Major and trace element abundances, and strontium isotopes in the Nyong basin rivers (Cameroon): constraints on chemical weathering processes and elements transport mechanisms in humid tropical environments

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Abstract

This paper aims to improve our understanding of chemical weathering processes and element transport mechanisms in the humid tropical environments. We studied the Nyong River basin (27,800 km^2) located on the northwestern part (Ntem Complex) of the Congo craton (central Africa). The dissolved concentrations (i.e., < 0.20 μm) of major and trace elements, dissolved organic carbon (DOC) and the $^{87}Sr/^{86}Sr$ ratios have been measured in more than 20 rivers draining watersheds with various surface areas (~ 1 to 28,000 km^2). All these rivers exhibit low major cations concentrations (i.e., Na, Mg, K, Ca) but high concentrations of some trace elements (Al, Fe, Th, Zr, Y, REE), silica, and DOC. The total dissolved load (TDS) is low (~ 20 mg l^{-1}) and dominated by silica and organic matter. The comparison of different watersheds shows us that chemical weathering is more efficient in the small unit-watersheds. All the sampled rivers exhibit a wide range of $^{87}Sr/^{86}Sr$ ratios and high Ca/Na ratio that can be explained by the heterogeneity of the crystalline rock constituting the cratonic basement.

Four selected rivers (Mengong, Awout, Soo, and Nyong) having different drainage areas and hydrological parameters were sampled over a 2-year period. Collected data show that all these rivers present the same monthly seasonal variations, with higher concentrations during rainy season and lower concentrations during dry season. This implies that the weathering and transport mechanisms of small watersheds can be extended to the whole Nyong basin. In the small unit-watersheds, chemical weathering mainly occurs in swamp zones where mineral dissolution is enhanced by humic substances. These swamp zones constitute a pool of organic-rich water, which can be quickly mobilized during rain seasons. In these waters, DOC and insoluble element concentrations (e.g., Al, Fe, and Th) were strongly correlated which show the key role of organic colloidal matter in the transport of some insoluble elements. Some other relationships (Al vs. Fe, REE vs. Al) were also examined in order to get information about chemical weathering or element transport.

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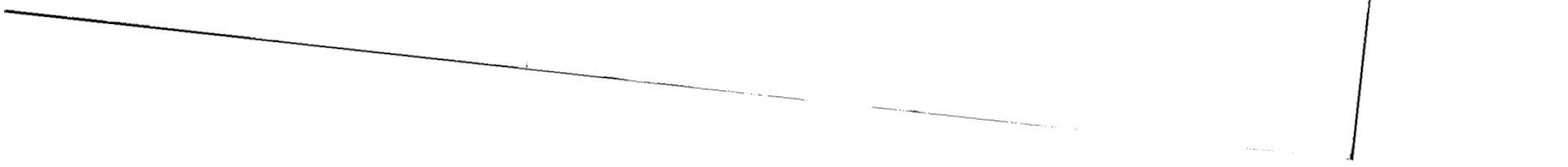E-mail address: viers@lucid.ups-tlse.fr (J. Viers).

Based on these data, it has been concluded that the chemical composition of these river waters is controlled by geomorphic and historic factors (e.g., thick cation-poor soil). In contrast, the present day climatic parameters (high rainfall and temperature) play a minor role in water chemistry regulation even though they are likely to enhance mineral dissolution. Even if organic matter favors mineral dissolution, chemical weathering in this area is low compared to other world regions, which suggest, on a global scale, a relatively small effect of these environments on the CO_2 consumption. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

In recent years, numerous field studies on both chemical and physical weathering have been performed in various parts of the world (e.g., Stallard and Edmond, 1983; Dethier, 1986; Berner and Berner, 1987; Meybeck, 1987; Probst et al., 1992; Drever and Zobrist, 1992; Amiotte-Suchet and Probst, 1993; Velbel, 1993; Bluth and Kump, 1994; Edmond et al., 1996; Gislason et al., 1996; Gaillardet et al., 1999; White et al., 1998; Land et al., 1999). These studies were directed at: (1) understanding the biogeochemical cycles of major and trace elements, (2) calculating chemical weathering rates, (3) estimating the role of major parameters like relief, climate, lithology, and vegetation that are likely to control chemical weathering processes, and (4) quantifying the effect of rock chemical weathering on the carbon cycle and its potential role on climate changes.

Studying river chemistry is fundamental since at the Earth's surface the erosion products are mainly transported by rivers (Milliman and Meade, 1983). For this purpose, various river basins should be investigated in order to take into account the diverse climatic, biotic, geomorphologic, and geologic parameters. Among different regions, tropical environments have received relatively little attention. This study represents a part of concerted efforts aimed at characterizing chemical weathering in the humid tropical environment. Up to now, mineralogical transformations of fresh rocks into weathering products have been the subject of numerous studies and are well understood for these tropical environments (Nahon, 1991; Tardy, 1993 and references therein). However, limited data are available on the geochemistry of surface- and groundwaters flowing through lateritic covers (Stallard and Edmond, 1983; Konhauser et al., 1994; Grout, 1995; Eyrolle et al., 1996; Dupré et al., 1996; Edmond et al., 1996; Viers et al.,

1997; Braun et al., 1998). On top of that, most of these studies were largely addressed to large river geochemistry without taking into account seasonal variations. The aim of the present work was to study the river basins of different length scales (small to large tributaries), and at different seasons. For this, more than 20 rivers of different hydrological characteristics (i.e., water discharge, and drainage area) were sampled during 1 week to give a global and "instantaneous" geochemical signature. Four representative rivers were selected and monthly sampling during a 2-year period. This allowed the construction of a comprehensive database (major and trace elements concentrations, Sr isotopes, and elemental ratios) for tropical rivers in order to apply it for quantifying element transport and chemical weathering processes. Finally, these results can be used to distinguish between different parameters controlling chemical weathering at the global scale.

2. General settings of the Nyong River basin

2.1. Location

The Nyong River basin is located in the Southern Cameroon (Africa) between the latitudes 2°48′N and 4°32′N and the longitudes 9°54′E and 13°30′E (Fig. 1). Although the Nyong is the second largest river of Cameroon in terms of length, its drainage area is relatively small (27,800 km², Olivry, 1986). The Nyong river basin is mainly located on the "Center South Cameroon Plateau", 600–900 m high, which corresponds to an erosion surface of Tertiary age (i.e., the First African Surface). This basin extends over three different physiographic regions. In the eastern part, the Nyong is flowing through large swamp zones of 2–3 km width. In the intermediate zone of the basin, the landscape is represented by a

succession of convex rounded hills separated by flat swamps of variable sizes and called "Collines en demi-orange". Finally, at about 100 km from the coast, the Nyong River leaves the South Cameroonian Plateau via a series of waterfalls, and finally flows through the coastal plain into the sea.

2.2. Climate

The Nyong basin is exposed to a humid equatorial climate marked by four different seasons. There is a continuous big wet season from September to November, and a continuous big dry season from December to March. The small wet season begins in April and lasts until June. Afterwards, the small dry season begins and lasts for a period of 2 months (July and August). Mean annual precipitation calculated over a period of 25 years varied from 1387 mm at Ayos to 1732 mm at Dehane (Olivry, 1986). Mean annual air temperature is about 24°C over the entire Nyong basin. The Nyong watershed is predominantly covered by tropical rain forest and is free of anthropogenic disturbance (industrial or agricultural) except in the region of Yaoundé (city of 1 million inhabitants).

2.3. Geology

A simplified geological map (Fig. 1) shows the main rock types present in the Nyong basin area. The parent rock consists of metamorphic and plutonic rocks. In the South of the basin, the Ntem complex that constitutes the northern boundary of the Congo craton (2896 ± 7 Ma, Toteu et al., 1994) is exposed. The following simplified description of the geology is based on different studies (Nédélec et al., 1990; Barbey et al., 1990; Vicat et al., 1998). Three main lithologic units characterize the Ntem complex: (1) granulitic gneisses (charnockites), (2) Soo tonalites, and (3) granitic group (granites and granodiorites). The mineralogical composition of these rocks is given in Nédélec et al. (1990) and Tchameni (1997). The Ntem complex is limited to the north by a major fault. In the north of the catchment, rocks attest migmatization processes dated from 600 Ma (Panafrican Chain) (Toteu et al., 1994). Two series are individualized: the Yaoundé series and the Mbalmayo series. Following the study of Barbey et al. (1990), the Yaoundé series (granulite facies) appears
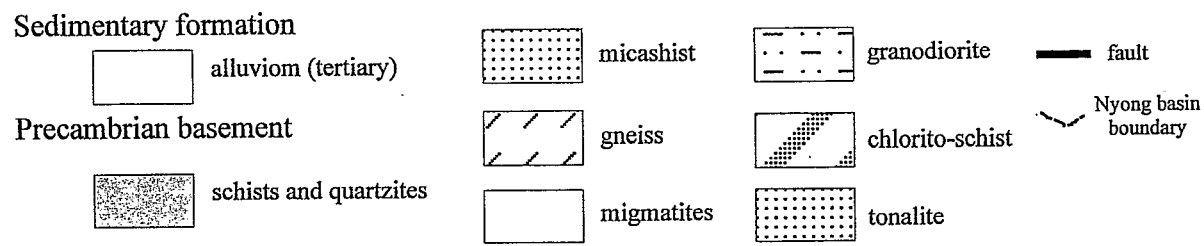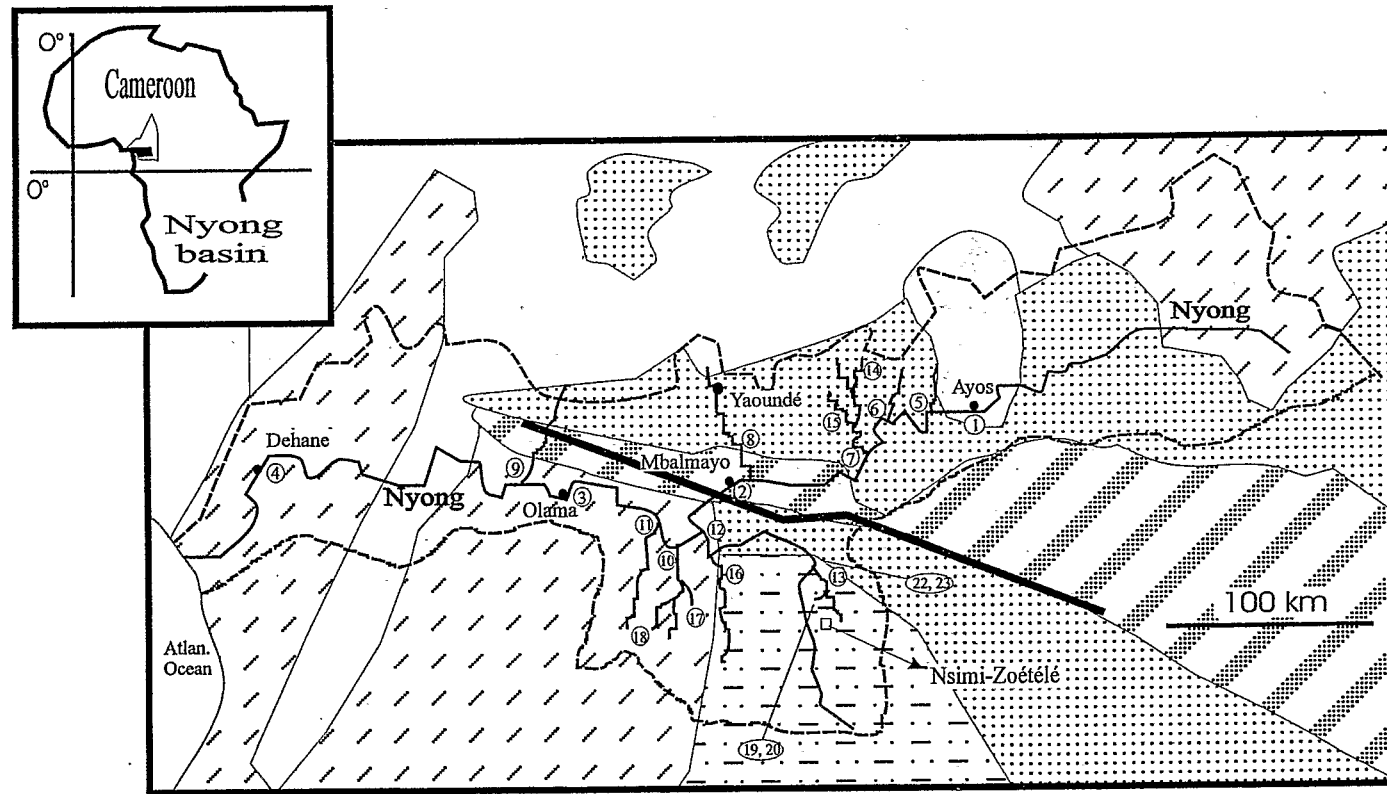
to be constituted by three types of migmatites rocks (i.e., leucosomes, quartzo-feldspathic differenciations, and garnet rocks). The Mbalmayo series is composed of schist rocks resulting in a low metamorphism (green schist facies) of detritic and clays rocks. From its metamorphism and structural features, the Mbalmayo series can be related to the Yaoundé series (Nédélec et al., 1986).

A pedological cover is developed on these rocks all over the basin. According to Robain (personal communication), the soils drained by the Nyong River and its tributaries can be classified in three major types: (i) thin humic horizon developed in the mountainous area, (ii) hydromorphic, and (iii) ferralitic. A forthcoming companion paper (Oliva et al., 1999) gives a description of these soils for the Nsimi-Zoétélé watershed (see Fig. 1). This watershed is a pilot site (PEGI and PROSE French programs) considered to be representative of the Nyong basin. Hydromorphic soils occupy the swamp zones while ferralitic soils are present in the hills. Ferralitic soils are the most widespread soils over the Nyong basin (about 80% of the humid forest zone). From bottom to top, the succession of the pedological horizons are (1) a saprolitic horizon where the structure of the parent rock is still present, (2) a mottled clay horizon, (3) a ferruginous horizon, and (4) a soft clayey (yellow or red) horizon. The ferruginous horizon can be either indurated (iron crust) or not (nodular horizon). These soils reach 40 m thick. Hydromorphic soils develop on truncated saprolite, outcropping parent materials, and sandy alluvial deposits. They exhibit sandy horizons covered by a brown silt clay horizon rich in organic matter. In this dark humic horizon, organic matter can reach up to 20% by weight. The major minerals of these soils are primary resistant minerals (i.e., quartz, and at a much lesser extent K-feldspar) and iron- and aluminum-rich weathering products (i.e., kaolinite, goethite, and hematite). Minor minerals are mainly Fe-oxides, Ti-oxides, and zircon (Oliva et al., 1999).

3. Sampling and analyses

3.1. Rivers

The map in Fig. 1 shows the sampling point locations within the Nyong River basin. Samples

Sedimentary formation

- alluviom (tertiary)

Precambrian basement

- schists and quartzites
- micashist
- gneiss
- migmatites
- granodiorite
- chlorito-schist
- tonalite
- fault
- Nyong basin boundary

Inset map: Cameroon, Nyong basin, 0°

Map labels: Nyong, Ayos, Yaoundé, Dehane, Nyong, Mbalmayo, Olama, Atlan. Ocean, Nsimi-Zoétélé, 100 km

from minor and major tributaries of the Nyong River were collected in October 1996 during the high water level season. Four of them (Mengong, Awout, Soo, and Nyong) were sampled on a monthly basis during the period from October 1994 to January 1997. One particular river is the Mefou, which drains the urbanized area of Yaoundé.

Among the rivers presented in this study, only the Nyong and the Mengong have been monitored to determine their water discharges. At the Nyong sampling point of Mbalmayo, the maximum monthly average discharge of 340×10^3 l s^{-1} is obtained in November and a minimum of 50×10^3 l s^{-1} in February over the period 1950–1993 (Olivry, 1986). At the opposite is the Mengong River, a first-order stream, which drains the pilot site Nsimi-Zoétélé and which has a mean water discharge of 6.7 l s^{-1} (Ndam Ngoupayou, 1997). In the other rivers, water discharge is intermediate between those of Nyong and Mengong rivers but they follow the same seasonal trend. Although the Nyong (27,800 km^2) and Mengong (< 1 km^2) rivers basins have very different drainage surfaces, their specific water discharge are similar (≈ 11 l s^{-1} km^{-2}; Ndam Ngoupayou, 1997).

3.2. Sampling and filtration

Three solution parameters (pH, temperature, and electrical conductivity) of the river waters were measured in the field. The pH was measured using a combined "Schott–Geräte" electrode calibrated using NIST standard buffer solutions (pH 4.00 and 6.86 at 25°C). The accuracy of the pH measurement was ±0.05 units. Samples were generally collected from bridges near the middle of the flow in 10-l High Density polyethylene (HDPE) containers. Water was immediately filtered using a Sartorius Teflon filtration unit (Ref.: SM 16540). The ester cellulose

Millipore filters used (ref.: GSWP) have a diameter of 142 mm and a pore size of 0.22 μm. The filtration is carried out under a pressure of 2 atm induced by a Masterflex peristaltic pump. The first 500-ml of the filtration were systematically discarded to clean the membrane. Filtered solution for cations and trace elements analyses was acidified (pH 1) with ultrapure 10 M HNO$_3$ and stored in HDPE bottles, previously washed with ultrapure (double-distilled) HCl diluted to 0.1 M and rinsed with MilliQ deionized water. Bacterial development was prevented by addition of HgCl$_2$ in the samples for DOC analyses. "Blank" tests were performed to control the level of pollution induced by the sampling and filtration protocols used (silicon tubes, membrane filter, filtration unit, and storage bottles). "Blank" tests on major and trace elements and DOC confirms that the contamination from sampling and filtration procedures is insignificant for the elements presented in this study. For several samples of Mengong and Nyong rivers, an aliquot of unfiltered solution was conserved to analyze the total concentration (i.e., bulk waters).

3.3. Analytical methods

Major cations (Na, Ca, K, Mg) and anions (Cl, NO$_3$, PO$_4$, SO$_4$) concentrations in the dissolved phase (< 0.20 μm) were measured by HPLC (respectively DX 100 and Dionex QIC). Aqueous silica concentrations were determined colorimetrically (molybdate blue method) using a Technicon automated analyzer. Trace elements concentrations were measured by ICP-MS (Perkin Elmer, Elan 5000 and 6000). Indium was used as an internal standard and corrections for oxide and hydroxide ions were made for the REE (Valladon et al., 1995). The international geostandards SLRS-3 (Riverine Water Reference Material for Trace Metals certified by the Na-

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Fig. 1. Location map of the Nyong basin, showing the bedrock geology and the stream sampling stations. The circles indicate the sample locations and must be related to the list reported thereafter: (1) Nyong-Ayos, (2) Nyong-Mbalmayo, (3) Nyong-Olama*, (4) Nyong-Dehane (order V), (5) Ntala, (6) Mbem, (7) Mfoumou, (8) Mefou, (9) Akono, (10) Kama, (11) Soumou, (12) Soo* (order IV), (13) Awout*, (14) Abe, (15) Ato, (16) Fala, (17) Nsono, (18) Bissi (order III), (19) Bives, (20) Minsamba (Order II), (21) Mengong*, (22) Ossue-Nsam, (23) Ossue-Bonva (order I). The "order" given for each river is a classification of the tributaries based on their hydrological parameters; from the order V to the order I, there is a decrease of the water discharge and drainage area of the river. An order I river will be a tributary of an order II river, an order II river a tributary of an order III river, and so on. The star (*) indicates that the river was monthly sampled during the period from October 1994 to January 1997.

Table 1

Major, trace elements, and DOC concentrations, and strontium isotopic ratios ($^{87}Sr/^{86}Sr$) measured in the dissolved phase (i.e., $< 0.20~\mu m$) of the Nyong basin rivers. < dl: signifies "below detection limit"; TDS: signifies "total dissolved solid"

	pH	Tempe-rature, °C	Conductance, $\mu S~cm^{-1}$	Mg, $\mu g~l^{-1}$	Ca, $\mu g~l^{-1}$	Na, $\mu g~l^{-1}$	K, $\mu g~l^{-1}$	Cl, $\mu g~l^{-1}$	NO_3, $\mu g~l^{-1}$	SO_4, $\mu g~l^{-1}$	H_4SiO_4, $mg~l^{-1}$	DOC, $mg~l^{-1}$	Al, $\mu g~l^{-1}$	Mn, $\mu g~l^{-1}$	Fe, $\mu g~l^{-1}$	Co, $\mu g~l^{-1}$	Rb, $\mu g~l^{-1}$	Sr, $\mu g~l^{-1}$	Ba, $\mu g~l^{-1}$	Y, $\mu g~l^{-1}$	La, $\mu g~l^{-1}$
Ayos	5.5	26	26.2	975	1314	758	1809	829	< dl	966	13.3	28.06	251	50.8	422	0.48	5.65	11.25	18.29	0.440	0.348
Mbalmayo	5.6	24.2	23.7	683	1273	1117	1487	1206	107	782	12.7	23.03	215	29.7	241	0.36	4.18	9.72	17.71	0.645	0.538
Olama	5.8	26	23.9	663	1296	1094	1193	970	< dl	667	13.6	23.7	252	27.8	281	0.31	3.41	13.36	23.77	0.543	0.528
Dehane	6.6	25.1	19.9	636	1034	1134	988	744	383	655	13.6	12.2	63	6.6	87	0.10	2.68	10.97	18.69	0.292	0.296
Ntala	5.3	25.3	22.7	853	1464	474	1380	493	247	364	8.2	24.4	749	54.4	1256	0.37	4.89	9.47	14.24	0.518	0.548
Mbem	5.2	22.5	17	530	1003	668	587	367	< dl	224	12.6	24.4	368	27.1	562	0.58	2.20	9.76	20.56	0.722	0.770
Mfoumou	5.4	22	16.8	562	990	614	815	482	< dl	233	12.2	23.6	567	33.0	929	0.59	2.90	8.81	19.10	0.863	0.866
Mefou	6.5	24.1	64.8	1097	3856	3677	4833	3295	1195	2994	17.4	21.6	1307	12.3	580	0.18	11.26	22.22	27.43	0.274	0.240
Akono	6.0	22.1	20.1	668	982	938	1233	925	160	619	15.1	21.3	275	35.9	402	0.34	4.09	10.37	22.10	0.633	0.398
Kama	6.3	22.5	20.4	578	1172	872	871	523	74	458	14.0	13.3	115	39.5	262	0.24	1.99	17.28	19.46	0.169	0.188
Soumou	5.8	22.1	22.9	613	1274	1283	955	–	< dl	–	18.1	22.9	586	40.3	499	0.30	2.12	21.40	36.13	0.383	0.543
Soo	5.3	22.3	20.4	606	1263	961	908	480	185	413	14.5	29.6	319	36.9	452	0.43	1.92	17.01	29.43	0.385	0.529
Awout	4.9	22.4	21.5	579	1324	895	776	485	< dl	274	12.9	34.1	405	24.8	414	0.28	1.52	16.10	20.83	0.327	0.454
Abe	6.1	22.1	17	743	781	740	778	337	382	1146	13.4	9.9	85	7.1	375	0.08	2.32	8.87	22.46	0.324	0.164
Ko	6.0	22.2	16.3	654	810	795	676	389	40	404	13.5	16.9	136	9.8	522	0.13	1.91	16.18	18.88	0.500	0.317
Fala	5.6	22.6	20.4	577	1090	1110	1005	468	< dl	497	15.3	25.9	199	31.7	357	0.37	2.36	17.10	32.81	0.306	0.448
Nsono	5.9	24.3	28.5	687	1556	1166	1247	525	< dl	265	14.1	19.8	111	38.5	487	0.24	2.50	22.61	24.45	0.161	0.175
Bissi	5.6	23.8	24.2	765	1540	1144	705	382	214	387	14.8	24.2	877	30.1	1147	0.42	1.52	23.95	26.94	0.327	0.472
Bives	4.8	23.4	18.7	474	1011	798	916	444	< dl	353	13.0	38.2	328	18.7	318	0.22	1.78	14.25	16.18	0.212	0.277
Minsamba	4.8	23.1	20.5	495	1066	758	901	698	< dl	498	11.5	27.4	369	20.5	311	0.28	2.17	11.01	15.59	0.269	0.349
Mengong	–	–	–	389	780	711	960	390	40	60	11.2	–	250	16.2	235	0.28	0.64	12.21	26.90	0.279	0.350
Ossue-Nsa	5.9	25.3	23.2	648	1252	1328	898	433	< dl	320	16.2	20.1	87	39.9	252	0.41	2.07	20.75	26.03	0.235	0.252
Ossu-bov	5.1	24.2	23.1	708	1685	637	887	558	< dl	276	10.0	28.3	345	60.8	846	0.74	2.46	12.76	18.11	0.368	0.424

	Ce, μg l⁻¹	Pr, μg l⁻¹	Nd, μg l⁻¹	Sm, μg l⁻¹	Eu, μg l⁻¹	Gd, μg l⁻¹	Tb, μg l⁻¹	Dy, μg l⁻¹	Ho, μg l⁻¹	Er, μg l⁻¹	Tm, μg l⁻¹	Yb, μg l⁻¹	Lu, μg l⁻¹	Zr, μg l⁻¹	Th, μg l⁻¹	U, μg l⁻¹	⁸⁷Sr/⁸⁶Sr	TDS, mg l⁻¹	NICB, %
Ayos	0.856	0.127	0.527	0.095	0.019	0.083	0.013	0.082	0.016	0.052	0.008	0.047	0.007	0.487	0.087	0.008	0.715360	22.5	80.6
Mbalmayo	1.317	0.179	0.690	0.136	0.025	0.134	0.018	0.119	0.020	0.071	0.009	0.060	0.008	0.395	0.121	0.029	0.716134	21.9	74.7
Olama	1.290	0.158	0.653	0.130	0.019	0.090	0.017	0.103	0.021	0.052	0.005	0.059	0.007	0.455	0.118	0.022	0.713782	21.6	79.0
Dehane	0.666	0.084	0.346	0.063	0.011	0.053	0.009	0.050	0.012	0.033	< dl	0.032	< dl	0.140	0.066	0.013	0.716372	21.1	77.1
Ntala	1.440	0.165	0.719	0.139	0.023	0.110	0.017	0.095	0.021	0.053	0.007	0.045	0.006	0.776	0.164	0.033	0.716044	16.5	87.2
Mbem	1.721	0.227	0.943	0.192	0.032	0.143	0.023	0.137	0.024	0.074	0.011	0.069	0.010	0.633	0.217	0.028	0.719310	17.5	89.1
Mfoumou	2.004	0.253	1.009	0.202	0.044	0.161	0.031	0.175	0.034	0.088	0.012	0.079	0.013	0.814	0.236	0.044	0.718397	18.1	87.1
Mefou	0.697	0.069	0.289	0.067	0.011	0.057	0.010	0.047	0.011	0.031	0.005	0.028	0.005	0.354	0.065	0.019	0.713353	47.7	69.1
Akono	1.134	0.139	0.571	0.119	0.029	0.124	0.018	0.115	0.023	0.065	0.012	0.075	0.011	0.353	0.109	0.023	0.716391	23.0	76.3
Kama	0.445	0.053	0.224	0.037	0.010	0.039	0.006	0.029	0.006	0.015	< dl	0.014	< dl	0.182	0.044	0.009	0.708885	20.0	84.6
Soumou	1.414	0.154	0.556	0.103	0.019	0.067	0.013	0.064	0.013	0.032	< dl	0.035	0.005	0.326	0.094	0.020	0.710324	~	–
Soo	1.306	0.146	0.559	0.114	0.014	0.090	0.013	0.073	0.013	0.037	0.006	0.033	0.005	0.436	0.151	0.022	0.712028	21.1	85.8
Awout	0.998	0.116	0.466	0.098	0.010	0.066	0.010	0.062	0.010	0.035	0.005	0.027	< dl	0.418	0.120	0.022	0.712448	18.8	88.7
Abe	0.381	0.048	0.205	0.057	0.006	0.053	0.007	0.048	0.011	0.032	0.005	0.037	0.007	0.089	< dl	0.005	0.718389	20.6	74.1
Ko	0.833	0.092	0.415	0.077	0.019	0.083	0.012	0.092	0.016	0.057	0.009	0.058	0.009	0.190	0.056	0.005	0.717732	18.7	86.3
Fala	1.080	0.116	0.456	0.079	0.015	0.062	0.010	0.053	0.009	0.031	< dl	0.028	< dl	0.389	0.152	0.016	0.713432	21.5	86.6
Nsono	0.472	0.054	0.212	0.031	0.010	0.044	< dl	0.029	0.005	0.018	< dl	0.013	< dl	0.342	0.072	0.006	0.710196	20.9	90.6
Bissi	1.180	0.128	0.504	0.104	0.015	0.072	0.010	0.068	0.013	0.032	< dl	0.034	0.005	0.790	0.114	0.026	0.710001	22.9	89.2
Bives	0.643	0.076	0.266	0.061	0.006	0.045	0.005	0.043	0.007	0.023	< dl	0.012	< dl	0.454	0.118	0.022	0.712077	18.4	86.5
Minsamba	0.817	0.093	0.371	0.072	0.015	0.060	0.007	0.052	0.009	0.024	< dl	0.023	< dl	0.524	0.120	0.018	0.711045	17.8	79.9
Mengong	0.757	0.099	0.366	0.080	0.023	0.075	0.007	0.055	0.011	0.027	< dl	0.020	< dl	0.379	0.092	0.021	0.711744	15.5	89.7
Ossue-Nsa	0.717	0.074	0.341	0.061	0.012	0.050	0.007	0.041	0.008	0.026	< dl	0.024	< dl	0.232	0.056	0.013	0.709989	22.2	90.4
Ossu-bov	1.021	0.125	0.510	0.111	0.020	0.084	0.013	0.071	0.012	0.029	0.005	0.037	0.005	0.571	0.076	0.014	0.717251	16.7	88.8

tional Research Council of Canada) was used to check the validity and reproducibility of the analyses by ICP-MS. A good agreement between our values and the certified data was obtained (relative difference < 8%) except for Co (35%) (see Viers et al., 1997). Dissolved organic carbon (DOC) was analyzed using a Carbon Total Analyzer (Shimadzu TOC 5000A).

Before analyses, unfiltered water samples are subjected to acid digestion ($HF + HNO_3$) in Savillex Teflon. Freydier et al. (1997) showed that the direct ICP-MS analyses of unfiltered rainwater induces an underestimation of Al and Fe concentrations (and maybe this is true for some other elements). Trace element concentrations were measured by ICP-MS. "Blank" tests were also performed to estimate the level of contamination induced by the acid attack procedure. The contamination from acid digestion procedure is found to be less than 2% of the concentrations. This was estimated by comparing the concentrations in the blank with concentrations in samples with very low elemental abundances.

Strontium isotopic ratios were measured by thermal ionization mass spectrometry (Finnigan Mat 261) at the CEREGE (Aix-en-Provence). Data correction was based on the systematic analysis of the NBS 987 standard $0.710178 \pm 12 \times 10^{-6}$) (Ref.: 0.7102215). The Sr concentrations in blanks (measured by ICP-MS) were insignificant compared to the Sr content of the water samples (9–30×10^{-6} g l^{-1}).

4. Results

4.1. The Nyong basin rivers

4.1.1. Major ion compositions

Measured solution parameters (pH, temperature, and specific conductance), major and trace elements concentrations, Sr isotopic compositions, and organic carbon concentration in the dissolved phase are presented in Table 1. The specific conductance of all these rivers is very low and lies between 17 and 28 μS cm^{-1} with the exception of the Mefou River, which shows a significantly higher value of 65 μS cm^{-1}. The pH is slightly acidic with values ranging from 4.8 to 6.6. There is no specific pH variation as a function of river order but there is a continuous

increase of pH along the Nyong River, from Ayos (5.5) to Dehane (6.56).

The total dissolved load (TDS, mg l^{-1}), expressed here as the sum of major inorganic species concentrations (Na, Ca, K, Mg, Al, Fe, H_4SiO_4, Cl, NO_3, and SO_4), is given in Table 1. Compared with the compiled data of Meybeck and Ragu (1997) for the major rivers of the world, the TDS values of our samples are among the lowest (15–23 mg l^{-1}). TDS in Mefou River is about twice higher (48 mg l^{-1}) than the average value calculated for all the other rivers. Finally, with the exception of Mefou River, the TDS of these rivers is dominated by silica. Indeed, the dissolved H_4SiO_4 concentrations range from 8.16 (Ntala) to 18.10 (Soumou) mg l^{-1}, which accounts for 50% to 70% of the TDS, respectively.

The concentration of each major cation (Na, Mg, K, Ca) varies between 400 and 1800 $\mu g\ l^{-1}$. Plotted in Fig. 2 is the magnesium vs. calcium concentrations. In the same figure we show for comparison the data for other major rivers of the world and a world average (Meybeck, 1979). Our set of rivers has the lowest elemental concentrations in the world. Mefou River presents much higher concentrations since the sum of the major cation concentrations exceeds 13 mg l^{-1}. There is a good agreement between our data and values given for other organic-rich rivers sam-
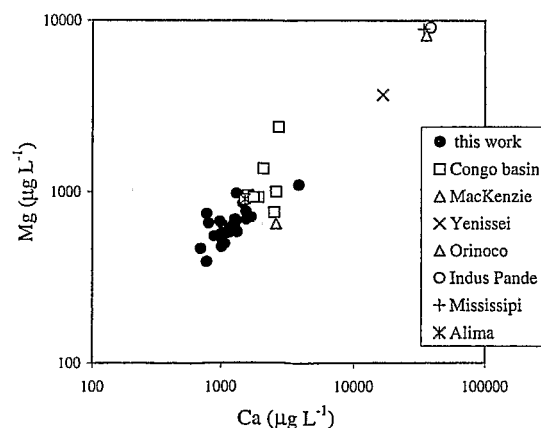

Fig. 2. Mg vs. Ca concentrations in the Nyong basin rivers. A comparison is made with other rivers representing different world areas (Congo basin rivers, Dupré et al., 1996; Amazon basin rivers, MacKenzie; Yenissei, Orinoco and Mississippi rivers, Meybeck and Ragu, 1997; Indus river, Pande et al., 1994; world average, Meybeck, 1979).

pled in Africa (Alima river, Dupré et al., 1996) or in South America (Orinoco river, Edmond et al., 1996; Rio Negro, Gaillardet et al., 1997). However, a rigorous comparison of the chemical composition of rivers requires a larger database, which takes into account the temporal variations.

For most sampled rivers the inorganic anions (Cl^- and SO_4^{2-}) content is in the range 200–1000 μg l^{-1}, while NO_3^- is much lower and often below the HPLC detection limit (about 10 μg l^{-1}). Alkalinity values are not reported in this study, because, due to the high content of organic acids, HCO_3^- concentration cannot be assessed easily by a classic acid titration. All rivers present a high content in organic carbon ($10 < DOC$ (mg l^{-1}) < 38) that is comparable to the values reported for other tropical (Thurman, 1985) or boreal rivers (Heikkinen, 1990).

The normalized inorganic charge balance, NICB, defined as ($TZ^+ - TZ^-/TZ^+$) is reported in Table 1. TZ^+ and TZ^- are the total cationic ($= Na^+ + K^+ + 2Mg^{2+} + 2Ca^{2+} + 3Al^{3+} + 3Fe^{3+}$) and anionic charges ($= Cl^- + NO_3^- + 2SO_4^{2-}$), respectively. The NICB shows for each river sample a large deficit (74–90%) of negative charges. At the pH of our samples, Al^{3+} and Fe^{3+} are not the species actually present in the solution. If we consider the true distribution of the hydrolyzed species of Al (Castet et al., 1993) and Fe (Diakonov, 1995) at the pH of these waters, the deficit of negative charges is reduced but remains high. This deficit of negative charges is balanced by the charge contribution of organic matter that is mainly constituted by high molecular weight organic acids such as humic substances. Measurement of small organic acids (e.g., acetic or oxalic acids) were performed by ionic chromatography; their level of concentrations are much too low to contribute significantly to the deficit of negative charges.

4.1.2. Trace element compositions

All these rivers present high concentrations in elements generally described as being slightly mobilized from weathered soil profiles (e.g., Al, Fe, Y, REE) or even considered as invariant (e.g., Th, Zr). For example, average Al and Fe concentrations are about 310 to 480 μg l^{-1}, respectively. For comparison, the Garonne River flowing in the south of France (temperate climate) present Al and Fe average concentrations that are below 50 μg l^{-1} (Baque, personal communication).

Yttrium and rare-earth elements concentrations fluctuate widely in the different rivers. For illustration, lanthanum concentration ranges from 175 (Nsono) to 866 ng l^{-1} (Mfoumou). These values are far above the typical concentrations reported for temperate rivers (e.g., Mississippi River, around 10 ng l^{-1} of La) (Sholkovitz, 1995). The REE patterns for some of the sampled rivers are plotted in Fig. 3. They are normalized to the estimated average composition of the upper crust (Taylor and McLennan, 1985). Some differences are observed in the REE patterns within the set of samples. Most of these rivers present a normalized La/Yb ratio that ranges from 0.8 to 1.2 indicating that there is no significant fractionation between light rare-earth elements (LREE) and heavy rare-earth elements (HREE) (see the pattern of the Ntala river in Fig. 3). However, the Nyong river ($[La/Yb]_N \cong 0.6$) and three other rivers (Akono, Abe, Ko; $[La/Yb]_N \cong 0.4$) exhibit a pronounced depletion in LREE (Fig. 3). As observed by several authors (Elderfield et al., 1990; Sholkovitz, 1993; Gaillardet et al., 1997) for some Amazonian rivers, the rivers that present a $[La/Yb]_N$ close to 1 have a significant upward convexity centered on the MREE (middle rare-earth elements).

Average concentrations of Th and Zr are 99 and 393 ng l^{-1}, respectively. These concentrations are similar to those reported by Konhauser et al. (1994) for Amazonian waters (Rio Negro) and by Dupré et
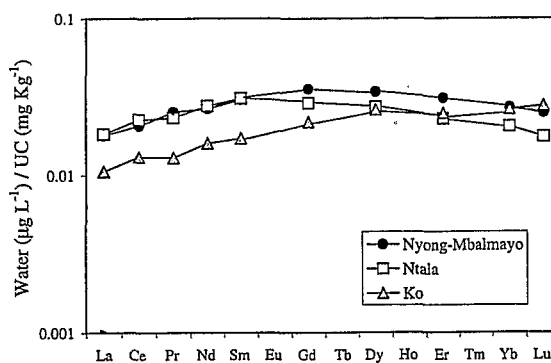

Fig. 3. REE patterns of the dissolved load for some rivers of this study. Data are normalized to the Upper Crust (average composition of the continental crust given by Taylor and MacLennan, 1985).

Table 2

Major, trace elements, and DOC concentrations measured in the dissolved phase (i.e., < 0.20 μm) of Mengong, Awout, Soo, and Nyong rivers. < dl: signifies "below detection limit"

Mengong	pH	Conductance, μS cm⁻¹	Temperature, °C	Mg	K	Ca	Na	NH₄	H₄SiO₄	Cl	NO₃	SO₄	DOC	Al	Mn	Fe	Co	Rb	Sr	Ba
O	5.6	12.8	22.1	365	100	695	791	87	10.4	319	< dl	< dl	13.4	260	12.7	278	0.27	0.37	13.14	14.10
N	5.6	13.4	21.9	474	82	822	552	78	10.4	248	< dl	< dl	14.0	243	13.2	274	0.31	0.26	14.84	16.64
D	5.8	13.2	21.4	612	82	1273	1128	< dl	10.4	102	< dl	79	12.0	142	8.5	216	0.20	0.27	12.90	13.98
J-95	5.8	19.8	22.4	272	89	490	426	35	10.5	165	420	118	11.6	133	6.9	209	0.11	0.29	8.35	10.10
F	not significant																			
M	5.5	29.6	24.3	827	468	1365	644	< dl	12.0	320	216	668	16.5	–	–	–	–	–	–	–
A	5.2	25.1	23.4	861	512	1868	1722	< dl	12.3	392	< dl	542	24.8	446	32.7	560	0.47	1.64	24.87	27.79
M	4.6	20	21.8	621	374	1388	1541	8	13.7	402	125	150	23.8	420	16.7	615	0.43	0.73	17.76	24.09
J	5.3	19.2	23.6	737	629	1644	1579	387	13.8	383	< dl	< dl	20.7	420	16.7	570	0.42	0.60	19.80	24.87
J	5.7	18.6	23.4	628	152	1281	1488	< dl	10.5	125	18	49	14.9	254	11.2	431	0.31	0.32	19.07	21.13
A	5.5	18	22.7	670	205	1207	1400	99	11.4	597	26	78	18.6	380	10.9	424	0.35	0.64	20.97	25.18
S	5.4	18.6	21.9	903	2004	2273	1567	305	12.8	859	41	232	18.6	388	21.8	553	0.58	0.90	22.46	27.35
O	5.2	19.8	21.1	669	813	1733	1059	< dl	13.5	829	252	179	20.2	393	15.0	577	0.28	2.44	20.61	24.53
N	5.7	15.5	21.8	576	229	1381	1183	< dl	12.7	140	< dl	< dl	11.0	194	0.8	172	0.07	0.35	16.40	18.49
D	5.9	17.4	21.9	637	253	1306	1226	17	12.3	94	93	38	13.7	209	15.6	361	0.38	0.30	20.22	21.68
J-96	6.0	17.3	22.5	564	298	1408	1539	< dl	12.0	112	499	108	11.4	157	6.8	256	0.17	0.46	15.40	15.61
F	not significant																			
M	5.4	29.4	23.6	1008	425	1416	889	184	13.0	841	290	638	18.9	274	13.0	322	0.22	1.11	24.04	25.74
A	5.2	21.5	22.5	674	343	1429	563	< dl	12.2	598	215	711	20.2	450	17.9	364	0.37	1.02	21.35	25.86
M	5.6	20	24.7	636	122	1165	1517	29	11.9	155	< dl	110	13.0	262	11.1	305	0.30	0.37	19.16	21.68
J	5.7	17.4	22.8	635	166	1534	1529	< dl	13.4	217	89	84	11.7	286	2.3	256	0.08	0.41	18.20	21.87
J	5.4	17.2	21.2	670	110	1454	1266	< dl	13.2	184	< dl	46	13.3	242	4.2	338	0.37	0.32	17.71	20.22
A	6.0	17.9	21.4	742	98	1480	1449	< dl	13.9	132	< dl	< dl	11.9	239	1.0	307	0.08	0.34	18.38	24.11
S	5.6	18.6	21.2	765	97	1559	1642	< dl	13.2	164	< dl	< dl	6.5	227	1.5	160	0.08	0.26	19.06	22.63
O	4.9	16	22.9	469	721	1202	557	< dl	9.0	469	507	122	17.8	223	2.8	216	0.11	1.84	14.36	16.69
N	not significant																			
D	6.1	15.1	21.8	583	119	1282	960	< dl	13.3	155	135	53	9.8	150	6.2	196	0.13	0.33	14.59	15.07
J-97	6.2	16.3	23.6	617	234	1279	1162	10	13.7	189	682	76	9.3	120	0.8	168	0.03	0.72	14.63	–

	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Zr	Th	U
O	0.243	0.247	0.588	0.071	0.292	0.065	0.013	0.038	< dl	0.040	0.007	0.016	< dl	0.019	< dl	–	0.050	0.007
N	0.193	0.224	0.534	0.062	0.257	0.047	0.014	0.035	< dl	0.032	0.006	0.023	< dl	0.014	< dl	–	0.030	0.007
D	0.099	0.121	0.279	0.032	0.131	0.025	0.010	0.023	< dl	0.018	< dl	0.010	< dl	0.008	< dl	–	0.068	0.015
J-95	0.068	0.077	0.184	0.024	0.106	0.009	0.005	0.015	< dl	0.017	0.005	0.011	< dl	< dl	< dl	0.160	0.026	0.008
M	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
A	0.264	0.287	0.725	0.087	0.394	0.076	0.022	0.057	0.011	0.036	0.008	0.023	0.005	0.025	0.005	0.592	0.129	0.018
M	0.282	0.348	0.827	0.096	0.399	0.079	0.027	0.055	0.008	0.058	0.012	0.027	0.005	0.032	0.005	0.594	0.136	0.022
J	0.258	0.328	0.752	0.087	0.384	0.097	0.020	0.064	0.011	0.046	0.008	0.030	< dl	0.025	< dl	0.570	0.123	0.021
J	0.183	0.178	0.440	0.053	0.208	0.049	0.011	0.018	0.006	0.040	0.005	0.016	< dl	0.012	< dl	0.441	0.104	0.014
A	0.262	0.293	0.724	0.086	0.310	0.062	0.020	0.050	0.006	0.042	0.006	0.027	< dl	0.022	< dl	0.540	0.136	0.021
S	0.314	0.400	0.942	0.108	0.422	0.113	0.017	0.074	0.009	0.058	0.011	0.036	< dl	0.033	0.005	0.574	0.147	0.021
O	0.267	0.334	0.805	0.087	0.346	0.056	0.021	0.072	0.010	0.048	0.009	0.026	< dl	0.028	< dl	0.603	0.142	0.016
N	0.155	0.173	0.414	0.046	0.195	< dl	0.009	0.029	0.005	0.034	0.007	0.014	< dl	0.022	< dl	0.398	0.075	0.013
D	0.169	0.191	0.463	0.049	0.213	0.034	0.011	0.041	0.009	0.025	0.007	0.019	< dl	0.019	< dl	0.409	0.079	0.014
J-96	0.110	0.118	0.298	0.035	0.166	0.029	0.010	0.045	0.005	0.024	0.006	0.011	< dl	0.011	< dl	0.336	0.068	0.012
M	0.210	0.220	0.550	0.067	0.263	0.058	0.014	0.045	0.007	0.042	0.009	0.019	< dl	0.022	< dl	0.078	0.095	0.015
A	0.245	0.326	0.742	0.087	0.351	0.073	0.020	0.080	0.009	0.052	0.010	0.025	< dl	0.023	< dl	0.391	0.129	0.016
M	0.197	0.264	0.510	0.063	0.247	0.061	0.010	0.044	0.007	0.033	0.007	0.014	< dl	0.013	< dl	0.082	0.091	0.016
J	0.270	0.332	0.741	0.088	0.393	0.076	0.011	0.062	0.006	0.056	0.011	0.023	< dl	0.024	< dl	0.472	0.123	0.023
J	0.264	0.312	0.739	0.087	0.350	0.068	0.020	0.069	0.009	0.048	0.009	0.027	< dl	0.023	0.005	0.499	0.136	0.021
A	0.191	0.241	0.522	0.060	0.227	0.068	0.005	0.028	0.005	0.041	0.007	0.020	< dl	0.020	< dl	0.447	0.104	0.017
S	0.207	0.226	0.467	0.057	0.259	0.071	0.006	0.033	0.003	0.050	0.007	0.021	< dl	0.015	< dl	0.399	0.086	0.018
O	0.209	0.288	0.659	0.080	0.307	0.061	0.016	0.058	0.008	0.037	0.008	0.021	< dl	0.017	< dl	0.306	0.080	0.013
D	0.155	0.184	0.421	0.052	0.217	0.042	0.012	0.040	0.006	0.032	0.005	0.016	< dl	0.015	< dl	0.301	0.073	0.013
J-97	0.118	0.129	0.265	0.036	0.143	0.029	0.014	0.026	0.004	0.020	< dl	0.012	< dl	0.010	< dl	0.268	0.067	0.008

Table 2 (*continued*)

Awout	pH	Conductance, μS cm^{-1}	Temperature, °C	Mg	K	Ca	Na	NH$_4$	H$_4$SiO$_4$	Cl	NO$_3$	SO$_4$	DOC	Al	Mn	Fe	Co	Rb	Sr	Ba
O	5.0	18.6	21.3	438	391	1263	230	< dl	12.0	709	310	144	21.9	404	24.9	365	0.36	1.54	15.59	19.48
N	4.8	17.5	21.7	413	274	1082	391	–	14.6	319	310	192	21.5	364	22.7	418	0.37	1.27	13.57	15.22
D	5.0	16.9	21.2	485	739	1370	1570	< dl	10.4	1375	1551	83	15.7	2978	18.6	579	0.33	1.55	14.85	16.08
J-95	5.6	35.5	25.3	272	743	666	858	117	15.4	1326	1350	84	11.5	161	28.2	381	0.30	1.89	8.01	6.90
F	not significant																			
M	5.3	36.5	24.5	1231	2704	3461	1801	< dl	20.8	1450	20	391		561	11.0	691	0.18	4.49	29.60	34.20
A	5.2	33.7	24.7	1011	2954	2902	1622	66	18.8	1246	< dl	252	40.8	515	27.8	830	0.39	4.72	29.29	32.80
M	4.8	29.7	22.4	769	1551	2146	1252	575	16.3	869	trace	232	32.2	656	33.2	743	0.47	2.59	23.24	31.52
J	4.6	23.4	21.8	619	907	1766	1310	637	14.9	683	588	297	27.3	537	29.1	701	0.44	1.97	20.52	27.91
J	4.6	24.2	22.1	660	845	1847	1302	< dl	12.8	485	< dl	164	22.3	612	35.1	808	0.51	2.10	22.96	27.53
A	4.9	27.3	22.3	702	902	1863	991	117	13.9	861	< dl	115	30.4	650	33.4	737	0.51	2.15	23.33	31.62
S	4.9	21.4	21.7	661	1000	1867	1121	217		565	< dl	117	25.0	482	24.2	509	0.34	2.24	16.10	133.49
O	5.0	19.5	21.6	600	778	1735	785	689	14.9	517	< dl	117	22.8	502	27.7	696	0.40	1.89	16.66	20.99
N	4.9	18	22	460	754	1322	965	< dl	16.9	310	459	132	16.1	510	15.7	576	0.30	1.51	14.52	17.47
D	5.2	17.9	22.3	489	627	1307	1141	< dl	17.4	302	14	111	8.2	510	20.9	643	0.35	1.46	14.53	17.33
J-96	5.4	20.1	23.2	532	1004	1604	1532	25	19.4	364	888	262	18.5	369	10.4	476	0.19	2.15	15.20	16.30
F	5.7	34.8	26.7	1084	3578	2854	2054	< dl	16.5	1629	62	139	23.2	186	1.8	600	0.16	6.25	22.41	24.15
M	5.4	38.1	23.9	1171	2835	3061	1625	28	18.6	1521	135	3625	29.0	379	8.7	445	0.15	4.80	28.24	34.01
A	4.7	34.5	23.9	798	1481	2335	1828	25	17.1	761	< dl	1460	39.4	1667	52.7	1068	0.79	2.79	29.17	36.08
M	4.5	22.5	22.6	623	911	1587	1079	50	16.5	402	< dl	172	23.6	640	30.2	832	0.47	1.90	19.68	27.42
J	4.5	21.3	23.1	586	694	1574	935	97	13.6	482	< dl	294	20.7	451	23.0	594	0.36	1.54	17.51	24.56
J	4.0	18.9	20.9	507	488	1419	932	< dl	15.8	346	< dl	126	–	458	21.3	539	0.34	1.04	15.31	19.47
A	5.2	16.6	20.9	462	427	1288	1209	7	17.5	167	492	130	11.1	729	15.5	516	0.28	1.12	13.95	46.32
S	–	21.8	21.7	570	822	1571	1352	< dl	16.7	572	287	406	8.7	1003	20.2	478	0.31	2.08	17.27	68.21
O	5.4	17	21	434	455	1226	992	< dl	17.2	374	459	189	16.1	299	14.8	409	0.27	1.07	11.29	12.15
J-97	5.5	17.4	23	458	597	1238	1190	< dl	18.1	313	5558	244	16.2	207	12.3	351	0.21	1.39	11.51	10.87

	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Zr	Th	U
O	0.289	0.362	0.866	0.100	0.414	0.080	0.020	0.066	0.009	0.050	0.010	0.033	0.004	0.023	0.005	–	0.440	0.134
N	0.282	0.320	0.775	0.094	0.377	0.066	0.017	0.065	0.007	0.048	0.010	0.030	0.005	0.025	0.004	–	0.124	0.035
D	0.240	0.386	0.793	0.091	0.352	0.079	0.017	0.053	0.007	0.042	0.008	0.027	0.003	0.022	0.002	–	0.107	0.036
J-95	0.078	0.110	0.262	0.031	0.109	0.021	0.005	0.028	0.006	0.023	0.003	0.007	< dl	< dl	< dl	0.331	0.046	0.013
M	0.383	0.373	0.992	0.121	0.488	0.099	0.013	0.065	0.012	0.083	0.016	0.031	0.003	0.036	0.007	0.711	0.151	0.019
A	0.346	0.401	0.931	0.114	0.419	0.086	0.025	0.090	0.011	0.059	0.015	0.028	0.006	0.032	0.002	0.728	0.162	0.027
M	0.448	0.594	1.375	0.153	0.628	0.124	0.040	0.119	0.020	0.087	0.013	0.040	0.006	0.039	0.005	0.837	0.195	0.030
J	0.365	0.496	1.154	0.134	0.527	0.103	0.027	0.099	0.018	0.074	0.013	0.036	0.005	0.033	0.003	0.667	0.169	0.025
J	0.365	0.480	1.059	0.125	0.457	0.096	0.020	0.102	0.012	0.069	0.010	0.031	0.002	0.032	0.004	0.765	0.142	0.027
A	0.420	0.595	1.288	0.146	0.587	0.118	0.029	0.089	0.015	0.077	0.015	0.051	0.002	0.044	0.006	0.794	0.188	0.026
S	0.351	0.328	0.874	0.105	0.435	0.079	0.046	0.082	0.011	0.055	0.011	0.032	0.004	0.026	0.004	0.690	0.116	0.023
O	0.331	0.441	1.013	0.119	0.450	0.086	0.030	0.085	0.015	0.052	0.013	0.041	0.004	0.025	0.003	0.748	0.158	0.027
N	0.313	0.373	0.886	0.108	0.398	0.105	0.027	0.084	0.010	0.062	0.011	0.026	0.003	0.032	0.002	0.689	0.142	0.022
D	0.281	0.393	0.869	0.101	0.390	0.078	0.024	0.069	0.011	0.049	0.013	0.031	< dl	0.018	< dl	0.726	0.146	0.024
J-96	0.226	0.279	0.659	0.077	0.312	0.060	0.015	0.057	0.010	0.033	0.009	0.027	0.001	0.017	< dl	0.578	0.107	0.028
F	0.170	–	0.468	0.056	0.206	0.052	0.011	0.036	0.004	0.037	0.006	0.019	0.002	0.017	0.001	0.120	0.123	0.033
M	0.249	0.316	0.690	0.080	0.339	0.071	0.019	0.054	0.009	0.048	0.008	0.028	0.004	0.023	0.004	0.085	0.105	0.015
A	0.497	1.178	1.542	0.175	0.705	0.130	− 0.001	0.130	0.019	0.101	0.019	0.046	0.005	0.047	0.006	0.545	0.239	0.039
M	0.370	0.520	1.111	0.134	0.547	0.102	0.019	0.067	0.015	0.068	0.014	0.034	0.004	0.031	0.004	0.170	0.187	0.034
J	0.317	0.522	0.945	0.113	0.449	0.098	0.014	0.056	0.014	0.062	0.011	0.036	0.004	0.028	0.004	0.104	0.119	0.025
J	0.315	0.415	0.969	0.116	0.414	0.078	0.011	0.056	0.011	0.057	0.013	0.028	0.003	0.027	0.002	0.636	0.157	0.030
A	0.290	0.428	0.866	0.091	0.372	0.088	0.006	0.055	0.007	0.048	0.009	0.021	0.001	0.023	0.003	0.869	0.146	0.033
S	0.363	0.544	1.093	0.126	0.450	0.096	0.011	0.049	0.007	0.070	0.011	0.036	0.004	0.025	0.005	1.096	0.137	0.035
O	0.209	0.267	0.614	0.069	0.277	0.053	0.015	0.052	0.007	0.036	0.007	0.021	0.003	0.016	0.002	0.572	0.090	0.022
J-97	0.153	0.164	0.409	0.048	0.187	0.034	0.010	0.035	0.005	0.027	0.005	0.014	0.002	0.011	0.002	0.382	0.065	0.010

Table 2 (*continued*)

Soo	pH	Conductance, $\mu S\ cm^{-1}$	Temperature, °C	Mg	K	Ca	Na	NH$_4$	H$_4$SiO$_4$	Cl	NO$_3$	SO$_4$	DOC	Al	Mn	Fe	Co	Rb	Sr
O	5.4	18.3	21.8	535	704	1283	276	< dl	11.3	532	–	288	18.2	278	21.3	325	0.26	2.28	17.22
N	5.8	18.3	22.5	535	469	1283	460	< dl	13.4	426	372	288	14.4	209	33.3	423	0.51	2.07	18.66
D	6.0	22.9	23.3	643	597	1229	1401	72	17.1	250	1155	366	12.5	100	48.8	251	0.59	1.75	20.15
J-95	6.1	25.8	25.2	827	668	1650	1363	70	18.2	318	989	394	13.0	67	72.2	195	0.66	2.19	22.34
F	not significant																		
M	5.7	28	23.9	691	1515	1359	1308	130	16.1	1057	278	2004		141	37.7	276	0.34	3.93	20.44
A	5.5	26.3	24.3	807	1204	2399	1786	968	16.5	856	45	1383	18.8	223	3.6	407	0.11	3.27	22.62
M	5.2	25.9	23.9	723	1028	1934	1263	173	17.5	773	50	259	22.6	336	5.0	582	0.17	2.84	22.15
J	5.4	21.3	23	663	990	1935	1444	877	16.2	841	201	280	21.8	286	26.6	503	0.40	2.49	20.81
J	5.7	21.7	23.2	700	663	1717	1147	< dl	17.1	509	10	1067	16.6	381	39.5	595	0.50	1.99	19.80
A	5.7	21.3	23.1	718	909	1843	1383	< dl	15.1	923	32	442	19.2	465	25.7	616	0.35	2.62	20.11
S	5.1	21.2	22.2	770	945	2064	1033	< dl	14.0	697	< dl	232	21.9	391	43.1	620	0.54	2.61	19.67
O	5.2	19.7	22.1	685	790	1807	1087	913	15.0	568	< dl	94	22.2	349	39.8	676	0.52	2.26	18.74
N	5.5	19.1	23.5	669	687	1718	1128	88	16.3	356	579	181	14.3	247	1.3	409	0.14	1.97	17.10
D	5.9	20.2	22.7	654	722	1651	1211	< dl	16.1	527	193	513	17.8	258	38.5	549	0.53	2.03	17.27
J-96	6.1	23	25.5	822	708	2040	1493	44	17.6	293	986	294	13.8	126	33.3	312	0.35	1.97	20.24
F	6.2	30.5	28	842	745	1759	1593	< dl	18.6	599	569	568	7.2	37	130.4	113	0.69	3.14	23.81
M	6.0	29.4	23.6	740	1070	1610	1422	< dl	15.2	1492	466	3361	9.2	92	5.1	157	0.09	4.10	22.41
A	5.5	20	23.5	604	785	1363	1027	29	15.2	503	71	307	15.8	275	34.8	539	0.47	2.17	17.89
M	significant																		
J	5.2	20.5	25.2	637	584	1640	1148	< dl	15.1	505	< dl	902	15.1	208	8.5	255	0.16	1.41	16.97
J	4.6	19.2	21.9	614	621	1676	1138	59	16.4	480	82	574	17.7	297	7.0	453	0.13	1.51	16.46
A	6.2	20.3	22	746	460	1713	1485	< dl	17.3	222	701	219	5.8	153	6.3	281	0.15	1.18	16.97
D	6.6	19	22.4	679	498	1661	1165	< dl	16.8	480	501	192	13.0	152	23.7	281	0.38	1.31	14.47
J-97	–	–	–	953	881	2109	1547	< dl		604	711	1653	–	60	61.5	159	0.50	2.10	20.33

	Ba	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Zr	Th	U
O	25.78	0.329	0.458	1.179	0.133	0.474	0.098	0.029	0.077	0.011	0.069	0.012	0.036	0.006	0.031	< dl	–	0.177	0.021
N	30.36	0.323	0.415	1.063	0.115	0.454	0.081	0.024	0.057	0.007	0.063	0.011	0.031	0.007	0.033	0.006	–	0.161	0.027
D	24.14	0.178	0.215	0.504	0.060	0.237	0.047	0.014	0.024	0.005	0.036	0.007	0.022	< dl	0.014	< dl	–	0.098	0.021
J-95	26.36	0.130	0.151	0.369	0.043	0.183	0.041	0.008	0.035	< dl	0.019	0.008	0.019	< dl	0.018	< dl	0.274	0.060	0.010
M	36.05	0.211	0.282	0.707	0.079	0.331	0.063	0.008	0.042	0.009	0.044	0.009	0.026	< dl	0.017	< dl	0.284	0.122	0.018
A	37.58	0.311	0.358	0.877	0.102	0.452	0.091	0.026	0.086	0.012	0.060	0.011	0.023	0.005	0.030	0.006	0.502	0.145	0.029
M	38.59	0.427	0.602	1.323	0.146	0.563	0.115	0.034	0.112	0.017	0.078	0.016	0.041	0.007	0.039	0.009	0.744	0.215	0.031
J	38.83	0.390	–	1.227	0.141	0.584	0.115	0.024	0.110	0.014	0.062	0.012	0.038	0.005	0.046	0.008	0.637	0.191	0.029
J	34.11	0.308	0.408	0.996	0.101	0.408	0.086	0.021	0.077	0.010	0.049	0.012	0.035	< dl	0.026	< dl	0.713	0.195	0.026
A	37.32	0.402	0.566	1.354	0.153	0.567	0.115	0.028	0.092	0.017	0.082	0.012	0.045	< dl	0.045	0.006	0.691	0.211	0.026
S	33.71	0.417	0.570	1.405	0.156	0.637	0.122	0.030	0.113	0.014	0.058	0.016	0.052	0.006	0.042	< dl	0.677	0.201	0.026
O	32.35	0.439	0.617	1.539	0.168	0.713	0.127	0.031	0.127	0.017	0.092	0.018	0.045	0.007	0.041	0.005	0.710	0.210	0.024
N	26.97	0.374	0.529	1.211	0.131	0.559	0.095	0.027	0.102	0.014	0.062	0.014	0.031	0.005	0.029	< dl	0.669	0.159	0.026
D	27.52	0.293	0.381	0.934	0.102	0.389	0.071	0.020	0.082	0.012	0.044	0.013	0.031	< dl	0.032	< dl	0.581	0.156	0.023
J-96	27.75	0.211	0.259	0.570	0.064	0.268	0.055	0.011	0.060	0.007	0.052	0.009	0.021	< dl	0.015	< dl	0.464	0.114	0.023
F	30.25	0.077	0.088	0.196	0.021	0.087	0.008	< dl	0.017	< dl	0.014	< dl	0.009	< dl	0.010	< dl	0.032	0.043	0.007
M	33.37	0.159	0.192	0.433	0.051	0.205	0.047	0.009	0.038	0.005	0.024	0.006	0.020	< dl	0.018	< dl	0.046	0.079	0.016
A	32.34	0.370	1.182	1.133	0.128	0.514	0.109	0.020	0.080	0.013	0.066	0.011	0.037	< dl	0.035	< dl	0.111	0.186	0.028
J	28.35	0.283	0.397	0.934	0.109	0.411	0.062	0.009	0.065	0.010	0.043	0.011	0.028	< dl	0.022	< dl	0.425	0.136	0.024
J	30.01	0.414	0.562	1.354	0.159	0.632	0.127	0.023	0.084	0.015	0.082	0.016	0.043	0.007	0.028	< dl	0.581	0.210	0.030
A	25.64	0.230	0.293	0.596	0.068	0.302	0.063	0.010	0.043	0.009	0.036	0.007	0.024	0.005	0.024	< dl	0.443	0.135	0.020
D	20.23	0.251	0.316	0.739	0.085	0.350	0.065	0.019	0.063	0.009	0.049	0.010	0.028	< dl	0.022	< dl	0.401	0.109	0.025
J-97	24.94	0.097	0.114	0.266	0.030	0.126	0.025	0.010	0.021	< dl	0.016	0.004	0.010	< dl	0.010	< dl	0.211	0.057	0.012

Table 2 (*continued*)

Nyong	pH	conductance, μS cm⁻¹	Tempe-rature, °C	Mg	K	Ca	Na	NH₄	H₄SiO₄	Cl	NO₃	SO₄	DOC	Al	Mn	Fe	Co	Rb	Sr	Ba
O	5.6	18.5	24.3	535	1134	1162	253	--	9.8	993	< dl	288	14.7	184	19.6	377	0.29	4.13	9.19	15.72
N	5.6	18.7	25.2	523	1095	1202	161	204	10.4	851	< dl	240	12.9	188	43.0	605	0.70	4.24	9.69	15.14
D	5.1	18.6	25.8	573	518	1325	873	< dl	11.9	563	162	96	16.3	123	34.6	345	0.60	1.88	9.48	12.72
J-95	5.3	16.4	26.3	506	363	1107	452	40	10.7	797	< dl	164	14.3	163	32.3	248	0.53	1.33	8.69	13.38
F	not significant																			
M	6.0	35.9	27.9	781	2054	1692	1924	53	13.3	2584	439	2038	17.8	138	25.4	266	0.19	5.68	14.55	22.53
A	6.0	31	28.1	826	2182	2383	2098	191	13.1	2225	214	1230	13.6	138	2.6	253	0.10	5.45	14.59	22.18
M	5.9	27.3	28.2	541	1036	1565	1315	135	15.5	1226	12	528	13.6	179	1.4	254	0.11	3.27	17.98	29.29
J	5.9	26.4	25.8	836	1158	2225	1658	718	14.0	1362	2059	339	22.6	177	11.7	195	0.15	3.89	13.59	22.00
J	5.9	21.4	25.7	639	656	1866	1190	642	12.7	819	11	144	12.9	186	27.3	220	0.31	2.55	11.42	19.45
A	5.9	24.6	25.5	698	1034	1828	1483	< dl	11.9	1317	435	911	14.0	183	14.7	214	0.18	3.40	11.19	18.68
S	5.8	20	25	658	924	1751	1027	487	11.2	871	< dl	193	14.3	220	25.3	209	0.36	3.26	10.44	17.64
O	5.6	20.7	24.3	827	1304	1891	1082	< dl	12.3	1098	< dl	220	18.7	240	35.7	327	0.51	4.27	10.29	18.38
N	5.4	20.2	25.1	730	902	1682	934	<	12.0	751	70	230	14.6	170	0.6	198	0.10	3.45	10.54	16.52
D	4.5	19.1	25.5	695	406	1606	878	15	10.1	459	< dl	< dl	18.9	198	48.4	353	0.71	1.44	10.73	16.63
J-96	5.6	18	26.1	654	452	1761	1226	43	11.8	529	341	151	15.8	184	38.5	259	0.60	1.02	10.05	15.84
F	6.5	35.3	29.6	962	1590	2483	2724	113	7.2	1847	966	665	9.2	62	14.5	72	0.18	3.67	15.11	16.45
M	6.3	44.1	26.9	997	2649	2701	2489	< dl	12.8	pol	746	3340	9.9	155	18.6	276	0.19	7.14	16.63	26.39
A	6.0	26.4	26.8	745	1336	1661	1310	31	13.2	1477	79	664	11.2	175	22.3	171	0.24	4.47	12.72	23.71
J	5.5	25.7	24.9	688	987	1634	1432	29	12.5	1225	494	598	8.8	137	2.1	116	0.08	3.10	12.42	38.73
J	5.3	23.6	24.3	816	1063	1997	1270	< dl	12.3	1049	< dl	625	13.4	176	1.6	122	0.06	2.96	11.41	39.87
A	6.3	23.7	24.1	743	649	1847	1472	< dl	11.7	794	< dl	326	5.1	147	18.8	141	0.22	2.02	12.16	18.60
O	5.6	22.3	23.1	485	571	1236	600	< dl	11.7	1043	< dl	175	15.0	169	11.3	202	0.17	3.23	9.63	15.08
D	6.0	22	24.6	807	732	1825	855	< dl	12.1	613	204	--	19.3	228	35.7	485	0.60	2.51	10.87	17.05
J-97	--	--	--	802	702	1953	1665	< dl		993	700	321	--	151	28.3	204	0.37	2.00	11.42	15.41

	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Zr	Th	U
O	0.481	0.364	0.919	0.123	0.528	0.096	0.027	0.086	0.013	0.077	0.018	0.055	0.007	0.043	0.009	–	0.101	0.026
N	0.488	0.379	0.939	0.124	0.532	0.098	0.024	0.082	0.013	0.090	0.018	0.051	0.007	0.043	0.007	–	0.100	0.020
D	0.329	0.275	0.706	0.097	0.426	0.090	0.017	0.060	0.009	0.064	0.012	0.034	0.005	0.032	0.004	–	0.114	< dl
J-95	0.347	0.289	0.674	0.093	0.600	0.058	0.017	0.080	0.009	0.051	0.011	0.033	< dl	< dl	< dl	0.352	0.055	0.003
M	0.313	0.259	0.582	0.075	0.290	0.055	0.014	0.054	0.007	0.060	0.013	0.030	0.005	0.019	0.003	0.267	0.064	0.016
A	0.367	0.289	0.621	0.088	0.414	0.072	0.024	0.089	0.013	0.058	0.013	0.039	0.006	0.039	0.010	0.367	0.081	0.024
M	0.406	0.390	0.857	0.118	0.454	0.104	0.028	0.086	0.014	0.044	0.016	0.039	0.008	0.045	0.007	0.552	0.119	0.026
J	0.558	0.491	0.974	0.129	0.621	0.124	0.031	0.123	0.019	0.086	0.018	0.052	0.009	0.067	0.010	0.521	0.116	0.026
J	0.450	0.369	0.834	0.109	0.483	0.106	0.022	0.076	0.015	0.067	0.015	0.047	0.006	0.041	0.007	0.479	0.101	0.011
A	0.473	0.382	0.877	0.119	0.550	0.107	0.021	0.080	0.013	0.085	0.013	0.046	0.005	0.046	0.005	0.446	0.110	0.021
S	0.570	0.485	1.107	0.154	0.559	0.114	0.031	0.128	0.023	0.092	0.016	0.054	0.007	0.058	0.006	0.459	0.111	0.021
O	0.678	0.551	1.310	0.176	0.745	0.148	0.036	0.154	0.022	0.131	0.025	0.074	0.011	0.075	0.009	0.531	0.151	0.023
N	0.494	0.393	0.877	0.121	0.481	0.110	0.018	0.111	0.016	0.075	0.019	0.039	0.005	0.043	0.005	0.485	0.100	0.018
D	0.405	0.350	0.820	0.104	0.478	0.090	0.023	0.089	0.012	0.069	0.012	0.035	< dl	0.044	0.006	0.419	0.073	0.007
J-96	0.377	0.313	0.710	0.098	0.435	0.063	0.022	0.101	0.009	0.057	0.014	0.039	0.003	0.035	0.006	0.397	0.063	0.010
F	0.098	–	0.146	0.021	0.086	0.020	0.001	0.021	0.002	0.015	0.004	0.009	0.002	0.012	0.001	0.027	0.026	0.008
M	0.269	0.210	0.476	0.061	0.250	0.055	0.015	0.049	0.010	0.050	0.008	0.027	0.005	0.034	0.004	0.050	0.063	0.016
A	0.522	0.471	0.904	0.125	0.531	0.104	0.022	0.082	0.016	0.083	0.017	0.053	0.008	0.048	0.008	0.079	0.125	0.024
J	0.415	0.316	0.667	0.098	0.425	0.098	0.017	0.073	0.013	0.074	0.017	0.040	0.005	0.043	0.007	0.078	0.087	0.024
J	0.559	0.467	1.025	0.132	0.603	0.114	0.021	0.091	0.017	0.113	0.022	0.051	0.011	0.055	0.007	0.459	0.119	0.030
A	0.350	0.278	0.611	0.092	0.394	0.074	0.012	0.073	0.010	0.062	0.013	0.041	0.007	0.036	0.004	0.355	0.076	0.014
O	0.519	0.419	0.994	0.132	0.572	0.117	0.030	0.115	0.017	0.089	0.019	0.054	0.008	0.049	0.008	0.493	0.114	0.021
D	0.521	0.420	0.965	0.134	0.569	0.112	0.028	0.112	0.016	0.085	0.018	0.052	0.007	0.047	0.007	0.519	0.080	0.012
J-97	0.312	0.251	0.588	0.083	0.345	0.071	0.018	0.068	0.010	0.055	0.012	0.034	0.004	0.032	0.005	0.284	0.059	0.013

al. (1996) for the Congo basin rivers (draining forested regions). The range of concentration for the other trace elements are also comparable to those given by Dupré et al. (1996) for the Congo basin rivers. Sr and Ba concentrations range from 9 to 33 $\mu g\ l^{-1}$ and Rb from 0.6 to 5.6 $\mu g\ l^{-1}$. Mn and Co concentrations vary from 6 to 61 $\mu g\ l^{-1}$ and 0.10 to 0.70 $\mu g\ l^{-1}$, respectively. Mefou River exhibits a similar range of trace element concentration but a much higher Rb concentration (about 11 $\mu g\ l^{-1}$).

4.1.3. Sr isotopes

The measured $^{87}Sr/^{86}Sr$ ratios are reported in Table 1. It can be seen that this ratio varies widely between different rivers. The lowest value is obtained for the Kama River (0.70888) and the highest for the Mbem River (0.71931). The rivers, which drain the northern part of the Nyong basin (Mbem, Abe, Ako, Mfoumou, Akono, and Ntala), present the more radiogenic values (0.71604–0.71931). In contrast, rivers flowing in the southern part of the basin exhibit lower $^{87}Sr/^{86}Sr$ ratios and can be divided in two groups. The first one, composed of Soo, Fala, Awout, Bives, Minsamba, and Mengong rivers, has isotopic ratios ranging between 0.71104 and 0.71343. The second one (Kama, Ossue-Nsam, Bissi, Nsono, and Soumou) exhibit slightly lower values with a range of 0.70888–0.71032. The Sr isotopic ratios measured in the four sampling points of the Nyong River (i.e., Ayos, Mbalmayo, Olama, and Dehane) range between 0.71378 and 0.71637 and lay between the extreme ratios of the tributaries. Ayos and Mbalmayo exhibit high $^{87}Sr/^{86}Sr$ ratios of 0.71536 and 0.71613, respectively. This isotopic ratio decreases downstream at Olama (0.71378) and increases again to the west at the Dehane station (0.71637).

4.2. Seasonal variability of major and trace elements in four representative rivers: Mengong, Awout, Soo, and Nyong rivers

The previous data give an "instantaneous" geochemical signature of the Nyong basin rivers because all the samples were collected at the same period. The important complementary information has been obtained in the course of monthly sampling performed on Mengong, Awout, Soo, and Nyong rivers

(Table 2). This sampling provides a large database that allows us to define possible inter-relationships between the trace and major elements and DOC in these rich-organic rivers. Besides, the seasonal variation of elemental concentrations in response to hydrological changes may give information about the mechanisms controlling the transport of these elements in rivers.

We have reported in Fig. 4 the variability of the DOC concentrations and water discharges over the studied period (October 1994–January 1997) for the Mengong River. Two different water discharges are reported: one is the monthly mean daily discharge and the other is the water discharge measured on the sampling date. The agreement between the two values of water discharge suggest that our monthly sampling can be taken as representative of the hydro-chemistry of the Mengong river. Ndam Ngoupayou (1997) has shown that there is no delay between the steep discharge maxima and the steep DOC concentration maxima during an increase of the Mengong River water discharge. DOC increases during rising stage, and then decreases during the comeback to a normal flow.

Some elements (i.e., Al, Fe, Y, REE, Zr, and Th) exhibit a good correlation with DOC. The Fig. 5 presents the Fe-DOC correlation for the four monthly sampling rivers. Mengong and Soo rivers present
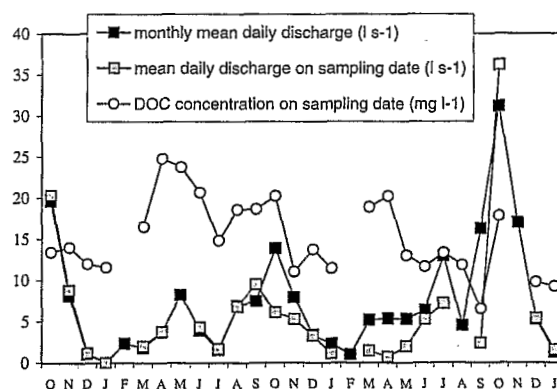
Fig. 4. Temporal variations of DOC concentrations and water discharge in the Mengong river waters. The letters O, N, D... stand for the monthly chronological order (i.e., October, November...) during the period from October 1994 to January 1997. Hydrological data are from Ndam Ngoupayou (1997).
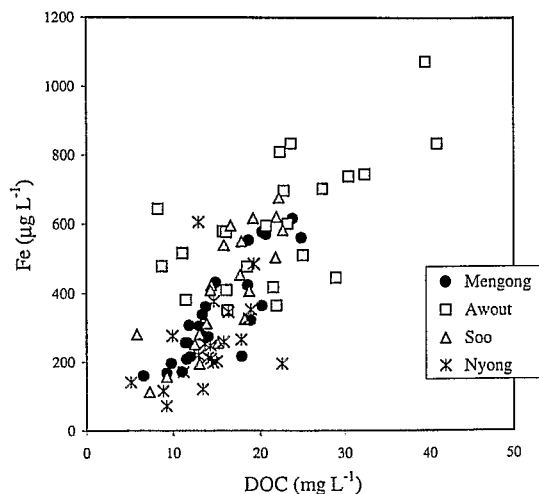
Fig. 5. Fe vs. DOC relationships in Mengong, Soo, Awout, and Nyong rivers.

clearly better correlation than Awout and Nyong rivers. The histogram drawn in Fig. 6 gives the variability (expressed in percent) of elements and DOC concentrations among seasonal samples for the Mengong waters. The variability is expressed as the standard deviation divided by the mean. This diagram enables us to recognize the elements that present the highest changes in their concentration in response to an increase of water discharge. Potassium and rubidium are the elements that exhibit the highest relative concentration variability (more than

80%). In contrast, dissolved silica content in Mengong River waters is much less variable with concentration variability lower than 20%. With the exception of K, the major cations (Na, Mg, and Ca) show the lowest variability (about 30%). All the other elements (Mn, Co, Al, Fe, Ba, REE, Y, Zr, Th, and U) and DOC have a concentration variability ranging from 35% to 60%.

We have reported in Fig. 7 the seasonal variation of the dissolved Th concentrations in Mengong, Awout, Soo, and Nyong rivers. All these rivers present the same temporal variations of Th concentrations. The dissolved concentrations increase during the period of high water level and decrease during the period of low water level.

4.3. Relation between dissolved and particulate phases in Mengong and Nyong rivers

Several water samples of the Mengong and Nyong rivers were also analyzed to study the bulk water composition (i.e., unfiltered water) (Table 3) in order to estimate the importance of the dissolved phase relative to the bulk waters. The bar chart diagram (Fig. 8) gives the percentage of the dissolved load with respect to the bulk phases for these two rivers. For the Mengong River, soluble elements represented in this diagram by Sr and Ba are exclusively in the dissolved load. The dissolved load carries
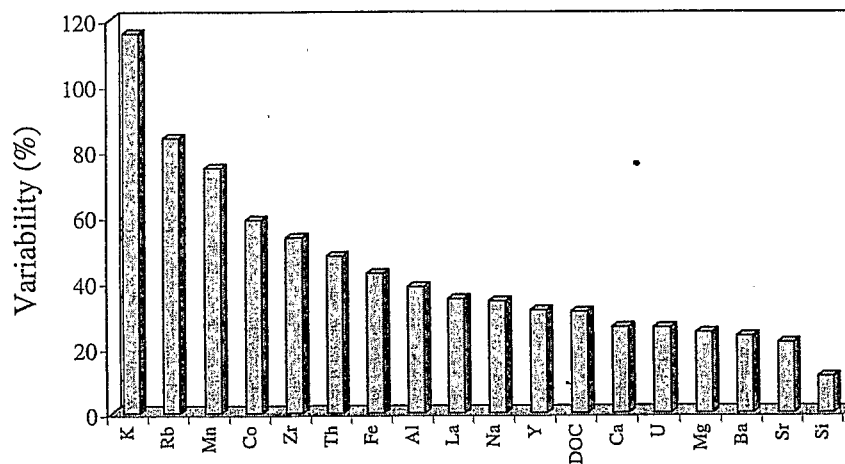
Fig. 6. Variability (in percent, standard deviation divided by the mean) of DOC and element concentrations during the 1994–1997 period of monthly sampling: Mengong river.
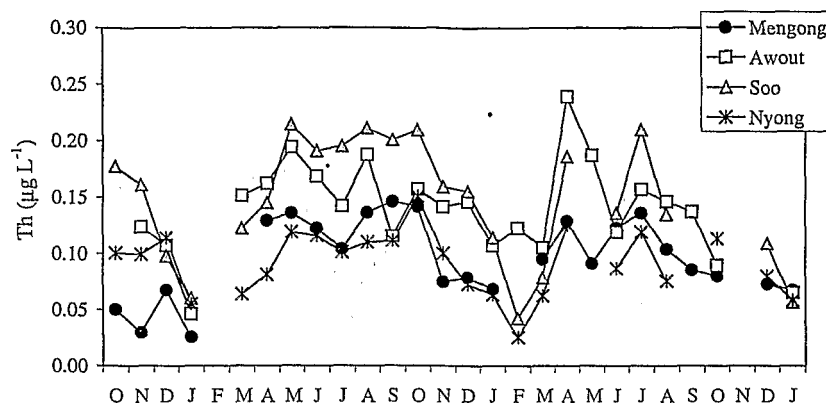
Fig. 7. Temporal variation of dissolved Th concentrations in the different rivers (Mengong, Awout, Soo, and Nyong).

between 45% and 65% of total Al, Fe, Mn, Co, and Zr. For the other elements (i.e., Y, REE, Th, and U), the dissolved load accounts for more than 70% of the total content. Generally, similar results are obtained for the Nyong River although the importance of the particulate load for Al, Fe, and REE for this river is higher compared to the Mengong River.

5. Discussion

5.1. Chemical weathering intensity

We have seen from several water samples of Mengong and Nyong rivers that the dissolved load (i.e., < 0.20 μm) dominates the total concentration (i.e., bulk water). Therefore, it can be concluded that the chemical weathering dominates over the physical (or mechanical) weathering in these environments. Consequently, the following discussion will mainly focus on the dissolved load.

The chemical composition of natural waters results from the contribution of several sources (soil/parent rock, vegetation, and atmosphere). To constrain the weathering term, we must correct the river water composition for the atmospheric contribution. From the knowledge of the geology of the Nyong basin, chloride has no bedrock source in the region because there are no evaporites and Cl content in granitoid rocks is very low (Garrels and MacKenzie, 1971). Thus, we can assume that the Cl content in river waters is entirely coming from the

atmosphere. Assuming the conservative behavior of this element, chloride normalization (Stallard and Edmond, 1981) can be used to correct the river water composition for atmospheric contribution and to estimate the intensity of chemical weathering. In Fig. 9 we show the normalized Na/Cl and Ca/Cl ratios $(X/Cl_{river\ water}/X/Cl_{rain\ water})$ for the whole set of rivers. The Na/Cl and Ca/Cl ratios in the rainwater (0.81 and 1.58, respectively) are the volume-weighted mean ratios of the local rainwater (wet deposits) measured by Freydier (1997) during our period of sampling (October 1996). The Nyong River sampling points (order V) exhibit normalized Na/Cl and Ca/Cl ratios close to 1 while the other rivers (order I, II, III, and IV) present distinctly higher ratios. This suggests that for the last rivers a significant fraction of Na and Ca can be attributed to chemical weathering of minerals constituting the soil and/or the parent rock of the basin. Fig. 9 also shows that Na/Cl and Ca/Cl ratios increase gradually with the decrease of the order of the river (watershed area). Because these rivers were sampled exactly at the same period, this result does not reflect seasonal variation. It should be interpreted therefore as a more efficient chemical weathering in the smaller watersheds compared to larger basins. This observation has an important consequence for the study of chemical weathering in tropical rivers. In the case of the Nyong River basin, consideration of only large tributaries would lead to an underestimation of chemical weathering intensity. Otherwise, in order to assess a geochemical signature that is truly representative of

Table 3
Element concentrations in the bulk waters (i.e., unfiltered waters) of some Mengong and Nyong samples

	Mengong											Nyong							
	Jul. 1995	Oct. 1995	Nov. 1995	Jan. 1996	Mar. 1996	Apr. 1996	May 1996	Aug. 1996	Sep. 1996	Dec. 1996	Jan. 1997	Jan. 1996	Feb. 1996	Mar. 1996	Apr. 1996	Jun. 1996	Aug. 1996	Dec. 1996	Jan. 1997
Al	433	626	428	415	361	511	342	379	372	348	578	404	208	448	729	836	235	445	379
Mn	7.2	22.3	7.9	4.4	18.7	16.5	12.3	9.9	11.4	17.7	25.0	34.3	26.1	47.0	38.7	36.4	28.7	57.3	35.9
Fe	671	762	457	603	406	331	407	685	598	723	797	1088	691	855	1320	1408	995	1779	1283
Co	0.19	0.43	0.22	0.15	0.33	0.36	0.32	0.32	0.33	0.33	0.39	0.59	0.33	0.46	0.55	0.52	0.35	0.93	0.51
Rb	0.23	2.45	0.36	0.60	1.29	0.97	0.39	0.37	0.39	0.42	0.84	1.53	3.95	7.51	4.89	3.87	2.24	3.25	2.30
Sr	13.15	19.72	16.50	15.58	24.44	19.54	19.78	19.02	20.02	16.12	16.60	11.61	15.23	16.96	13.18	12.92	12.70	12.61	12.57
Ba	16.05	25.73	20.80	18.17	26.19	24.28	23.58	23.43	24.63	20.02	19.29	19.31	17.33	27.73	25.29	23.18	20.27	23.06	22.46
Y	0.134	0.305	0.186	0.140	0.180	0.231	0.199	0.237	0.225	0.202	0.168	0.514	0.227	0.427	0.768	0.708	0.543	0.746	0.516
La	0.215	0.504	0.435	0.247	0.237	0.354	0.265	0.334	0.337	0.309	0.321	0.541	0.227	0.451	0.816	0.806	0.482	0.743	0.509
Ce	0.455	1.085	0.625	0.500	0.554	0.786	0.612	0.733	0.732	0.683	0.646	1.168	0.490	1.024	1.783	1.688	1.090	1.676	1.170
Pr	0.052	0.124	0.070	0.055	0.062	0.087	0.069	0.084	0.085	0.077	0.068	0.153	0.064	0.119	0.221	0.211	0.145	0.213	0.149
Nd	0.197	0.484	0.282	0.218	0.253	0.349	0.276	0.328	0.340	0.300	0.261	0.632	0.265	0.498	0.891	0.860	0.615	0.889	0.631
Sm	0.037	0.088	0.052	0.039	0.049	0.067	0.048	0.060	0.063	0.057	0.045	0.123	0.056	0.097	0.182	0.169	0.121	0.173	0.127
Dy	0.024	0.058	0.038	0.029	0.033	0.045	0.037	0.044	0.042	0.038	0.033	0.092	0.037	0.079	0.143	0.133	0.092	0.129	0.092
Er	0.013	0.032	0.019	0.015	0.019	0.024	0.020	0.025	0.043	0.022	0.019	0.053	0.023	0.045	0.082	0.076	0.058	0.077	0.054
Yb	0.014	0.029	0.017	0.016	0.015	0.019	0.016	0.021	0.021	0.019	0.017	0.046	0.020	0.042	0.074	0.071	0.052	0.069	0.050
Zr	0.568	0.948	0.599	0.660	0.437	0.782	0.477	1.036	0.737	0.621	0.892	0.510	0.247	0.395	1.089	1.240	0.413	0.740	0.510
Th	0.093	0.182	0.105	0.085	0.084	0.111	0.091	0.117	0.112	0.111	0.127	0.088	0.041	0.076	0.218	0.229	0.075	0.117	0.091
U	0.015	0.036	0.023	0.018	0.015	0.023	0.016	0.026	0.023	0.025	0.026	0.016	0.015	0.028	0.045	0.042	0.023	0.021	0.020
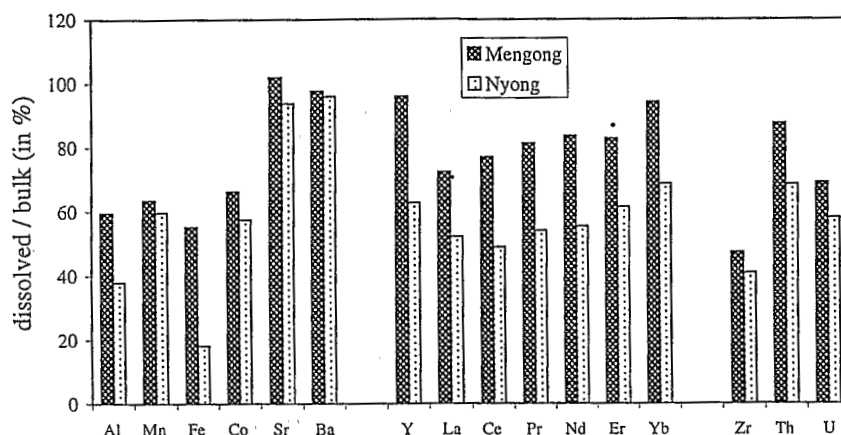
Fig. 8. Relative importance of the dissolved phase (i.e., < 0.20 μm) with respect to the bulk waters (i.e., unfiltered waters) in Mengong and Nyong rivers. The comparison is based on the averages of 10 samples (see text).

the chemical weathering for the whole basin area, one should take into account the contribution from rivers of different hydrologic orders.

5.2. Contribution of the lithology

From the comparison of the $^{87}Sr/^{86}Sr$ and element concentration ratios (e.g., Ca/Na, Mg/Na, and HCO_3/Na) for the rivers draining various monolithological watersheds (i.e., silicate, carbonate, and evaporite), the respective contribution of each lithol-
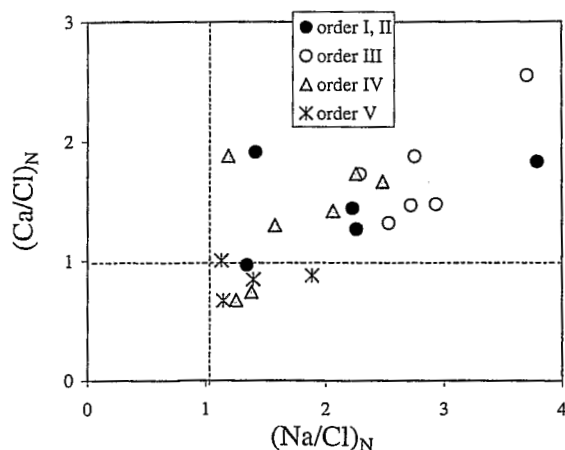
Fig. 9. Ca/Cl vs. Na/Cl ratios in the Nyong basin rivers. The ratios are normalized to the same ratios measured in local rainwater (Freydier, 1997).

ogy can be deciphered (Négrel et al., 1993; Gaillardet et al., 1999). Concentration ratios are rather used since they are more conservative than absolute concentrations, which are strongly dependent on dilution and evaporation processes. Bicarbonate content (HCO_3^-), which is usually used to quantify the weathering intensity (Bluth and Kump, 1994; Gislason et al., 1996), is not considered here because of the analytical difficulty in isolating HCO_3^- resulting from the decay of organic matter from HCO_3^- resulting from silicate weathering. All the ratios have been corrected from the atmospheric input using the following methodology:

$$X_{atm} = Cl_r (X/Cl)_{rw}$$

where X_{atm} is the percentage of element coming from the atmosphere, Cl_r is the chloride concentration in the river, and $(X/Cl)_{rw}$ is the ratio measured in the local rainwater (data in Freydier, 1997).

We have reported in Fig. 10 the Ca/Na vs. Mg/Na and Ca/Na vs. Sr/Na diagrams obtained for the river waters along with the silicate and carbonate end-members reported by Gaillardet et al. (1999). A close look at these diagrams clearly shows that the investigated set of rivers lays out of the silicate end-member. Moreover, the set of rivers seems to be located on a mixing line between the silicate and carbonate end-members although no evidence of carbonate formation was described in this area. The use of $^{87}Sr/^{86}Sr$ ratio is a good way to
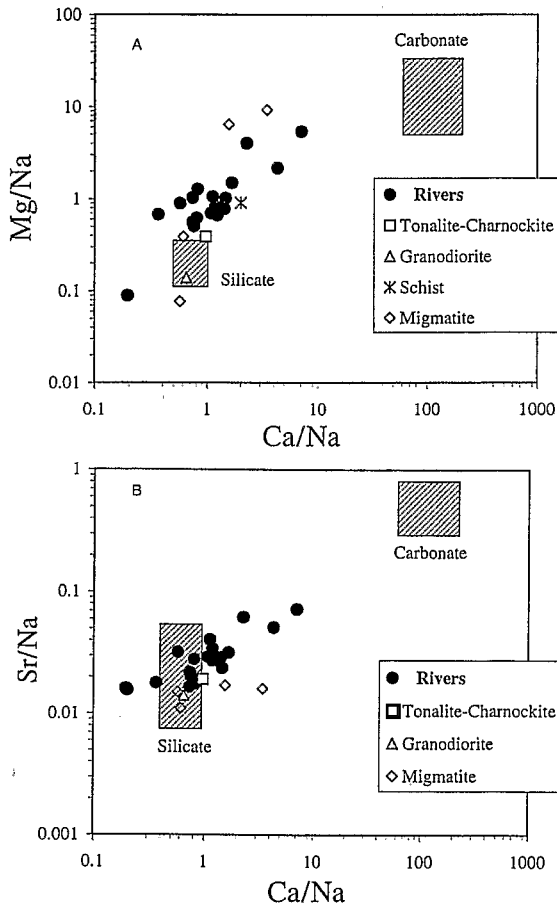
Fig. 10. Ca/Na mass ratios as a function of Mg/Na (A) and Sr/Na (B) mass ratios in the dissolved load (< 0.20 μm) of the Nyong basin rivers. Comparison with the corresponding ratios of the carbonate and silicate end-member as defined in Gaillardet et al. (1999), and of the main rock types of the Nyong basin (charnockite–tonalite: Nédélec et al., 1990; granodiorite: Nédélec, 1990; schist: Nédélec et al., 1986; migmatite: Barbey et al., 1990).

detect a possible contribution of carbonate. Indeed, an increasing contribution of carbonate rocks to the dissolved load of river waters results in an increase of the Ca/Na ratio while there is simultaneously a decrease of the $^{87}Sr/^{86}Sr$ ratio. We have reported in Fig. 11 the variation of the $^{87}Sr/^{86}Sr$ as a function of the Ca/Na in the various rivers of the Nyong basin. For comparison, the data for the Congo basin rivers (Négrel et al., 1993) have been reported on the same plot. The $^{87}Sr/^{86}Sr$ ratio of the Nyong basin rivers varies independently of their Ca/Na ratios contrary to the Congo basin case where carbonate rocks rep-

resent a significant source of solutes. This result indicates that the high Ca/Na ratio found in the Nyong basin rivers cannot be explained by a carbonate contribution. Therefore, the high Ca/Na ratio may result from lithological particularities of the Nyong watershed substratum. To check this hypothesis, the Ca/Na, Mg/Na and Sr/Na ratios of the main crystalline rocks of the Nyong basin have been plotted on Fig. 10 (data from Barbey et al., 1990; Nédélec et al., 1986, 1990; Nédélec, 1990). These specific rock compositions can explain why the Nyong basin river waters lay out of the silicate end-member defined by rivers draining homogeneous granitic rocks (Gaillardet et al., 1999). Note that this heterogeneity could be also provided by calcite veins, which are common in metamorphic formation. Besides, a recent work by White et al. (1999) points out the possible role of disseminated calcite in granitoid rocks to explain their high Ca/Na ratios. We think that contribution of calcite is not responsible for the observed heterogeneity. As also shown by White et al. (1999), calcite would contribute mainly in the former stage of fresh rock alteration when chemical weathering is highly selective. The basin is dominated by old weathering surface, where the most reactive minerals (e.g., plagioclase) have been depleted. So it is unlikely that the Ca/Na results from the selective and preferential dissolution of mineral(s)
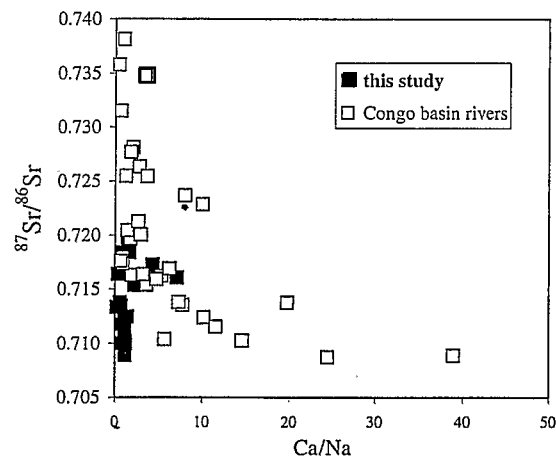
Fig. 11. A $^{87}Sr/^{86}Sr$ ratios as a function of the Ca/Na ratios in the dissolved load of the Nyong basin rivers. Comparison with the corresponding values measured by Négrel et al. (1993) for the Congo basin rivers.

like calcite. Therefore, we propose an alternative explanation to the fact that the Nyong rivers plot outside river ratio end-member as defined by Gaillardet et al. (1999) for the weathering of silica rocks. The Nyong river waters present pHs (4.5–6.5) that are very low compared to global river water chemistry. The weathering of mineral containing Ca, Sr, and Mg is more pH dependent than that of mineral containing Na (Gislason et al., 1996). The relatively low pH might account for the enhanced mobility of Ca, Mg, and Sr relative to that of Na in the Nyong basin rivers.

5.3. Sr isotopes

Another feature of the geochemistry of these rivers is the large variation in their Sr isotopic composition. On Fig. 12, which presents the isotopic composition of the dissolved Sr vs. Rb/Sr ratio, two main groups of rivers can be distinguished. The tributaries from the south define the first one, which exhibits both low $^{87}Sr/^{86}Sr$ and Rb/Sr ratios. These rivers drain the basin area underlained by gneiss, tonalites, and granodiorites of the Ntem complex. Within this set of rivers, those, which drain the gneissic formations, present lower $^{87}Sr/^{86}Sr$ ratios. The opposite tendency is obtained for the tributaries from the north, which drain micashists and migmatites of the Yaoundé series. The high $^{87}Sr/^{86}Sr$ ratios of these

waters are consistent with the high Rb/Sr ratios of their source rocks (see Barbey et al., 1990). However, three rivers (Mefou, Ossue-Bonva, and Nyong) lay out of these two domains. The Nyong River has intermediate isotopic composition since it is fed by a mixing of rivers with different isotopic characteristics. Ayos and Mbalmayo sampling points have a Sr isotopic ratio of 0.715 and 0.716, respectively. These high values result from the contribution of important tributaries coming from the north. Between Mbalmayo and Olama are the confluences of the major tributaries coming from the south (e.g., Soo, Fala, and Soumou), which induces a lower $^{87}Sr/^{86}Sr$ ratio at Olama. At Dehane, the $^{87}Sr/^{86}Sr$ ratio is higher than that measured upstream at Mbalmayo or Olama. This surprising result can be explained by the confluence, downstream Olama, of an important tributary from the north (i.e., Kelle) that was not sampled in the present study. The high Rb/Sr ratio of Mefou River must be due in part to an excess of anthropogenic Rb delivered by the city of Yaoundé and which obscured a pure lithologic signature.

The relationships obtained between Sr isotopic composition and major and trace (Na, Ca, Mg, Rb, and Sr) elements suggest that the large range of $^{87}Sr/^{86}Sr$ in the Nyong basin rivers is due to heterogeneous silicate basement. Recent works (Blum et al., 1994; Bullen et al., 1997; Blum and Erel, 1997)
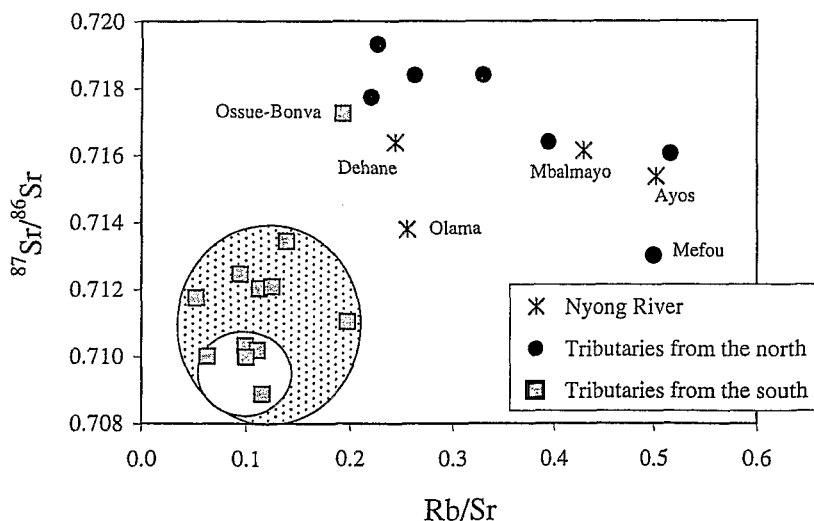
Fig. 12. Scatter diagram of $^{87}Sr/^{86}Sr$ vs. Rb/Sr for the whole set of rivers.

showed that the ^{87}Sr/^{86}Sr released by weathering of crystalline rocks does not necessarily reflect the bedrock value. Based on the study of a granitic glacial soil chronosequence, Blum and Erel (1997) demonstrated that the ^{87}Sr/^{86}Sr ratio of both the Sr exchangeable pool and the Sr soil digest vary with the age of the weathering surface. These ratios are higher in the youngest soil compared to the oldest soils in response to the different weathering rates of the bedrock-forming minerals. They reported also a difference of Sr isotopic value between the Sr exchangeable pool and the Sr soil digest, which is decreasing with increasing soil age. With regard to these results, the exact nature of the Sr carried by the draining rivers should be questioned; does it reflect exchangeable Sr (as in the study of Blum and Erel, 1997) or rather digest soil Sr? These last remarks enlighten the difficulty at getting at precise information about chemical weathering using solely the Sr isotopic composition of rivers and/or of whole rock or soil. In the case of the Nyong basin, the age of the weathering surface is very old, so it is likely that the Sr carried by rivers should reflect pretty well the Sr of the whole soil system. In accord with this, the higher Rb/Sr, ^{87}Sr/^{86}Sr ratios for the tributaries coming from the north can be explained by the higher abundance of micas and K-feldspars in the parent rocks for this area (i.e., migmatite, micashist, and schist). Indeed, these minerals are known for their high Rb/Sr and ^{87}Sr/^{86}Sr ratios (Douglas et al., 1995).

5.4. Element transport in the Nyong basin rivers

Section 4 showed that all the rivers sampled in the whole Nyong basin present similar ranges of concentration for DOC and major and trace elements. The main geochemical features of these surface waters are low major cation concentrations and high concentrations of some "insoluble" elements (e.g., Al, Fe, and Th), silica, and DOC.

To constrain more precisely the weathering mechanisms responsible for release into the solution and transport of these elements, we will focus on the monthly sampling database obtained for the Mengong, Awout, Soo, and Nyong rivers. Without extensive discussion of this database (see Ndam Ngoupayou, 1997; Viers, 1998), we will analyze the correlation coefficients (Pearson Product–Moment correlation) between each pair of elements in order to extract the most significant relationships.

Some elements (i.e., Al, Fe, Y, REE, and Th) exhibit a positive correlation with DOC (see Fe–DOC relationship in Fig. 5), suggesting a close association with organic matter (i.e., humic substances). Viers et al. (1997) and, more recently, Dupré et al. (1999) have demonstrated, by using ultrafiltration experiments on Mengong and Awout river waters, that these elements were entirely associated with organic colloidal material. However, one of the difficulties consist in distinguishing between two fractions of each element, one which is dissolved organo-metallic complexes and second which is adsorbed on mineral colloids or which constitutes the mineral colloids themselves. On top of that, natural organic matter and mineral colloids (e.g., clays and oxyhydroxides) are often intimately associated in natural waters (Sholkovitz, 1976; McKnight et al., 1992). Inspection of Fig. 5 reveals that the Fe–DOC correlation is higher in Mengong and Soo river waters compared to Awout and Nyong river waters. A higher proportion of metal associated with mineral colloids can explain the lesser correlation in Awout and Nyong rivers as shown in Dupré et al. (1999). This is consistent with the higher proportion of particulate matter, and consequently, mineral colloids in Nyong river waters compared to the Mengong river waters. Olivié-Lauquet et al. (1999) reach the same conclusion in a comparative study of the iron transport forms in Mengong and Nyong rivers using spectroscopic methods. These considerations suggest that the natural organic matter strongly enhances the mobility of some elements (i.e., Al, Fe, Th, Zr, Y, and REE) in the humid tropical environments.

Strong specific correlations between some elements were also observed in these river waters. As can be seen on Fig. 13, the dissolved concentrations of Al and Fe show a clear positive correlation. These two elements comprise the main secondary phases present in the soils of these tropical environments: kaolinite ($Al_2Si_2O_5OH_4$) and iron oxyhydroxides and oxides (goethite: FeOOH, hematite: Fe_2O_3). Because the Fe/Al ratio remains constant for the different rivers, it may be concluded that these two elements do not fractionate during their transport through the hydrographic network. In the same fig-
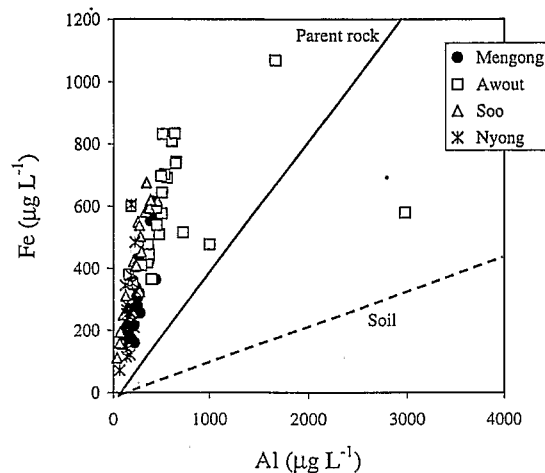
Fig. 13. Fe vs. Al relationship in the river waters (Mengong, Awout, Soo, and Nyong). Comparison between the same ratios in soils and rock parental samples collected in the Nsimi-Zoétélé watershed (Viers, 1998).

ure, average ratios of parent rocks and soils have been plotted for comparison. The Fe/Al ratio of the parent granitoid rocks is intermediate between those of waters and soils, which indicate a preferential Fe export ("mobility"); consequently, weathered soils are enriched in Al with respect to Fe. According to the recent work of Dupré et al. (1999) on these organic-rich natural waters, the enhanced mobility of Fe (with respect to Al) cannot be explained by a difference in the affinity between humic substances and these two elements. In our opinion, two different processes can account for this result. First is the remobilization of iron in the form of Fe^{2+} in reduced conditions arising from the decay of organic matter. The second process concerns aluminum precipitation in the form of new-formed kaolinite like it has been reported for soils of the Nsimi-Zoétélé (Oliva et al., 1999). Alternative mechanism, which can reduce Al mobilization, is the precipitation of gibbsite during kaolinite dissolution (Nahon, 1991; Tardy, 1993). However, only a trace of gibbsite has been found in the soil of the Nsimi-Zoétélé watershed (Viers, unpublished data).

Another important observation concerns lanthanum, thorium, and the rare-earth elements behavior. Fig. 14 shows the relationship between Al and La concentrations in Nyong basin rivers. The dissolved concentrations of La and Al exhibit a good

positive correlation in all the rivers. However, Soo and Nyong rivers present a La/Al ratio, which is significantly higher than that of the Mengong and Awout rivers. Among the factors responsible for this fractionation, pH variation must be considered since it is a master parameter controlling the speciation of elements, their degree of complexation by organic matter, and their adsorption onto particle surfaces. The average pH values are the highest for the Soo and Nyong rivers (about 0.5 unit pH). With the increase of pH, the percentage of neutral and negatively charged species of aluminum ($Al(OH)_3^0$, $Al(OH)_4^-$) increases (Castet et al., 1993), which can result in a lower complexation by organic ligands. Contrary to Al, the pH variation noted in our river waters should not influence the REE speciation since the trivalent species (REE^{3+}) dominates up to pH 9–10 for La (Deberdt et al., 1998). This difference in speciation and complexation by organic ligands may induce a higher La/Al ratio in the river waters having the higher pH.

5.5. Hydro-geochemistry functioning of the Nyong basin

The seasonal variations of the element concentrations in response to an increase of water discharge give indications on the mechanisms that control the
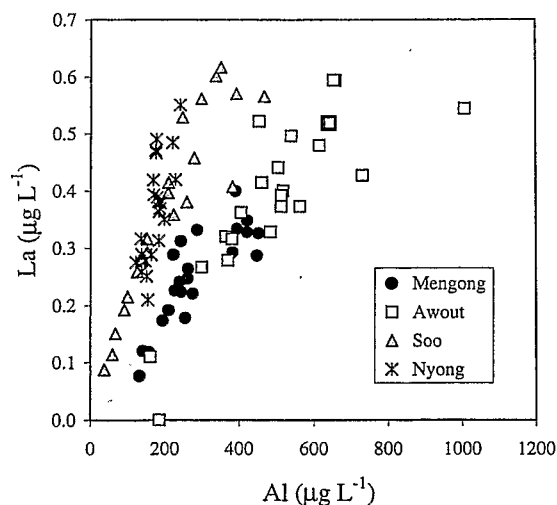
Fig. 14. La vs. Al relationships in the river waters (Mengong, Awout, Soo, and Nyong).

dissolved load of these rivers. In the Nyong basin rivers, dissolved concentrations increase during an increase of water discharge. In principle, this result can appear surprising since we may expect a dilution process by a higher flow of water. However, we must always keep in mind that there is no general rule to describe the variation of element concentrations in natural systems (Shafer et al., 1997; Shiller, 1997). The behavior of a given element in a watershed depends on several factors, which could be classified in two types. Firstly, there are the specific characteristics of the watershed (e.g., climate, hydrological pathways, vegetation, and size of the watershed). Secondly, there is the factors directly related to the elements and the mechanisms that control their release (e.g., differential breakdown of rock and/or soil minerals) and their transport into the solution (e.g., organic and inorganic complexation, and sorption onto mineral surfaces).

We will use an example of the Mengong brook watershed (also called Nsimi-Zoétélé), representative of the Nyong basin, in order to explain the geochemical and hydrological functioning of the whole Nyong basin. This catchment has been described as presenting a swamp zone where the high concentration of humic substances favors the dissolution of soil minerals (i.e., kaolinite, goethite, hematite, zircon, and rutile) by releasing protons and complexing elements (i.e., Al, Fe, Th, and Zr) (Viers et al., 1997; Oliva et al., 1999). These dissolution processes were confirmed by Oliva et al. (1999) who observed various weathered minerals (i.e., kaolinite, zircon, and rutile) using SEM microscopy. This explains the high dissolved concentration of some elements (i.e., Al, Fe, Th, Zr, and REE) in these river waters. Interestingly, Th or Zr that are generally considered as "invariant" in soil profiles and used as a reference to calculate exportation rates of elements can be very mobile for some organic-rich zones as demonstrated in this study.

Contrary to Al and Fe, we do not observe a positive correlation between silica and DOC. It implies that silica do not form complexes, at least in significant quantity, with humic substances in these surface waters. This is in good agreement with recent results of potentiometric titration of model solutions (Pokrovsky and Schott, 1998) and ultrafiltration experiments (Dupré et al., 1999). Silica concentration

$(8–21$ mg 1^{-1} $H_4SiO_4)$ is higher than quartz solubility $(9.6$ mg 1^{-1}, Walther and Helgeson, 1977). In studied watersheds, silica concentration is controlled both by dissolution of quartz grains and kaolinite and phytolythes (Alexandre et al., 1997).

Another important feature of studied rivers geochemistry is the very low concentrations of major cations. In the pilot site of Nsimi-Zoétélé, Oliva et al. (1999) did not find primary minerals (e.g., plagioclase) in the thick pedological cover that could deliver a large amount of major cations to the soil solutions.

Finally, the hydromorphic soils of the swamp constitute a pool of water rich in inorganic and organic compounds, which can be quickly mobilized ("flushed") during rain seasons. During periods of low base flow (i.e., dry seasons) the Mengong brook is mainly fed by organic-poor ground waters flooding the hill soils. In contrast, during high flow period the major source of waters is the swamp (Ndam Ngoupayou, 1997). The functioning of the Mengong watershed can be extended to the whole Nyong basin area since we have seen previously that rivers of higher importance (Awout, Soo, and Nyong) behave similarly than the Mengong River. In fact, the geochemical signature of large rivers is given by small tributaries, which drain swamp areas where chemical weathering mainly occurs.

5.6. Weathering regime

The geochemical features of the Nyong basin river waters are determined by two factors: firstly, chemical weathering operates mainly within a thick lateritic cover where primary and secondary minerals are cation-deficient, and secondly, the lateritic mantle prevents significant interactions between the fresh crystalline basement and the percolating waters. A recent study (Braun, personal communication) shows that the water in contact with the fresh rock at the weathering front do not participate strongly to the basin budget because of its high residence time. In such an environment, erosion regime is said to be *Transport-Limited* as defined by Stallard (1985) for the lowland shield of the Amazon basin or more recently by Gaillardet et al. (1995) for the Congo basin.

An increase of the chemical weathering in these environments would require a stronger interaction of

meteoric water with fresh materials. For two reasons, it seems unlikely that chemical weathering will change in the near future. Firstly, the Nyong basin belongs to the Congo craton, which is tectonically very stable. Secondly, the basin is completely covered by rain forest that stabilizes the thick pedological cover and thus minimizes the mechanical erosion. The absence of physical erosion prevents the creation of new contact surfaces between water and fresh minerals. Therefore, although the chemical weathering in these environments is potentially high (high temperature and precipitation), it is strongly restricted due to thick soil and vegetation and lack of tectonic uplift. Finally, in the humid tropical environments of south Cameroon, chemical weathering appears to be controlled by historical and geomorphologic parameters rather than by present-day climatic parameters. Even if natural organic matter favors mineral dissolution in the swamp zones of the Nyong basin, chemical weathering is low compared to other regions in the world.

6. Conclusion

(1) The study of river waters collected at the same time shows us that there is a progressive increase of the present day chemical weathering intensity with the decrease of the watershed drainage area. This result requires careful estimation of the hydrological parameters for the chemical weathering studies based on the river waters chemistry. The high Ca/Na ratio and the wide range of $^{87}Sr/^{86}Sr$ ratio measured in the Nyong basin rivers does not reveal a significant carbonate contribution but originates from the heterogeneity of the basement crystalline rocks. This result should be kept in mind in studies that use defined silicate end-member to decipher the lithologic contribution in the composition of river waters.

(2) Chemical weathering mainly occurs in swamp zones where organic matter favors mineral dissolution. The dissolved load of these waters (high contents of silica and insoluble elements and low contents of soluble elements) is explained by the weathering of the thick lateritic cover constituted by cation-depleted phases (i.e., quartz, clays, and oxyhydroxides). The same seasonal variations observed in rivers with different drainage surfaces indicate that the main chemical weathering mechanisms identified in small watersheds can be generalized for the whole Nyong basin.

(3) Finally, high rainfall and high temperature are not the major factors controlling chemical weathering. Local parameters such as soil thickness and vegetative cover are more important than present day climatic parameters.

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