the upper Niger rivers in Mali, although dissolved trace element data exist for other unpolluted tropical hydrosystems like the Congo (e.g., Négrel et al., 1993; Dupré et al., 1996) and the Amazon (e.g., Gaillardet et al., 1997) systems.

Similar to what was found for the major elements, the Niger and the Bani show slight differences in absolute concentrations of trace elements (Table 2): Rb, U, La, Ce, Zr and Sm are higher, whereas Pb, Ba, Cr and Ni are lower in the Niger at Banankoro than in the Bani at Douna. The other elements present similar concentrations in the two rivers. In general, these concentrations are within the range found in other large rivers. When compared to the Amazon and Congo (Négrel et al., 1993; Dupré et al., 1996; Gaillardet et al., 1997), differences are found for Sr and Ba. For example, the concentration of Ba varies from 12.9 to 60.9 ppb, while in the Amazon and Congo basins, values of 6.1 to 28 ppb were measured.

In order to investigate the relations between the elements in the dissolved phase, a correlation matrix was calculated. For all gauging stations, the results lead to the same conclusions (all for concentrations).

(1) Sr and Ba are strongly correlated with the major elements Na, Ca, Mg and alkalinity (Fig. 5). These elements generally decrease with discharge as do major elements.

(2) Rb and U are slightly correlated with these same major elements. This indicates that Rb and U participate in or are controlled by processes other than those that control the quantity of major ion chemistry. For example, the close correlation observed between Rb and K (Fig. 5) could be explained by their closely linked behaviour in the vegetation cycle. The same clockwise hysteresis in the relationship between discharge and concentration for K can be recognised for Rb (Fig. 5).

(3) All other trace elements do not show systematic relations with Na, Mg, Ca, alkalinity and water discharge. Th and Co are more or less well correlated with rare earth elements.

For rare earth elements (REE), absolute concentrations in the dissolved phase fluctuate widely but are generally lower than those observed in the Congo and Amazon basins. For example, at Banankoro, individual concentrations range from 0.0095 to 0.116 ppb (Table 2) with a mean of 0.076 ppb. Increasing con-

centrations were observed going from the Niger at Banankoro to the Bani at Douna for most of the rare earth elements. As a result, all REE concentrations show a high correlation, with a majority of coefficients greater than $r=0.9$ (e.g., La and Ce in Fig. 6a). As pH values are similar for the samples, a possible dependence on pH of the REEs in the dissolved phase could not be detected. However, compared to the world's major rivers (Fig. 6b), the upper Niger river concentrations of La are in good agreement with the La concentration for water with pH near neutrality. As suggested by many authors, the general decrease of dissolved REE concentrations with increasing pH indicates that pH is a major factor controlling the REE quantities and the shape of REE distribution patterns in the dissolved load (Goldstein and Jacobsen, 1988; Dupré et al., 1996; Gaillardet et al., 1997; Tricca et al., 1999).

In order to get information on the upper continental crust composition in this large African basin, the data were normalised to the mean upper crust composition (UCC) as proposed by Taylor and McLennan (1985) (Figs. 7 and 8). Such a representation has previously been used for the Congo basin by Dupré et al. (1996) and for the Amazon Basin by Gaillardet et al. (1997). In these diagrams, the order of elements corresponds to the progressive enrichment from Ni to Cs of elements in the upper continental crust compared to the mantle of the earth. In spite of variations in absolute concentrations, the observed patterns are remarkably similar, but they are neither linear nor regular. All elements are strongly deficient with respect to the upper continental crust. Fig. 7 presents these UCC normalised patterns for the average of water samples. These graphs indicate the differences between the elements Rb, U, Ba, Sr, Zr, Hf and the other elements: the elements Rb, Ba, Sr and Ca, known as soluble, are all enriched in the dissolved phase relative to the neighbouring element, whereas Th, Pb, Fe, Co, Ni and REEs are depleted. The element Zr and Hf are also strongly depleted in the dissolved phase of the Niger rivers. The same was described for the Congo and Amazon systems (Dupré et al., 1996; Gaillardet et al., 1997).

In Fig. 8, the mean dissolved REE concentrations display a more or less pronounced upward convexity centered on the intermediate REEs (Sm, Eu and Gd). Values for heavy REEs are often under the detection

Table 2

Trace element concentrations in the dissolved phase (C_D) of upper Niger rivers in ppb

(a)											
Station (river)	Detection limits	Banankoro (Niger)									
Sample		1	2	3	4	5	6	7	8	9	Mean*
V ^a	0.013 ^b	0.63	0.70	0.31	0.29	0.28	0.31	0.73	0.66	0.37	0.43
Cr	0.025	0.35	0.55	0.61	0.41	0.28	0.49		0.74	1.28	0.68
Mn	0.010	0.59	0.99	0.18	1.83	0.64	0.37	4.56	1.04	0.45	0.94
Fe	1.181	40	122	19	144	157	15	37	182	139	126.9
Co	0.004	0.023	0.056	0.044	0.047	0.036	0.012	0.051	0.053	0.035	0.05
Ni	0.39	0.53	0.53	0.52	0.61			0.45	0.58	0.44	0.55
Cu	0.01	0.47	0.64	0.78	0.82	0.37	0.32	0.85	0.65	0.51	0.67
Zn	0.139		2.59	1.97	5.27	0.17	1.11	3.05	0.57	1.21	2.16
Rb	0.003	5.8	5.1	3.4	3.1	3.0	4.0	5.6	4.0	3.3	3.66
Sr	0.007	38.4	33.4	21.1	28.5	37.3	39.6	50.8	24.6	27.2	26.6
Zr	0.01	0.045	0.135	0.040				0.019	0.125	0.061	
Cs	0.001	0.010	0.012	0.009	0.003	0.003	0.009	0.013	0.013	0.010	0.01
Ba	0.017	42.4	38.6	28.9	30.7	37.9	39.7	51.4	28.8	27.7	30.2
La	0.001	0.050	0.106	0.046	0.064	0.057	0.010	0.039	0.116	0.068	0.076
Ce	0.001	0.075	0.185	0.088	0.142	0.118	0.014	0.135	0.234	0.146	0.155
Nd	0.011	0.034	0.080	0.060	0.052	0.043		0.045	0.110	0.068	0.072
Sm	0.011	0.016	0.016	0.013					0.024	0.012	
Eu	0.003		0.006	0.007			0.015	0.018	0.008		
Tb	0.001		0.002	0.002					0.003		
Yb	0.003		0.006	0.004							
Hf						0.005	0.002		0.002	0.004	
Pb	0.013	0.018	0.032		0.153		0.019	0.284	0.046	0.091	0.091
Th	0.002	0.013	0.023	0.007	0.005	0.003		0.006	0.020	0.011	0.011
U	0.002	0.016	0.023	0.019	0.006	0.008	0.012	0.024	0.021	0.012	0.015
Ca ^c			2.5	1.8	2.2	2.5		3.9		2.3	
Mg			1.3	1.0	1.3	1.3		2.4		1.3	
K			1.8	1.4	0.9	1.0		2.0		1.0	
Na			3.3	2.3	2.5	3.5		5.4		2.6	
Alkalinity			26.1	18.7	23	26.8		42.6		22.7	
Cl			0.5	0.4	0.2	0.2		0.6		0.4	
SiO ₂			7.5	5.9	6.5	8.2		8.1		7.1	
pH			6.9	6.8	7	7.2		7.4		6.9	
DOC ^d					1.81	0.92		1.7	7.64		
Discharge ^e		80	233	1560	1950	485	49.9	10.7	2160	1340	

limit. A positive Eu deviation is found for all gauging stations: $[Eu/Sm]_N$ ratios (dissolved Eu/Sm ratio UCC normalised) range from 1.3 to 1.7.

4.2. Suspended load

4.2.1. General features

On a global scale, the Niger belongs to the group of the lowland African rivers with very low suspended sediment matter concentrations. Calculated for the eight hydrological years, the average suspended sediment concentration (weighted by discharge) varied

between 24 and 43 mg/l for the Niger (from Banankoro to Ké-Macina); it was 59 mg/l for the Bani. The relationships between discharge and sediment concentration during the annual flood are described by clockwise hysteresis loops (e.g., Fig. 9). These temporal variations in suspended sediment transport would be related mainly to the decrease of sediment availability during the rainy season and the increased portion of base flow during the recession limb of the hydrograph (Picouet et al., 2001). Maximum concentrations ranged from 80 mg/l at Banankoro to 250 mg/l at Douna, all during high discharge periods. The

Banankoro (Niger)									
1	2	3	4	5	6	7	8	9	Mean*
0.56	0.47	0.40	0.41	0.43	0.45	0.73	0.40	0.42	0.46
0.33	0.63	0.30	0.27	0.41		0.46	0.55	0.00	0.42
0.51	0.34	1.65	1.06	0.46	1.01	0.42	0.96	0.49	0.87
69	52	186	183	14	36	44	109	132	112.0
0.048	0.043	0.036	0.037	0.023	0.029	0.029	0.043	0.031	0.04
0.59	0.46					0.41	0.44	0.33	
0.64	0.81	0.52	0.47	0.37	0.46	0.64	0.57	0.48	0.59
1.19	1.12	0.37	0.20	0.16	1.01	0.39	0.63	0.33	0.58
5.7	3.6	3.7	3.3	4.1	4.7	4.1	3.9	3.5	3.81
34.2	21.9	30.6	34.5	35.8	34.2	20.2	23.9	28.2	26.0
0.095	0.083				0.019	0.086	0.075	0.056	
0.011	0.008	0.006	0.009	0.006	0.012	0.010	0.012	0.010	0.010
36.9	27.9	34.3	35.6	33.8	38.0	23.0	30.7	29.2	30.4
0.068	0.085	0.099	0.083	0.011	0.017	0.084	0.073	0.073	0.081
0.107	0.151	0.216	0.183	0.019	0.038	0.168	0.165	0.156	0.169
0.040	0.084	0.086	0.071	0.017		0.096	0.071	0.062	0.076
	0.018		0.014			0.025	0.014	0.015	
	0.010			0.014	0.015	0.008	0.004		
0.000	0.003								
	0.005						0.004		
	0.002							0.003	
0.054	0.028	0.038	0.046			0.047	0.049	0.036	0.042
0.016	0.012	0.004	0.005			0.011	0.012	0.010	0.010
0.014	0.017	0.011	0.009	0.015	0.008	0.019	0.014	0.014	0.014
2.8	1.9	2.2		3.1	2.9			2.3	
1.3	1.0	1.1		1.5	1.4			1.2	
2.0	1.4	1.0		1.5	1.5			1.1	
3.7	2.6	2.7		4.0	3.8			2.6	
27.8	20.6	21.6		30.8	29.2			22.7	
0.7	0.3	0.5		0.5	0.5			0.4	
4.8	6.2	6.9		6.6	6.6			7.5	
6.9	6.8	6.9		7	7			7.1	
	1.6	1.6	1.22	1.7	1.25		2.48		
424	1680	2460	574	92.1	99.6	1560	4340	1460	

(continued on next page)

higher suspended sediment concentrations found in the Bani probably reflect the sensitivity to erosion of the soils (ferruginous soils) and the larger agricultural areas (Picouet, 1999). Although the annual discharge decreases slightly between Koulikoro and Ké-Macina, the mean annual sediment concentration increases. This is probably due to inputs of the intermediate basin which is underlain by sandstones and quaternary deposits more susceptible to mechanical erosion (Picouet, 1999).

The mineralogy of the suspended sediments determined by X-ray diffraction analysis is mainly quartz

with minor kaolinite and illite (Gourcy, 1994; Censier et al., 1995). The average proportions of clay minerals are kaolinite (70–85%) and illite (15–25%). Particulate organic carbon (POC in wt.%), determined by Picouet (1999) using different aliquots with a 0.45- μm site filtration, varied from 1.3% to 20%. The proportions of particulate organic carbon and corresponding sediment concentration values confirm the expected inverse correlation between POC and sediment content in rivers reported at a world scale by Meybeck (1982): organic matter is diluted by mineral matter transported by the flood wave.

Table 2 (continued)

Station Sample	Ké-Macina (Niger)								Mean*
	2	3	4	5	6	7	8	9	
V ^a	0.73	0.66	0.50	0.43	0.42	0.69	0.64	0.53	0.59
Cr	0.51	0.72	0.31	0.21	0.63		0.46	0.00	0.45
Mn	0.70	0.32	0.88	0.53	0.26	0.44	0.27	0.59	0.50
Fe	75	71	176	88	22	39	55	166	105.1
Co	0.060	0.052	0.031	0.028	0.019	0.030	0.039	0.030	0.04
Ni	0.67							0.29	
Cu	0.68	0.78	0.59	0.44	0.41	0.46	0.61	0.44	0.63
Zn	0.45	0.89	0.47			0.21	0.28		
Rb	5.5	3.9	3.6	3.4	3.7	5.0	4.1	3.6	3.86
Sr	33.4	22.8	30.7	35.2	36.6	41.3	20.9	29.2	26.4
Zr	0.157	0.135			0.018	0.023	0.114	0.075	0.12
Cs	0.021	0.011	0.009	0.008	0.006	0.008	0.010	0.009	0.01
Ba	42.3	28.1	33.9	35.5	37.5	41.4	25.1	30.0	30.2
La	0.114	0.096	0.109	0.065	0.020	0.029	0.058	0.103	0.091
Ce	0.171	0.164	0.235	0.130	0.030	0.057	0.104	0.202	0.171
Nd	0.092	0.097	0.089	0.049	0.020	0.040	0.056	0.101	0.085
Sm	0.026	0.018	0.017	0.017				0.018	
Eu		0.008			0.017	0.023	0.005		
Tb	0.002	0.003					0.002	0.002	
Yb		0.007						0.005	
Hf	0.003	0.001	0.006		0.001			0.003	
Pb	0.027	0.028	0.044	0.017			0.054	0.052	0.039
Th	0.021	0.017	0.007	0.003	0.004	0.003	0.012	0.014	0.013
U	0.022	0.025	0.016	0.012	0.017	0.021	0.022	0.016	0.020
Ca ^c			2.3	2.5				2.4	
Mg			1.1	1.3				1.2	
K			1.1	0.9				1.1	
Na			2.7	3.3				2.6	
Tac			22.8	25.9				23.2	
Cl			0.3	0.2				0.4	
SiO ₂			7.4	7.6				7.1	
pH			6.9	7				7	
DOC ^d	1	1.94	1.2	0.84	1.72	1.46	2	0.95	
Discharge ^e	279	3170	1860	570	69	38.4	1430	1210	

^a Trace elements in the dissolved phase in ppb (determined by ICP-MS).

^b Detection limits for trace element concentrations are calculated according to normal conventions with 12 HNO₃ blanks, see text for major elements.

^c Major elements in the dissolved phase in mg/l.

^d Dissolved Organic Carbon, DOC, in mg/l.

^e Discharge in m³/s.

* Volume weighted values (calculated for the elements where 70% of the values are higher than the detection limit).

4.2.2. Trace elements

Trace element concentrations in the particulate phase were obtained in an indirect way as explained before. The results obtained for the total phase are difficult to interpret because of the strong correlation between the concentration of elements in the total phase with suspended sediment matter (except Sr). It

is thus necessary to know the values in the two phases. Nevertheless, an important result of this study showed that enrichment factors (Table 3) calculated from total trace metal concentrations of Co, Cu, Fe, Mn, Ni and Pb were close to one. These results confirm that the upper Niger rivers, where there is less human activity compared to other large rivers in

Douna (Bani)								
2	3	4	5	6	7	8	9	Mean*
1.54	0.70	0.67	0.58	0.67	1.62	0.72	0.63	0.71
0.42	0.58	0.30	0.21	0.57	0.00	0.26	0.00	0.35
0.64	0.28	1.43	1.01	0.48	2.03	0.35	0.65	0.62
63	41	251	134	35	53	22	164	98.1
0.099	0.054	0.039	0.038	0.035	0.068	0.026	0.040	0.04
0.61				0.43	0.55		0.31	
0.98	0.93	0.72	0.65	0.54	0.72	0.64	0.59	0.76
0.63	1.26	0.75		0.33	0.16	0.28	0.20	0.73
9.9	4.0	5.2	5.1	5.1	7.7	3.2	5.2	4.4
69.7	17.4	35.9	37.2	42.2	57.9	9.9	35.1	23.68
0.111	0.114			0.042	0.038	0.066	0.125	0.099
0.029	0.019	0.014	0.012	0.013	0.021	0.015	0.018	0.017
60.9	19.1	28.3	29.8	35.2	42.4	12.9	27.3	21.9
0.075	0.137	0.163	0.093	0.024	0.038	0.080	0.122	0.121
0.100	0.261	0.357	0.201	0.048	0.072	0.165	0.228	0.244
0.048	0.188	0.254	0.135	0.016	0.034	0.121	0.133	0.170
0.016	0.034	0.041	0.034		0.002	0.023	0.023	0.031
0.006	0.010	0.010		0.019	0.022	0.007	0.005	0.008
0.001	0.004	0.004			0.001	0.002	0.003	0.003
	0.006						0.007	
	0.007			0.001			0.004	
0.032	0.021	0.078	0.023		0.027	0.017	0.047	0.035
0.017	0.021	0.005	0.006	0.003	0.004	0.007	0.015	0.013
0.217	0.040	0.032	0.028	0.060	0.134	0.019	0.033	0.036
	3.7		3.0	3.1			3.9	
	2.4		1.4	1.6			2.0	
	4.2		1.6	1.6			1.8	
	2.0		3.3	3.7			3.1	
	36.2		27.5	30			33.2	
	0.6		0.3	0.5			0.6	
	5.5		7.9	7.9			8.2	
	7.2		7	7.1			7.4	
	1.7	4.75	4.95	3.95	6.65	1.3	4.6	
42.2	572	325	83.2	2.2	1.5	427	210	

the world, are still unpolluted with respect to heavy metals.

Mean trace element concentrations of the upper Niger rivers are similar to those found in the Congo and Amazon systems (Table 3). For example, absolute La concentrations range from 25 to 64 ppm on the Niger, while it varies between 37 and 57 for the two

others large rivers (except in the ‘Coca-Cola’ rivers rich in organic matter). Most other REE are consistent with this range of variation, which is related to high correlation coefficients between the elements. Only Pb concentrations are lower, while Sr, Cr, Ni and Co concentrations are higher than in the other two big river systems. The major difference between the Niger

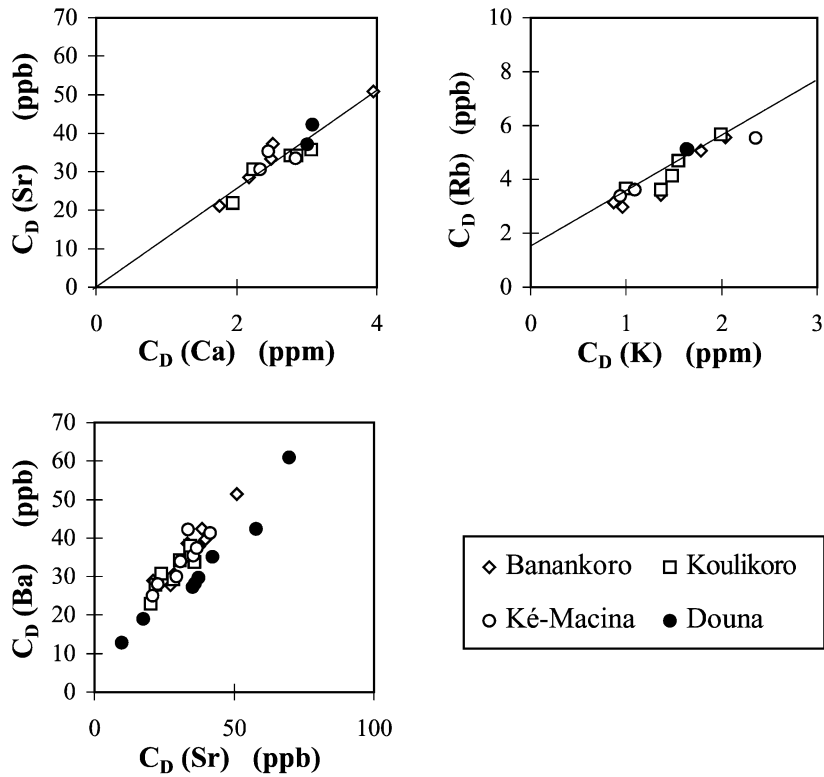


Fig. 5. Relationships between some trace element concentrations in the dissolved phase (C_D in ppm) of the upper Niger rivers.

and the Bani is total particulate matter concentration, which is highest in the Bani. Furthermore, Ba, Sr, Co, Cr and Ni are less concentrated in the Bani particulate matter than in the Niger particulate matter.

In spite of these variations in absolute concentrations, all patterns for the UCC normalised suspended sediment concentrations of the Niger rivers are remarkably similar (except for Pb and Ta) (Fig. 7).

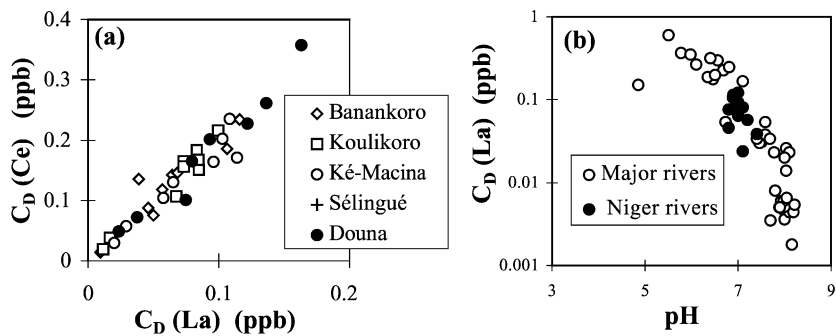


Fig. 6. (a) Plot of Ce concentrations in the dissolved phase ($C_D(\text{Ce})$), against La concentrations in the dissolved phase ($C_D(\text{La})$), for the upper Niger rivers. (b) La concentrations in the dissolved phase as a function of pH. Comparison with data from the literature (Goldstein and Jacobsen, 1988; Dupré et al., 1996; Gaillardet et al., 1997).

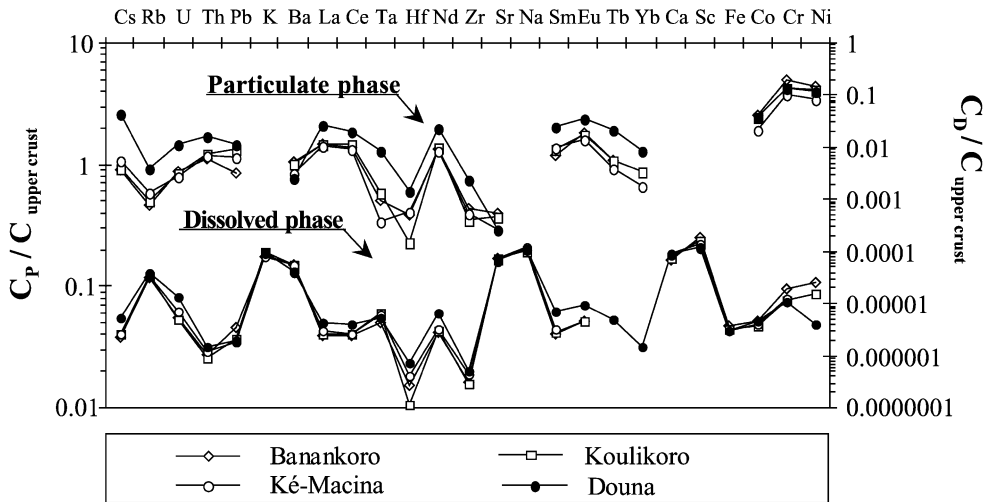


Fig. 7. Diagram showing the mean composition of the upper Niger rivers normalised to the upper continental crust (Taylor and McLennan, 1985), both in the dissolved phase and in the particulate phase. With respect to the continental crust, elements such as U, Rb, Ba and Sr are depleted in the sediment and enriched in the particulate phase.

Important deviations from the normalised upper crust values are also observed. These findings lead to several observations and interpretations (Fig. 7) (all UCC normalised).

(1) Rb, U, Ba, Sr are depleted in the suspended load with respect to their neighbouring elements: Rb

and Sr are strongly depleted while U and Ba are less depleted. The major elements Ca and Na also belong to this group (Dupré et al., 1996; Gaillardet et al., 1997). The strong depletion in the suspended phase and the associated enrichment in the dissolved phase (Fig. 7) suggest that these elements are the most

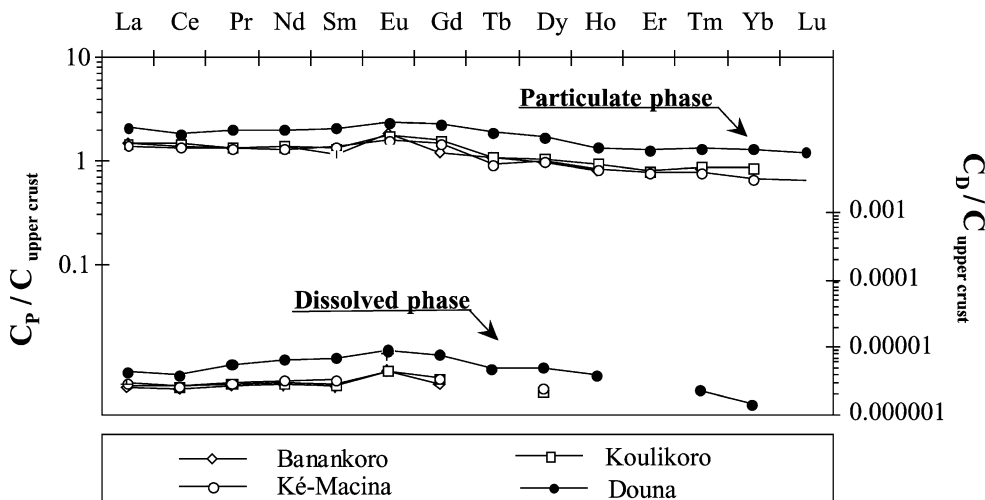


Fig. 8. Diagram showing the REE mean composition of the upper Niger rivers normalised to the upper continental crust (Taylor and McLennan, 1985), both in the dissolved phase (C_D) and in the particulate phase (C_P).

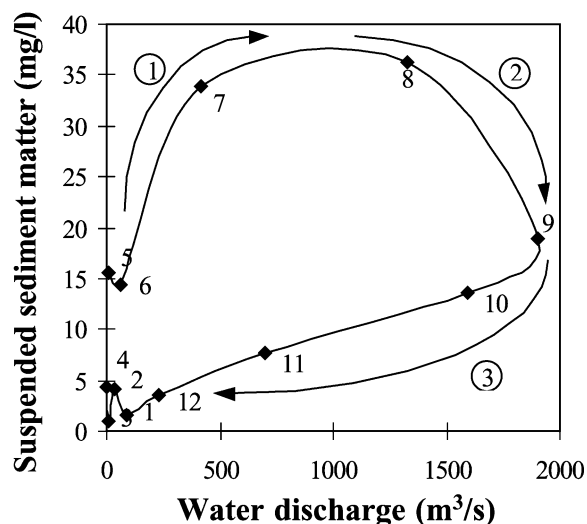


Fig. 9. Relationships between mean monthly water discharge and mean monthly suspended sediment concentration at Banankoro gauging station for the hydrological year 1991–1992 (each number corresponds to a month). The clockwise hysteresis cycle suggests that the sediment transport dynamics of the river can be described in three periods. (1) At the beginning of the rainfall season, sediments come from the surface runoff occurring on slopes, from suspension of sediments deposited in the channel network and from river bed erosion. The two first sources make up the “easily mobilized material” at maximum availability at the beginning of the rainy season. (2) Sediment availability thereafter decreases with time: the protection of soil against erosion increases with growth of a vegetation cover. Erosion is slowed down. (3) During the recession limb of the hydrograph, the “easily mobilized material” has disappeared or is not available anymore due to a halt in rainfall and, therefore, to surface runoff, plus soil protection by vegetation cover. The sediment material in the river comes from sediment originating upstream and from bank and bed erosion.

mobile elements during the weathering processes (Dupré et al., 1996). The removal of the most mobile elements from the bedrock concentrates all remaining elements in the weathered phases of the soils, from whence it can be removed mechanically. These relationships between suspended and dissolved phases for the most soluble elements (U, Rb, K, Ba, Na, Sr and Ca) can be used to model weathering processes and to determine erosion rates (Gaillardet et al., 1995, 1997, 1999a,b). Elbaz-Poulichet et al. (1999) suggest that depletions of some of these elements may be a result from the sorting of feldspars, which concentrates alkali and alkaline earth elements.

(2) Zr and Hf are strongly depleted in suspended sediments, which was also found previously on the Congo and Amazon. These elements are also depleted in the dissolved phase. These two negative deviations could indicate their preferential transport in bed load material (not sampled). Dupré et al. (1996) reported a similar proportioning between suspended and sandy phases. The elements Zr and Hf are not mobile in the weathering processes and are preferentially incorporated by mechanical sorting into zircons (heavy grains).

(3) The other elements, Cs, Th, Pb, REE, Ta, Co, Cr and Ni are slightly enriched relative to the continental crust and have, at a first order, UCC-like pattern. This enrichment is more important for the Bani river where the sediment content is highest. The discrepancies between the mean suspended phase and the mean upper crust for these elements can be attributed to the local chemical heterogeneities in the composition of the source material. Fig. 7 shows the strong enrichment for Co, Ni and Cr relative to the other elements. For the Congo basin, Dupré et al. (1996) explained this enrichment in suspended sediment by contributions of Ni, Co and other transition elements originating from organic material.

The average patterns of REE in suspended sediments (UCC normalised) are shown in Fig. 8. A slight enrichment in light REE (La, Ce) is observed and a depletion in heavy REE (Tb, Yb). The enrichment is more important for the Bani river. The mean $[La/Yb]_N$ ratios (normalised) range from 1.5 to 2.1. All average patterns show a small positive deviation for Eu (as in the dissolved phase): particulate $[Eu/Sm]_N$ ratios range from 1.2 to 1.6. However, this deviation disappears when the suspended sediment concentrations of the Niger river system are normalised to the suspended sediment concentration of the Congo system. This suggests there is a problem of normalisation: the mean upper crust composition defined by Taylor and McLennan (1985) might not reflect the composition of the upper crust in West Africa with respect to Eu. For Douna, the average patterns also show a small negative deviation for Ce.

Table 3 shows important variations in absolute quantities of suspended sediments. For each gauging station, there is a high degree of correlation among the trace elements in the suspended phase, the only exception being Sr. Some of these correlations are

illustrated in Fig. 10. The highest correlation exists between REE, Th, U, Ba and Co. The correlation coefficient is 0.96 between $C_p(\text{Th})$ and $C_p(\text{La})$ and 0.86 between $C_p(\text{Ba})$ and $C_p(\text{Co})$. For the other elements (Rb, U, Pb, Zr, Mn, Cu and Ni), the correlations are more varied. The correlations also depend on the gauging station. For example, the correlation coefficient between $C_p(\text{Ni})$ and $C_p(\text{La})$ is 0.56 using all data, while it is 0.93 with Douna data only, 0.91 with Ké-Macina data, 0.56 with Koulikoro data and not significant with Banankoro data. The plot of trace elements in the suspended phase passes through the origin of the axes, which suggests a dilution due to the variable quantity of quartz. This trend is a common feature in suspended sediment in many rivers and lakes. Deviations from this trend are mainly due to the low concentrations observed during the period of base flow.

Because of the effects caused by dilution due to the presence of organic material and quartz, element ratios should be used to model the weathering processes and to determine erosion rates.

5. Partitioning of elements

The partitioning of elements in the dissolved and the particulate phases in the upper Niger ($S\%$) can be estimated with the following formula:

$$S\% = 100 \times \frac{C_D}{C_T} \quad (2)$$

where $S\%$ is the proportion of total concentration in the dissolved phase and C_D and C_T are the dissolved and total concentration in ppb for the element.

For each gauging station, these percentages were calculated for the samples where values are higher than five times the detection limit (Fig. 11). The volume weighted mean percentages are also plotted. The elements are separated into three groups. (1) A first group with the highest $S\%$ values ($\geq 70\%$) is the set of most soluble elements (Sr, Ba, Rb). These elements are enriched in the dissolved phase with respect to the suspended phase. (2) A second group with the lowest $S\%$ values ($S\% < 50\%$) is the elements less mobile during weathering (e.g., REE, Sc, Th,

Cr...). (3) A third group shows very irregular $S\%$ values (V, U, Cu and Sb).

Similar to the results obtained for absolute concentrations, considerable variability is observed between samples for all elements. Although samples were obtained at different stages of the hydrological cycle, pH values are similar and near neutrality. However, suspended sediment concentrations and particulate organic carbon values (POC) (Picouet, 1999) vary widely from one sample to another. Therefore, the relationships between $S\%$ and suspended sediment concentration were studied. For example, in Fig. 12, $S\%$ of Rb and La are plotted versus suspended sediment concentration. Similar results are obtained when $S\%$ is plotted against POC (in %) because of the good inverse correlation between POC and suspended sediment matter (Picouet, 1999).

The proportion of total concentration in the dissolved phase generally decreases with the increase of the sediment load and follows a hyperbolic law (e.g., Rb and La in Fig. 12). This trend is clearly observed for Sr, Ba, Rb, Co, V, U and La. For Sb, Cu, Pb, Cr, Mn and Th, the lowest values are more scattered but the trend is still visible. The lowest values of $S\%$ are therefore explained by the highest values of suspended load. During the peak discharges, this contains many suspended bed load minerals, principally quartz. These relationships may imply that the three gauging stations of the upper Niger (Banankoro, Koulikoro, Ké-Macina), which present the lowest variability of sediment load, always show more stable values of $S\%$, relative to the Bani where the sediment load varies more than 200 mg/l during the rising stage.

Both for the lowest values of suspended sediment matter and for the insoluble elements (REE, Sc, Th, Cr), $S\%$ values are more scattered. This is probably linked to the fact that the lowest sediment concentrations are observed during the recession curve and during base flow. In the first case, the suspended sediment concentration is diluted by water originating from the groundwater, which is poor in sediment. In the second case, suspended sediments in the river could have other origins such as plankton development and diatom blooms; the organic matter could also represent an important proportion of the particulate matter (POC% is high). It is also possible that the presence of less soluble elements (like REE) in the

Table 3

Trace element concentrations in the particulate phase (C_P) of upper Niger rivers in ppm (calculated from C_T and C_D and suspended sediment concentrations) and mean enrichment factor (EF) (calculated from C_T)

(a)											
Station (river)	Banankoro (Niger)									Mean*	Mean EF**
Sample	1	2	3	4	5	6	7	8	9		
V ^a	94	37	105	95	106	12	58	130	122	103	1.6
Cr	754	248	161	93	112		51	179	200	172	4.5
Mn	1197	823	1082	956	1961	138	1764	1358	1499	1205	1.6
Co	24	13	23	20	34	6	22	30	36	26	2.1
Ni	60	69	74	71	117		104	97	126	88	3.2
Cu	61	92	39		24	3		50	49	34	2.1
Zn	120	534	75		57			81	104	88	1.4
Rb	125	41	51	42	50	21	66	64	49	51	1.4
Sr	271	75	84	155	298	244	304	126	119	137	2.8
Zr	229	104	119	43	59	9	26	63	91	83	0.4
Cs	3.1	1.6	3.0	3.8	3.5	0.2	2.9	4.1	3.0	3.3	0.8
Ba	485	251	421	519	1070	144	212	795	655	575	2.6
La	40	20	44	37	52	3	19	61	52	45	1.3
Ce	78	42	91	71	108	4	34	121	105	89	1.2
Pr	8.6	4.0	9.3	8.3	11.2	0.4	4.0	12.4	10.8	9.4	1.2
Nd	33	15	34	33	39	4	21	48	39	35	1.2
Sm	4.7	2.6	5.9	3.0	7.0	2.8	4.2	7.9	6.5	5.3	
Eu	1.22	0.37	1.22	1.93	2.88	0.59	1.83	1.77	1.64	1.62	1.4
Gd	4.3	1.2	4.4	3.9	6.1	1.6	6.7	7.5	4.8	4.6	1.1
Tb	0.84	0.31	0.69	0.70	0.74		0.48	0.65	0.83	0.70	0.9
Dy	3.5	1.4	3.5	3.0	4.2		3.2	4.6	3.6	3.5	0.9
Ho	0.8	0.4	0.69	0.47	0.65		1	0.8	0.82	0.65	0.7
Er	1.6	0.6	2.0		3.0			2.1	2.2	2.0	0.5
Tm	0.28	0.02	0.26	0.25	0.62	0.65		0.29	0.25	0.27	0.4
Yb	2.7	0.7	1.6	0.8	2.2			1.9	2.0	1.5	0.6
Lu	0.27	0.10	0.24	0.25				0.26	0.23		0.5
Hf	8.3	3.6	4.0			5.9	3.2	2.1	2.5	2.4	
Ta	3.2	4.9	1.7	0.9	0.9	0.3		0.0		1.1	0.5
Pb	34	21	21		16			26	29		0.9
Th	16.0	6.9	12.9	9.0	11.6	1.5	4.3	16.5	14.0	24.1	
U	2.9	0.8	2.9	1.9	2.9		1.0	2.7	2.8	12.1	0.9
%POC ^b			2.9	6.7	12.6	11.8	12.5	4.5	5.7		
SSM ^c	8.6	18.1	57.6	11.6	7.5	6.6	85.4	29.4	13.8		
Discharge ^c	80	233	1560	1950	485	49.9	10.7	2160	1340		

dissolved phase is due to the combination of a 'true' dissolved phase with a colloidal phase when measuring. The composition of the latter is similar to the suspended sediment phase. Ultra-filtration experiments carried out by Viers et al. (1997) confirmed this filtration artefact. Analytical errors and propagation of these errors due to the low values of suspended matter concentrations (<10 mg/l) are also possible. Because of the low volumes discharged, data collected during base flow hardly participate in the overall average concentrations and in the element budgets.

6. Chemical weathering

The following analysis focuses on the Niger at Banankoro and the Bani at Douna. These two gauging stations have a more natural flow regime and the best data set.

6.1. Atmospheric input to river chemistry

The importance of atmospheric input for the chemical composition of rivers has been emphasised

Koulikoro (Niger)									
2	3	4	5	6	7	8	9	Mean*	Mean EF**
68	73	149	77	14	26	143	126	123	1.6
282	107	186	98	0	45	154	291	151	3.6
2761	819	2328	1889	712	1930	1658	1793	1531	1.9
19	15	37	23	6	11	30	30	25	2
73	48	119	99	66	86	81	153	83	2.1
41	33	62	57	0	49	34	141	49	2.2
352	62	104	139	31		54	146	94	1.1
60	46	66	74	40	25	73	60	56	1.6
114	82	148	229	285	149	166	165	133	2.9
69	64	126	51	10	10	54	90	67	0.3
3.1	2.6	4.7	4.1	1.3	0.8	4.2	3.6	3.4	0.8
524	306	838	751	325	242	661	734	569	2.7
31	32	62	33	5	8	56	58	45	1.2
72	68	134	66	12	19	119	115	94	1.2
6.8	6.6	13.8	6.6	1.0	1.6	12.1	12.0	9.6	1.1
27	24	51	31	4	9	46	47	37	1.2
5.4	4.2	8.5	6.4	2.6	0.0	7.3	7.3	6.0	1.1
1.00	0.79	2.69	1.37	0.53	0.78	1.87	1.81	1.58	1.4
2.6	3.2	8.9	6.4	1.9	3.1	8.6	5.6	6.1	1.3
0.67	0.50	0.94	1.31			0.71	1.01	0.80	0.8
2.2	2.7	5.4	2.8	1.6	1.1	4.6	4.3	3.7	0.9
0.6	0.53	1.02	0.94	0.31		0.93	0.96	0.88	0.7
1.1	1.5	2.2	2.8	0.6	0.4	2.2	2.6	1.9	0.6
0.04	0.19	0.51	0.54			0.31	0.32	0.34	0.3
1.5	1.2	3.4	2.8	1.0		2.0	2.1	2.2	0.7
0.17	0.17	0.32				0.24	0.28		0.5
2.7	2.1			3.0	3.3	1.8	2.8	2.1	
19.2	0.8	1.2	1.0	0.4			2.2	1.5	0.4
56	25	33	14	7	10	26	52	27	1.1
10.0	10.1	18.0	11.6	1.8	3.2	16.3	16.3	13.2	
1.7	2.2	3.4	3.1		0.2	2.6	3.2	2.8	0.8
	3.2	4.6	6.7	9.1	18.5	9.1	18.5		
12.4	51.7	17.2	7	7	7.0	17.7	13.1		
424	1680	2460	574	92.1	99.6	4340	1460		

(continued on next page)

in the literature (e.g., Stallard and Edmond, 1981; Meybeck, 1983). Chloride concentration is the most useful parameter for evaluating the atmospheric input to rivers since it shows little fractionation (Appelo and Postma, 1993). Two complementary methods can be used. The first method uses a correction of the dissolved load for total atmospheric inputs (Meybeck, 1983) originated both from the basin itself and outside, using local rainwater composition. The method consists of multiplying the mean chloride concentration in rainwater at a given point in the

basin by the evapo-transpiration factor. This factor can be calculated for each river basin as the ratio of the discharge over precipitation. The Cl content of rainwater in the upper Niger basin has been measured during 2 years (1997 and 1998); the average is close to 20 $\mu\text{mol/l}$ (Picouet, 1999). The main problem with this method is that the real evapo-transpiration factor is unknown.

The second method uses different assumptions. It applies a marine correction to the dissolved load, using element ratios found in seawater (Stallard and

Table 3 (continued)

Station (river)	Ké-Macina (Niger)										
Sample	2	3	4	5	6	7	8	9	Mean*	Mean EF**	
V ^a	89	64	150	179	119	102	104	100	103	1.4	
Cr	175	91	200	202	50	136	123	257	153	3	
Mn	544	427	2543	3677	1178	2086	656	2207	1403	0.9	
Co	19	12	39	45	27	24	19	27	24	1.4	
Ni	59	50	131	158	100	93	70	70	82	2.6	
Cu	39	27	40	58	403	33	38	48	40	1.6	
Zn	107	51	75	151	206	76	94	174	90	1.1	
Rb	66	43	82	91	85	99	81	59	64	1	
Sr	91	74	181	241	283	188	76	116	117	1.3	
Zr	83	59	110	132	73	61	78	82	82	0.3	
Cs	4.1	2.6	4.3	5.0	5.0	3.2	5.3	3.5	3.8	0.9	
Ba	351	310	891	1409	631	600	472	702	595	1.5	
La	46	27	73	75	50	42	44	47	47	1.1	
Ce	85	55	151	174	104	82	95	96	97	1.1	
Pr	9.9	6.0	17.0	16.5	11.8	9.4	10.0	9.5	10.4	1	
Nd	36	22	59	59	39	32	36	34	37	1	
Sm	6.4	3.8	12.7	8.6	7.7	8.1	6.5	6.2	6.9	1.1	
Eu	1.46	0.74	3.17	2.86	2.04	0.47	1.56	1.54	1.68	1.3	
Gd	4.7	2.8	12.1	12.1	11.0	5.9	6.5	4.7	6.4	1.1	
Tb	0.78	0.47	1.23	0.95	1.28		0.51		0.72	0.7	
Dy	3.7	2.3	6.3	2.0	4.4	1.9	3.9	3.5	3.7	0.8	
Ho	0.79	0.43	1.07	1.32	0.82	0.7	0.67	0.69	0.72	0.6	
Er	2.0	1.2	3.7	3.9		1.8	1.8	2.4	2.2	0.6	
Tm	0.25	0.16	0.44		0.61	0.39	0.27	0.29	0.27	0.6	
Yb	1.8	1.0	2.8		1.3	0.9	1.6	1.6	1.6	0.5	
Lu	0.24	0.15	0.33				0.27	0.23	0.23	0.6	
Hf	2.7	1.9			5.7	5.2	2.6	2.4	1.7		
Ta	1.8	0.7	1.5		1.5	1.5		0.8	0.8	0.3	
Pb	26	19	30		22		27	29	25	1	
Th	13.9	8.5	20.1		11.5	11.0	15.5	13.4	13.3		
U	2.8	1.7	3.7		2.7	2.5	2.1	3.0	2.5	0.7	
%POC ^b		2.9	4.7	6.7	5.1	10.6	2.1	7.1			
SSM ^c	41.9	68.7	15.0	5.7	7.5	7.4	75.7	9.9			
Discharge ^c	279	3170	1860	570	69	38.4	1430	1210			

^a Trace elements in the particulate phase in ppm (determined from trace element concentrations in the dissolved phase and in the total phase and Suspended Sediment Matter (SSM) concentrations as follows: $C_p = (C_T - C_D) / \text{SSM}$).

^b Particulate Organic Carbon, POC, in %.

^c Suspended Sediment Matter (SSM) in mg/l and discharge in m³/s.

* Volume weighted values (calculated for the elements where 70% of the values are higher than the detection limit).

** The enrichment factor (EF) of the element in the total phase is defined by: $(X_{\text{total}} / \text{Th}_{\text{total}}) \text{ ppm} / (X_{\text{crust}} / \text{Th}_{\text{crust}}) \text{ ppm}$ where X_{total} and X_{crust} are, respectively, the concentrations of the element X in the total phase (our data) and in the continental crust (data are from Taylor and McLennan, 1985).

Edmond, 1981). It assumes that the surpluses of major and trace elements observed in river water relative to seawater originate from the basin itself and are part of the continental weathering flux. This method requires a river that does not drain saline formations. Then, all Cl in the river is considered derived from marine aerosols. The amount of other major elements in the

river originating from marine contribution can then be expressed with the following equation:

$$X_a = \text{Cl}_{\text{riv}} \times \left(\frac{X}{\text{Cl}} \right)_a \quad (3)$$

where X_a is the atmospheric contribution of X in stream water; Cl_{riv} is the Cl concentration in the river and $(X/\text{Cl})_a$

Douna (Bani)									
1	3	4	5	6	7	8	9	Mean*	Mean EF**
83	134	156	209	36	100	124	189	142	1.5
316	142	124	192	0	116	127	218	148	2.5
2680	601	2004	3947	1328	2941	378	2787	1290	0.6
19	22	29	46	10	23	18	35	25	1.32
45	74	95	144	15	35	59	105	79	1.9
29	48	38	42	11	37	36	109	49	1.2
913	102	64	121	47	92	65	417	143	0.8
105	103	110	155	36	106	88	112	102	0.8
201	77	139	216	88	300	57	147	101	0.6
102	163	126	167	23	64	106	186	139	0.4
5.4	10.3	10.0	13.3	2.2	7.1	8.7	10.1	9.6	1.6
247	312	526	865	122	564	314	694	420	0.6
40	57	71	92	15	40	53	90	63	1.2
89	103	131	173	32	100	107	163	118	1.1
9.2	12.6	15.5	22.6	3.5	10.4	12.0	21.3	14.2	1.2
35	46	57	72	13	40	44	81	52	1.2
6.1	8.4	9.1	14.4	2.8	8.9	8.1	14.8	9.3	1.2
0.94	1.79	2.50	3.14	0.51	1.39	1.80	3.06	2.09	1.4
4.4	6.2	11.9	14.3	2.9	9.9	8.6	10.9	8.7	1.4
0.78	1.04	1.42	2.37	0.25	0.48	0.98	1.67	1.21	1.1
3.7	5.3	7.0	7.4	1.6	4.7	5.0	8.4	5.9	1
0.85	0.99	1.22	1.25	0.26	1	0.86	1.64	1.07	0.7
2.0	2.8	2.4	5.3	1.0	2.8	2.6	4.6	2.9	0.8
0.18	0.37	0.52	0.63	0.22	0.52	0.33	0.72	0.43	0.7
2.2	2.5	3.9	3.9	0.4	2.1	2.1	3.7	2.8	0.7
0.26	0.36	0.40	0.56			0.30	0.62	0.39	0.6
5.0	5.1	0.0	0.0	1.6	3.8	3.5	5.8	3.4	
2.9	4.7	1.7	2.3	0.4	3.0	0.6	4.3	2.8	0.7
21	30	25	38	7	18	22	49	29	0.8
12.2	17.6	20.4	25.1	3.7	12.0	15.7	22.5	18.1	
3.2	4.8	3.9	6.0	0.2	2.2	2.6	5.1	4.0	0.9
	1.7	4.8	5.0	4.0	6.7	1.3	4.6		
16.9	106.4	18.7	9.2	19.8	9.9	221.7	9.7		
42.2	572	325	83.2	2.2	1.5	427	210		

Cl)_a, the element ratio normalised to Cl in the atmosphere (seawater ratio).

No salt rocks or evaporites are known in the upper Niger basin. The proposed correction of river water composition for atmospheric inputs can thus be applied since it can be assumed that all chloride measured in the river originates from atmospheric precipitation. In this

paper, a marine correction was applied to all data (Table 4). The marine normalised ratio for Cl was deduced using element ratios of seawater from Berner and Berner (1987).

Marine contributions to river chemistry are insignificant, i.e., less than 5%, for Ca, K and Mg. For Na, marine input range from 9.7% to 20% depending on

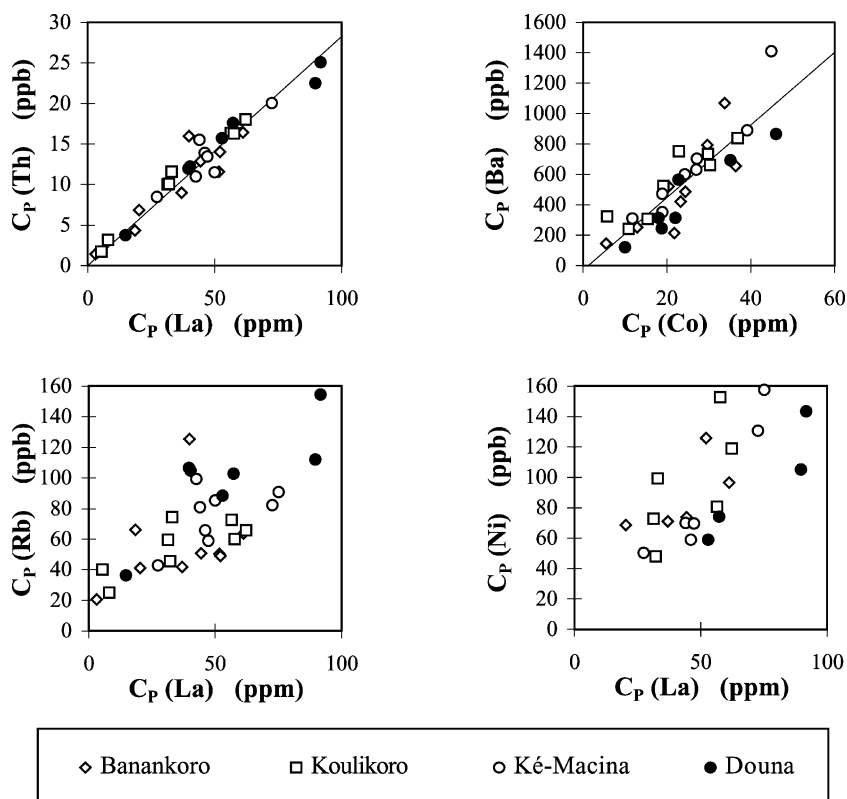


Fig. 10. Relationships between some trace elements in the suspended phase (C_p) of the upper Niger rivers.

the gauging station, with an average of 12.5%. All concentrations or fluxes mentioned below are data corrected in this way.

6.2. Rock weathering inputs

After correction for precipitation inputs, the dissolved load of a river represents the result of mixing of water derived from the weathering of the main lithologies, here silicates and limestones. Water draining in each of these rock types is characterised by its own chemical signature (e.g., Meybeck, 1983, 1994; Berner and Berner, 1987).

Following the method described by Négrel et al. (1993) for the Congo basin, relationships between molar ratios Ca/Na , HCO_3/Na and Mg/Na were studied (Fig. 13). The same element (Na) is used for normalisation to eliminate dilution and evaporation processes from the relationships (see Section 4.1.1).

For the upper Niger rivers, the best correlations observed between elemental ratios are those between Ca/Na vs. Mg/Na ($r=0.89$, $n=120$) and Ca/Na vs. HCO_3/Na ($r=0.94$, $n=120$). These correlations are shown on log–log scales in Fig. 13a for individual samples and in Fig. 13b for the average ratios on the Niger rivers and on other large rivers (using data from Gaillardet et al., 1999a). Similar relationships have been reported for the Congo and Amazon basins (Négrel et al., 1993; Gaillardet et al., 1997) and for other large unpolluted rivers (Gaillardet et al., 1999a). In such diagrams, the mixing between the two main end members are represented by a straight line. The probable range of rock weathering end members for silicates, carbonates and evaporites is represented in Fig. 13 by the shaded areas. These values have been estimated by Gaillardet et al. (1999a) using literature databases on simple or well-confined lithologies. The carbonate end member is characterised by $Ca/Na=$

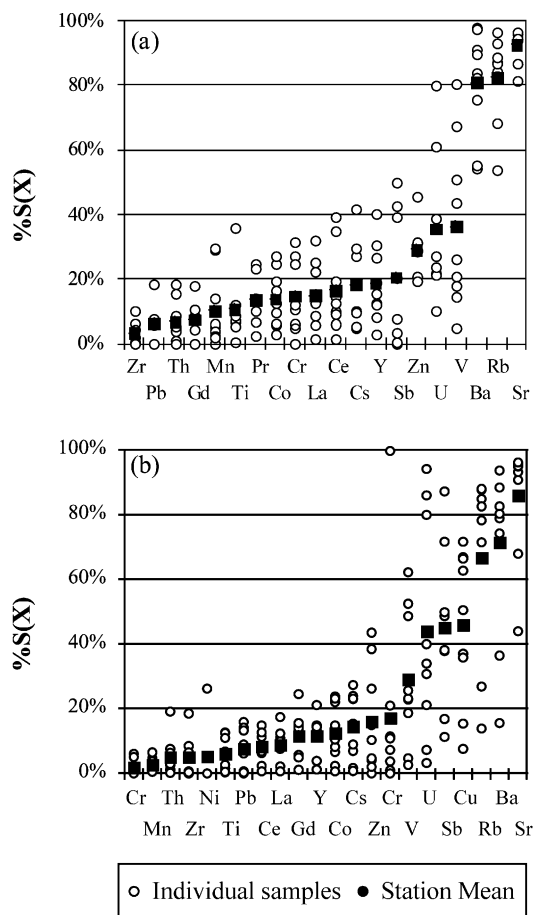


Fig. 11. Element distributions in dissolved and total load in the river water (%S) from two sampling sites: (a) the Niger at Banankoro and (b) the Bani at Douna.

45 ± 25 , $Mg/Na = 15 \pm 10$ and $HCO_3/Na = 90 \pm 40$. The chemical composition of water draining silicates is: $Ca/Na = 0.35 \pm 0.15$; $Mg/Na = 0.24 \pm 0.12$; $HCO_3/Na = 2 \pm 1$. The chemical composition for water draining evaporites is less relevant in this area, as there are no evaporite rocks in the basin.

For the upper Niger rivers, the Ca/Na ratios vary from 0.3 to 2.2, but 80% of the values varies from 0.4 to 0.7. For the Mg/Na ratio, 80% of the values varies from 0.4 to 0.7 and for HCO_3/Na ratio, this is 2.9 to 4.3. It is clear from Fig. 13 that the silicate and carbonate end members explain all variability in the data. However, it is found that silicate weathering contributes to a large extent to the chemical composition the

Niger rivers whereas carbonate dissolution is insignificant. Several observations support these results: (1) carbonate outcrops are insignificant (Fig. 1); (2) the range of variation of the silicate draining water end member can be too restrictive: according to Fig. 13, the granite and schist end member for the upper Niger rivers is characterised by a Ca/Na ratio reaching 1; (3) the few high values observed during the recession limb are probably due to the high mineral concentration in the base flow.

Thus, the geochemistry of the upper Niger rivers is strongly influenced by the silicate weathering and, to a lesser extent, by the marine inputs. Therefore, the mixing model previously described for the Congo and Amazon river basin (Négrelet et al., 1993; Gaillardet et al., 1997) can be applied with confidence to the Niger Basin. The main purpose of the model is to calculate the contribution of silicate weathering to the present dissolved load. It is based on several mass budget equations (using elemental molar ratios) given by Négrelet et al. (1993). The general form of such a mixing equation is ($X=Cl, Ca, Mg, HCO_3$):

$$\left(\frac{X}{Na}\right)_{riv} = \sum_i \left(\frac{X}{Na}\right)_i \alpha(Na)_i \quad (4)$$

for i =silicates, carbonates, evaporites and rain water; the $\alpha(Na)_i$ is the mixing proportion of Na ($\alpha_{pluie} + \alpha_{silicate} + \alpha_{carbonate} + \alpha_{evaporite} = 1$) from which the mixing proportions of the other elements are easily deduced. Usually, an inverse method is applied to resolve this model (Négrelet et al., 1993).

For the upper Niger rivers, the proportions of Na, Ca, HCO_3 and Mg that originate from the silicate reservoir were obtained from their mean annual dissolved concentrations with data corrected for marine contribution (Table 4).

6.3. Silicate weathering flux and inorganic CO_2 consumption

For the upper Niger rivers, the annual silicate weathering flux (F_{TDS}) in 10^3 tons/year was calculated from the TDS corrected for marine contribution using annual average concentrations (Table 4). For comparison, in Fig. 14, silicate weathering flux and cationic weathering rates ($Na+K+Ca+Mg$) are given for other large rivers in the world (Gaillardet et al.,

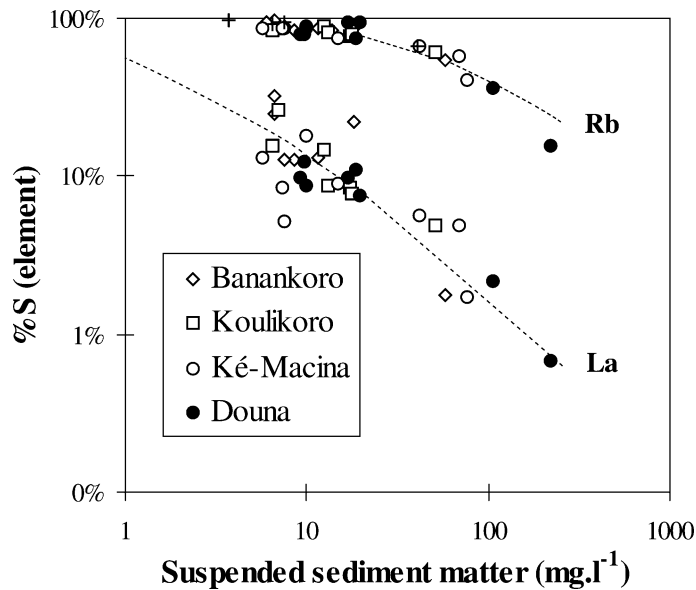


Fig. 12. Rb and La phase distribution vs. suspended sediment (in mg/l) in the upper Niger rivers. The parameters of the curve (dashed lines) are estimated by fitting visually a hyperbolic law to all experimental points (SSM, %S).

1999a). A clear general agreement is observed between the upper Niger rivers and the rivers where the dissolved silica represents a dominant part of the TDS, being the result of silicate weathering (Amazon, Congo, Orinoco, Niger, Zambesi). The silicate weathering fluxes for the upper Niger rivers range from 0.2 to $1.9 \cdot 10^6$ tons/year and are the lowest values observed. The low annual runoff is the main explanation

for the low silicate weathering loads observed on these catchments, especially in the Bani basin. It was found elsewhere, too, that runoff is an important controlling parameter for weathering rates (e.g., Bluth and Kump, 1994; Gaillardet et al., 1999a).

Of course, the basin surface area plays an important role in the interpretation of these fluxes. For this reason, however, the silicate weathering fluxes, ex-

Table 4

Correction for atmospheric inputs (marine contribution)—annual volume weighted mean concentrations (in $\mu\text{mol/l}$) and fluxes (in 10^3 tons/year) before and after correction for the period 1991–1997

X_i	Sea	Banankoro (Niger)				Douna (Bani)			
	X_i/Cl ratio	C_{before} $\mu\text{mol/l}$	C_{after} $\mu\text{mol/l}$	$F_{\text{before}} 10^3$ tons/year	$F_{\text{after}} 10^3$ tons/year	C_{before} $\mu\text{mol/l}$	C_{after} $\mu\text{mol/l}$	$F_{\text{before}} 10^3$ tons/year	$F_{\text{after}} 10^3$ tons/year
Ca	0.019	51.14	50.85	49.92	49.65	69.11	68.80	20.34	20.25
Mg	0.099	47.01	45.49	27.69	26.83	51.01	49.38	8.93	8.65
K	0.018	35.27	34.99	31.61	31.36	53.66	53.36	14.95	14.87
Na	0.87	106.68	93.23	55.59	48.29	112.49	98.05	17.46	15.13
Alkalinity	0	333.6	333.6	480.4	480.4	389.50	389.50	171.24	171.24
Cl	1	15.45	15.45	—	—	20.38	20.38	—	—
SO ₄	0.052	1.57	0.77	3.93	2.03	3.01	2.15	2.02	1.42
SiO ₂	0	261.1	261.1	345	345	210.90	210.90	69.33	69.33
Σ^{+a}	—	7.0	6.63	164.9	156.2	8.67	8.27	61.70	58.85
TDS ^a	—	41.9	41.2	976	964	45.58	45.89	269.53	267.49
SSM ^a	—	24.5	24.5	579	579	57	57	390	390

^a Concentration in mg/l.

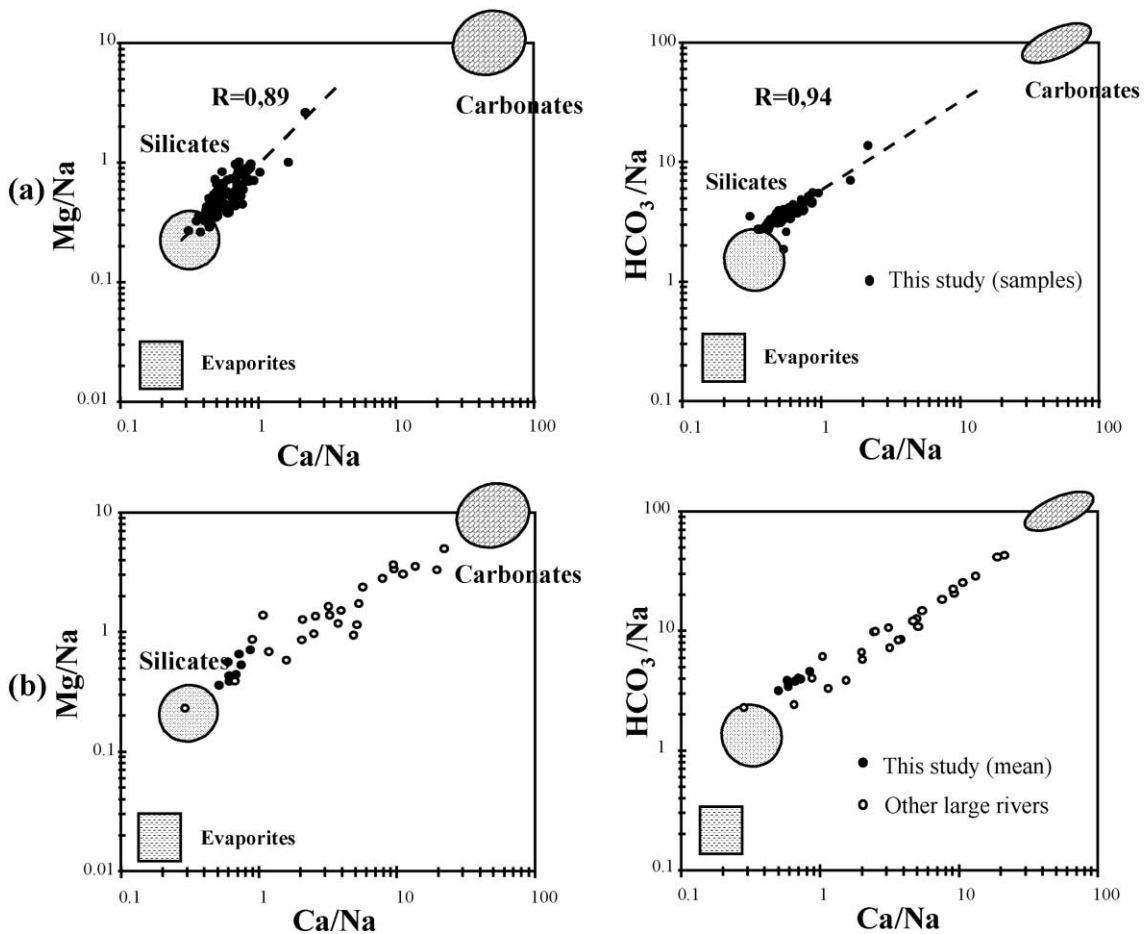


Fig. 13. Mg/Na vs. Ca/Na and HCO₃⁻/Na vs. Ca/Na. Mixing diagrams for silicate, carbonates and evaporite end-members in the upper Niger rivers. (a) Individual samples. (b) Annual mean values and comparison with data from literature on other large rivers (Gaillardet et al., 1999a).

pressed as tons of dissolved solids washed off in 1 km²/year (specific silicate weathering fluxes), cannot be used to compare to large basins. They are an underestimation because the surface area of silicate rocks is less than the total basin area.

Chemical weathering processes require CO₂ and produce HCO₃⁻. All bicarbonate ions produced by silicate weathering are derived from atmospheric/soil CO₂, but only half of the bicarbonate ions derived from carbonate dissolution originate from the atmospheric/soil CO₂, the other half originating from carbonate mineral dissolution. Moreover, calcite and aragonite precipitation in the ocean, through biological processes, produces closely the CO₂ consumption due to the

weathering of limestones on the continents (Broecker and Peng, 1998). Thus, only silicate weathering represents a net consumption of atmospheric/soil CO₂.

As carbonate outcrops are insignificant in the upper Niger basins, the concentration of HCO₃⁻ in the river and its fluxes (see Table 4) are due to silicate weathering and can be directly related to the atmospheric/soil CO₂. It can therefore be estimated that the interannual flux of CO₂ removed from the atmosphere by silicate weathering ranges from 2.6×10^9 mol/year (26×10^3 mol/km²/year) for the Bani at Douna to 7×10^9 mol/year (100×10^3 mol/km²/year) for the Niger at Banankoro. These are in agreement with a previous estimate by Boeglin and Probst (1998) of

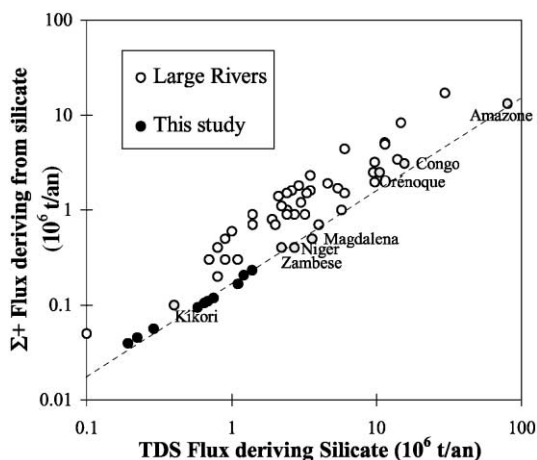


Fig. 14. Relationships between silicate weathering flux and cationic weathering rates (Na+K+Ca+Mg). Comparison with the largest rivers in the world (data from Gaillardet et al., 1999a). A good general agreement is observed between the upper Niger rivers and the rivers where the dissolved silica represents a dominant part of the TDS and results from silicate weathering (Amazon, Congo, Orinoco, Niger, Zambese).

59×10^3 mol/km²/year on the Niger at Bamako for a dry period (from 1990 to 1992). As chemical weathering rates are low, the consumption of atmospheric CO₂ by weathering processes over the upper Niger basin is low, especially in the Bani basin.

7. Physical weathering rates

7.1. Measured suspended sediment yields

Suspended load is classically used to provide an estimate of the mechanical denudation, although there are many limitations to this method (e.g., Walling, 1983; Milliman and Meade, 1983; Walling and Webb, 1996). Using the data of suspended load, Picouet (1999) has calculated the specific mean annual suspended sediment load as 8.2 tons/km²/year for the Niger at Banankoro and 3.9 tons/km²/year for the Bani at Douna. These values are very low compared to other large rivers in the world (Summerfield and Hulton, 1994; Meybeck and Ragu, 1996), but they are close to those observed for other large unpolluted African rivers like the Congo (8.8 tons/km²/year, Laraque et al., 1995) or the Niger at its mouth (19 tons/km²/year, Milliman and Meade, 1983). On a global scale, these

low physical weathering rates have been linked to the low relief in these non-mountainous basins (Milliman and Meade, 1983; Milliman and Syvitski, 1992; Summerfield and Hulton, 1994). The correlation between sediment load and topographic relief underlies the relation between sediment rates and tectonism, a factor less amenable to a numerical description (Milliman and Syvitski, 1992). As we saw in previous paragraphs, the low physical weathering rate observed on the Bani basin is related to the low annual runoff in this catchment.

7.2. Predicted suspended sediments yields according to a steady state model

Assuming that at the scale of large drainage basins weathering occurs in steady state conditions, physical erosion rates can be predicted using the composition of bedrock, the chemical composition of suspended sediment and dissolved load (corrected for atmospheric inputs). This mass budget has been described in the Congo basin by Gaillardet et al. (1995) and has since been applied to other large rivers (Gaillardet et al., 1999b). The concept of steady state, understood as the stream equilibrium concept by geomorphologists, assumes that the amount of bedrock which is eroded in a given drainage basin per unit of time equals the fluxes of solids and dissolved materials (corrected for non-weathering inputs) leaving the drainage basin. Thus, a balance should exist between solutes (produced continuously by rock chemical weathering) and solids (released physically from soils especially during periods of high floods). In this study, the mass of sands transported over the bottom of the river is ignored because bed load usually represents less than 10% of the suspended flux (Nouvelot, 1969). For the silicate part of the continental crust, the steady state equation can be written as follows for individual chemical components:

$$M_c C_c(X) = M_p C_p(X) + M_w C_w^{\text{sil}}(X) \quad (5)$$

where M_c is the mass of bedrock being eroded per unit of time, M_p is the flux of suspended material in the river and M_w is the water discharge. $C_c(X)$, $C_p(X)$ and $C_w^{\text{sil}}(X)$ are the concentration of X , respectively, in the continental crust (in ppm), the concentration of X in suspended sediments (in ppm) and the dissolved

load derived from silicates (in g/l). Dividing by discharge, Eq. (5) becomes:

$$\tau_{\text{sil}} C_c(X) = P C_p(X) + C_w^{\text{sil}}(X) \quad (6)$$

where P (in mg/l) is the modelled suspended sediments concentration (mechanical erosion rate) and τ_{sil} the mass of eroded silicate continental crust per litre of water (the model total erosion rate).

This equation applies to all elements, from the most soluble that are divided between suspended and dissolved load (see Section 5) to the most insoluble elements, for which dissolved concentration is negligible (in this case Eq. (6) becomes more simple). The solution of such equations can be obtained by an inverse method as detailed in Gaillardet et al. (1995), or by a graphical method (Gaillardet et al., 1999b). The results of using the second method are reported here.

Because of the size of the drainage basins studied, it was initially assumed that the continental rocks within the drainage basin had an average composition close to that of the upper crust defined by Taylor and McLennan (1985). Weathering indices were defined for each mobile element by comparing its concentration to the concentration of an immobile element whose magmatic compatibility is close to that of the mobile element. For example, for the mobile element Na, the ratio, $\alpha_{\text{Na}} = [\text{Th}/\text{Na}]_{\text{sed}}/[\text{Th}/\text{Na}]_{\text{ucc}}$ can be used. The main advantage of this method is to minimise the uncertainty that exists

about the continental crust composition. This normalisation to non-mobile elements removes the variations in absolute concentrations in suspended sediments generally due to a dilution by quartz or organic matter. In this way, the amplitude of the negative deviation with respect to the continental crust is quantified (Fig. 15). The notation α_X is now introduced, i.e., the average composition of drainage bedrock, similar to Taylor and McLennan's UCC. Eq. (6) then becomes, for each mobile element X :

$$\alpha = 1 + \frac{1}{P} \frac{C_w^{\text{sil}}(X)}{C_p(X)} \quad (7)$$

For a soluble element X , if we call $C_p^*(X)$ the concentration of X in suspended sediment if no dissolution of this element had occurred, then the ratio of $C_p^*(\text{Na})$ over $C_p(\text{Th})$ is close to that of Taylor and McLennan's upper crust (in the same way for any other couple soluble/insoluble). Eq. (6) then becomes, for any soluble element X :

$$\frac{C_p(X)}{C_p^*(X)} = \frac{1}{\alpha} = 1 - \frac{1}{P} \frac{C_w^{\text{sil}}(X)}{C_p^*(X)} \quad (8)$$

The graph of this equation in a C_p/C_p^* vs. C_w/C_p^* plot is a straight line crossing the X -axis at P (in g/l) and the Y -axis at 1. Schematically, this figure is a plot of weathering intensity versus dissolved fluxes for the different soluble elements (Gaillardet et al., 1999b).

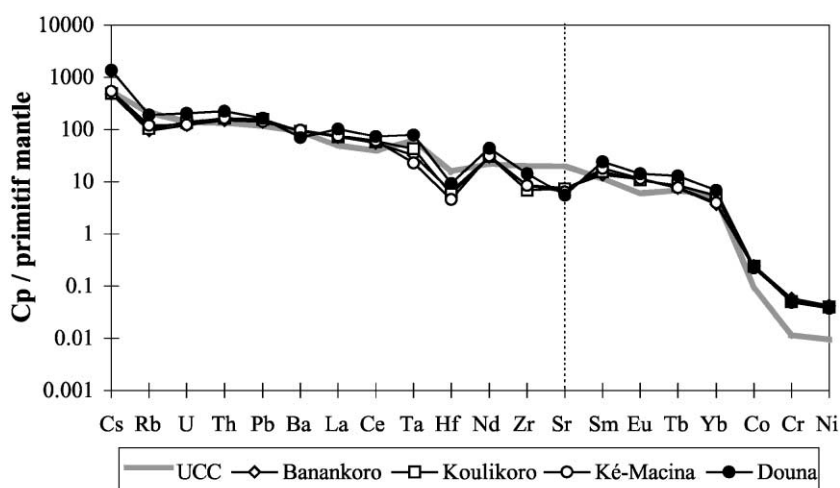


Fig. 15. Diagrams of mean suspended sediments from upper Niger rivers normalised to the primitive mantle.

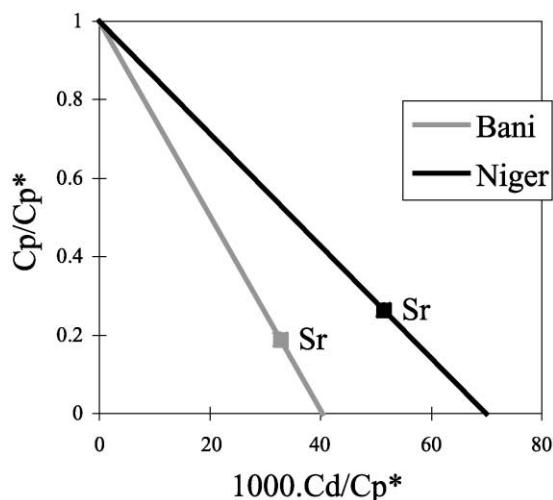


Fig. 16. Silicate weathering steady state diagrams for the Bani and Niger rivers. C_p and C_D denote the concentrations in the suspended and dissolved load, respectively. C_p^* is the concentration that suspended sediments would have in the absence of chemical weathering. The theoretical value of the river-suspended-sediment concentration (P in mg/l) is given by the intersection of the steady state line with the X -axis (in black for the Niger and in grey for the Bani).

This method was applied to La and Sr concentrations with data corrected for non-silicate inputs and a crust ratio La/Sr varying between 9 and 14 (Fig. 16). The modelled average suspended concentrations were compared with the measured values. Fig. 17 shows little discrepancy between P derived from the mass budget and P measured in the field. For the Niger at Banankoro, Koulikoro and Ké-Macina, the model predicted similar P values of 74 ± 22 mg/l, while the observed values vary from 25 mg/l at Banankoro and Koulikoro to 43 mg/l at Ké-Macina. The presence of sandstone and quaternary fluvio-lacustrine sediments between Koulikoro and Ké-Macina could explain the increase of the average sediment concentration between these two stations. For the Bani at Douna, the predicted P value of 43 ± 12 mg/l is close to the measured concentration of 59 mg/l.

Thus, within uncertainties, the Bani at Douna and the Niger at Ké-Macina (third station on the Niger) have similar predicted and measured concentrations of suspended sediments (Fig. 17). This result implies that these rivers are in apparent agreement with the steady state. In other words, it indicates that at a global scale, the soil thickness is close to the dynamic equilibrium:

the amount of particles removed from the top of the soil by mechanical erosion is balanced by approximately the same amount of residual particles created by chemical weathering at the top of the weathering front. A second observation is that the sediment concentrations measured for the Niger at Banankoro and Koulikoro (the upstream part of the catchment) are smaller than those predicted by the steady state. This would suggest that here, sediments are transported at a smaller rate than the rate at which they are produced. In the absence of major lakes, reservoirs or floodplains, this cannot be attributed to sediment trapping. The discrepancies for Banankoro and Koulikoro would mean that on average and under the present climatic conditions, soils here continue to develop in depth.

Comparison between the predicted values for the upper Niger and for other large rivers (Fig. 18; data from Gaillardet et al., 1999b) indicates that all the upper Niger rivers might indeed belong to the group of lowland rivers where the steady state hypothesis is confirmed (Zaire, Lena, Nile, Ob, Seine). As described by geomorphologists, these basins are characterised by a limited transport regime where the low physical denudation rate leads to excess soil formation

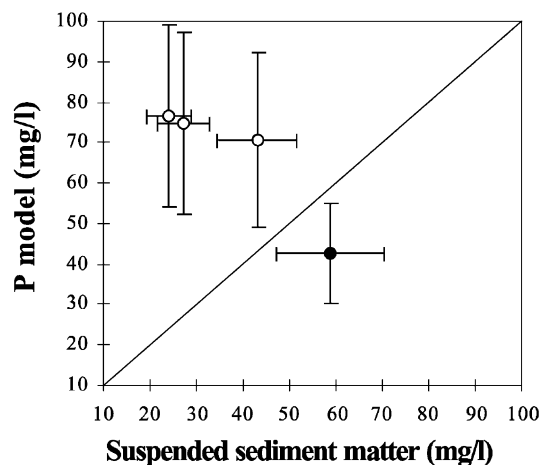


Fig. 17. Comparison between observed mean annual suspended concentrations and the predicted values calculated using a steady state erosion model and assuming that the drainage basin average composition is similar to the upper crust of Taylor and McLennan (1985). Sr/La is taken between 9 and 14 and calculations propagate uncertainties close to 40%. A 20%-uncertainty was assigned to the measured concentrations.

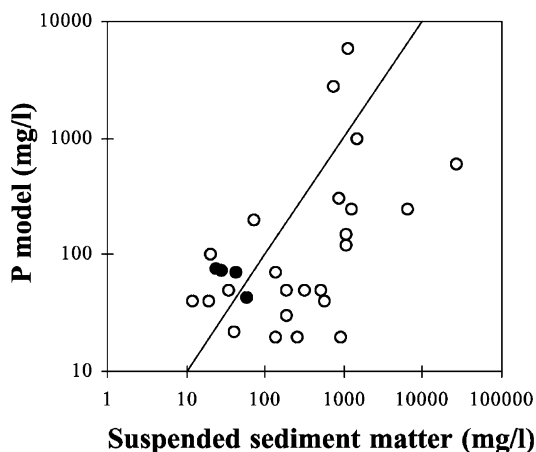


Fig. 18. Comparison between observed mean annual suspended concentrations and predicted values calculated using a steady state erosion model: for this study (black circles) and for other large rivers (white circles) (data from Gaillardet et al., 1999b). Compared to other large rivers, the upper Niger rivers show a reasonable agreement between predicted and measured values.

which protects bedrock from weathering. Gaillardet et al. (1995) have emphasised this effect for the Congo, where it explains that in spite of its optimal climatic conditions, low rates of chemical weathering occur.

8. Conclusions

This study presents the results of the systematic analysis of major and trace elements in dissolved ($0.2 \mu\text{m}$) and suspended matter in the upper Niger rivers. The composition of both phases is the result of the mineralogy and petrology over the drainage areas (silicate rocks and sandstone). Slight differences were detected between the chemical composition of the Niger and the Bani rivers depending on the differences in their drainage basin characteristics (lithology, land use cover...). The contribution of atmospheric precipitation to the rivers' chemistry, using the technique of marine contribution, is very low. Weathering of superficial rocks and soils is very important, affecting the chemistry of major ions and trace elements such as U, Rb, Ba and Sr. Comparing the chemistry of the upper Niger rivers with other rivers indicates that the upper Niger rivers are among the least mineralised. As was observed by other authors in two other unpolluted large

rivers (Amazon and Congo), one of the obvious results of the trace element analysis is the decoupling between the most soluble element (U, Rb, Ba, K, Ca, Na and Sr) and the other trace elements. Relative to the mean continental crust composition of Taylor and McLennan (1985), the most soluble elements show chemical complementarities between the dissolved and particulate phases.

The observations on the distribution ratio of dissolved and particulate phases in the upper Niger, which is among the least 'organic' rivers in the world, allow two main results to be concluded. (1) Suspended sediment concentrations control the presence of elements in the dissolved phase for the majority of elements. For the different samples with variable sediment contents, the proportion of total load in the dissolved phase decreases with increasing suspended sediment content. This process reflects the dilution of suspended sediment. In fact, for the suspended phase, the variability over the hydrological year is mainly related to the dilution of other minerals by quartz. (2) Colloids and/or adsorption processes are additional factors controlling the REE concentrations in the dissolved phase and those of associated elements, in the low flow period (base flows).

Estimates of chemical and physical denudation rates in the upper Niger basins were proposed. Silicate erosion rates and associated CO_2 consumption were obtained with TDS and HCO_3^- values corrected for atmospheric input, which is a valid method since there are no carbonate rocks or evaporites in the basin. These rates range from 0.2 to 1.9×10^6 tons/year and from 26×10^3 to 100×10^3 mol/ km^2 /year, respectively. Using the data on suspended load, physical denudation rates were estimated between 3.9 and 8.2 tons/ km^2 /year. On a basin scale, these low rates are related to the combination of lithology (silicate rocks), lack of tectonism which permitted an excess of soil formation limiting bedrock weathering and the climate and related hydrological regime (relatively little runoff).

Finally, the suspended sediment concentration (in mg/l), which would indicate steady state erosion, was calculated using the chemical composition of dissolved and solid products of silicate weathering. These predicted values were compared to measured data, showing that observations in the upper Niger basin, within uncertainties, validate the steady state hypoth-

esis. This basin is therefore characterised, like other lowlands rivers, by a ‘transport limited regime’.

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