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Chapter 7

Geochemical cycling of trace and rare earth elements in Lake Tanganyika and its major tributaries

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Abstract

Fe and Mn and light rare earth elements (LREE) were used to evaluate the biogeochemical factors affecting trace element distribution and cycling in Lake Tanganyika, East Africa. Dissolved trace elements were measured in samples from the lake and its three major tributaries (the Ruzizi, Malagarasi and Lufubu rivers) by ICP-MS. The river waters were relatively trace element—and REE—enriched compared to the lake waters. Ce-anomalies varied among the rivers and within the lake. Normalized REE patterns of the lake waters to the average upper continental crust were more similar to those of the Ruzizi River, which might be due to the relatively high pH values in the two systems. Hydrodynamics, Fe, and Mn coating and biogenic activity appeared to be the major biogeochemical factors that affect horizontal distribution of trace elements in the lake. Vertical fractionation of LREE was greater in the Southern Basin than the Northern Basin. The high-trace element and REE concentrations near the surface in the Southern Basin might be due to upwelling in this basin during the dry season. The coincidence of Ce/Ce* and $\mathrm{Sm_{UCC}/Yb_{UCC}}$ maxima with those of Fe and Mn (60 m) suggested that Fe- and Mn-oxyhydroxides were responsible for the vertical distribution of trace elements in Lake Tanganyika. The occurrence of nutrient profile minima at 60 m also suggested that trace elements and LREE cycling may be enhanced by bacterial reduction process. This study highlighted the importance of riverine inputs, Fe, Mn and LREE geochemistry and hydrodynamics in spatial abundance, and cycling of trace elements across Lake Tanganyika.

7.1. Introduction

The cycling and distribution of trace elements in lacustrine systems are a function of various geochemical and biological processes, which are governed by environmental factors such as pH, dissolved oxygen contents (DO), nutrient availability and the extent of vertical mixing (Heaney et al., 1986). Because of the disproportional distribution of nutrients, DO and spatial variations in hydrodynamics (e.g., wind strength), the distribution of certain trace elements is likely to vary across large and semi-productive tropical lakes such as Lake Tanganyika. Although a large dataset of dissolved major element geochemistry of the lake and its main tributaries is available (e.g., Plisnier, 1996; Langenberg et al., 2003), those on dissolved trace elements are scarce. The data presented in this paper may therefore contribute to the assessment of the factors that govern dissolved trace element cycling and distribution in Lake Tanganyika.

The geochemical composition of rivers is the primary source of trace element loadings into large waterbodies, such as lakes and oceans (e.g., Garrels and Mackenzie, 1971; Meybeck, 1987). To better understand the processes that control the chemical composition of lakes, an investigation of the geochemical continuity between lakes and rivers is therefore needed. Fe and Mn play a crucial role in controlling trace element distribution in freshwater systems, as riverine dissolved trace elements are generally associated with organically stable Fe- and Mn-oxyhydroxides (Hoyle et al., 1984). Although at river mouths the behavior of Fe and Mn may be altered, following variations in DO and pH, Fe and Mn may allow an accurate evaluation of changes in trace element distribution and their fate after mixing with lake waters (Haberyan and Hecky, 1987; Green et al., 1989).

Furthermore, the vertical distribution of lacustrine trace elements is a function of the oxidative states of Fe and Mn (Haberyan and Hecky, 1987; Viollier et al., 1995; De Carlo and Green, 2002). Because of high DO contents at epilimnion, Fe and Mn may precipitate as oxyhydroxides upon their entry to lakes and sink. As a result, the surface water is generally depleted in dissolved Fe and Mn (e.g., Viollier et al., 1995; Coffey et al., 1997). A subsequent increase in organic matter decompositions with depth may follow, leading to a substantial decrease in pH and DO and reductions of Fe(III) to Fe(II) and Mn(IV) to Mn(II) (De Carlo and Green, 2002). Fe and Mn redox reactions are then accompanied by the release of previously coated trace elements into the water column, resulting in a considerable increase in dissolved Fe(II), Mn(II) and other trace elements with depth (Viollier et al., 1995; De Carlo and Green, 2002).

REE behave in a coherent and predictable manner in natural environments, and they have been used to investigate mixing between various water sources (e.g., Sholkovitz, 1993; Johannesson et al., 1997; Elbaz-Poulichet and Dupuy, 1999; Barrat et al., 2000). Like other trace elements, REE tend to be adsorbed onto the surface sites of clay and organic particles (Byrne and Kim, 1990; Atsuyuki and Kawabe, 2001; Shan et al., 2002). However, their affinity for these ligands is mainly dependent on the decreasing pattern of their ionic radii from LREE to HREE. Hence, HREE, with smaller ionic radii, and which are relatively compatible with organic and inorganic ligands, are less susceptible to adsorption onto oxyhydroxides and are more resistant to scavenging than LREE (Aagaard, 1974; Johannesson et al., 1996). Owing to these unique characteristics, the normalized REE patterns in natural waters compared to their average upper continental crust (UCC) (Taylor and McLennan, 1985) compositions commonly show HREE-enrichment relative to LREE. Dissolved Fe, Mn and LREE, which are non-conservative elements in most aquatic systems, can therefore be used to study the fate and behavior of riverine trace elements in an adjacent lacustrine environment (Webster, 1993; De Carlo and Green, 2002).

The objectives of this study are therefore to (1) use dissolved Fe, Mn and LREE concentrations to investigate the fate and behavior of trace elements from the Ruzizi, Malagarasi and Lufubu rivers coming into Lake Tanganyika; (2) evaluate surface distributions of trace elements in different sub-basins of the lake and (3) study the vertical cycling of trace elements in the Kigoma and Mpulungu sub-basins.

7.2. Hydrogeological setting

Lake Tanganyika, located in the Western Branch of the East African Rift Valley, is the second deepest lake (maximum depth of 1470 m) in the world after Lake Baïkal (Coulter and Spigel, 1991). The lake is 50 km wide and approximately 650 km long in a north–south direction. Lake Tanganyika has a total surface area of 34,000 km^2 and a water volume of 18,880 km^3. The bottom waters of the lake are divided into Northern and Southern basins by a naturally occurring sill of 600 m depth and several sub-basins by minor sills (Tiercelin and Mondeguer, 1991). The annual inflow of Lake Tanganyika is estimated to be 53 cm cm^{-2} lake surface, whereas the difference between its annual evaporation and outflow is 127 cm cm^{-2} lake surface (Haberyan and Hecky, 1987).

Although the thermal stratification varies seasonally from one basin to another, Lake Tanganyika has been classified as a meromictic lake with a thermocline depth varying between 50 m and 80 m in the Northern Basin and up to 150 m in the Southern Basin (Coulter and Spigel, 1991). The

Southern Basin is characterized by a deeper oxycline (*ca.* 250 m) than the Northern Basin (*ca.* 100 m; Tiercelin and Mondeguer, 1991).

Three major rivers, the Malagarasi, Ruzizi and the Lufubu, contribute to the lake recharge. The Lukuga River, which flows into the Congo River and later into the Atlantic Ocean, is the only outlet from Lake Tanganyika. The temperature of the Malagarasi and Lufubu river waters at their mouths is similar to the surface water of the lake (26.5–28.1°C), and thus their waters mix with the lake water. In contrast, the Ruzizi River water is generally denser (i.e., high-sediment loading) than the surface water of the lake, and does not immediately mix with the lake water (Hecky et al., 1991). The Malagarasi River has the greatest annual flow (*ca.* $300\,m^3\,s^{-1}$; Langenberg et al., 2003), followed by the Ruzizi River (*ca.* $200\,m^3\,s^{-1}$; Devroey, 1954; Cazenave-Piarrot, 1981) and Lufubu rivers (*ca.* $100\,m^3\,s^{-1}$; Sichingabula, 1999).

7.3. Materials and methods

7.3.1. Water sampling

Fourteen surface water samples were collected at the mouths of the three rivers and upstream. Samples were collected once in the rainy and once in the dry season (2003). Because of the large size of the lake, twenty water samples were collected inshore and offshore of four sub-basins (Bujumbura, Kigoma, Moba and Mpulungu sub-basins). The Northern and Southern basins of the lake are characterized by different hydrodynamics, and thus replicate profile samples were collected in the Northern (the Kigoma Sub-basin) and Southern basins (the Mpulungu Sub-basin; Fig. 7.1), respectively.

Surface waters were directly filtered (0.45-μm membrane pore diameter) by a hand pump into pre-acid-washed polyethylene bottles. The tubing system was thoroughly flushed with lake or river waters between samples. Profile samples were collected by a conductivity–temperature–depth (CTD) meter. One sample from each profile was transferred into a clean, pre-acidified polyethylene container, and a portion was filtered and acidified (pH 2). The sampling was carried out under ultra-trace element conditions (Patterson and Settle, 1976). Thus, plastic gloves were worn through out the sampling, and contact with metallic tools was minimized. Samples were subsequently stored in double-zip loc bags.

7.3.2. Water analysis

Cadmium reduction and ascorbic acid methods were used to measure nitrate (NO_3^-) and orthophosphate (PO_4^{3-}) concentrations on the filtered

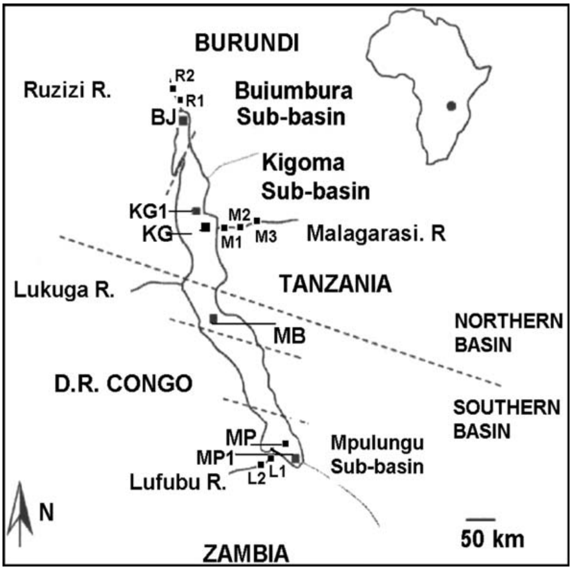

Figure 7.1. Schematic map of Lake Tanganyika, showing the sampling sites; BJ and MB stand for the Bujumbura and Moba sub-basins, whereas KG and MP are profile samples from the Kigoma and Mpulungu sub-basins, respectively.

water samples, using spectrophotometry (Hach DR/2000), whereas pH was measured by a portable Hach pH meter. The analytical precision for the methods was $\pm 0.01\,\mathrm{mg\,l^{-1}}$.

The Finnigan Element 2 high-resolution inductively coupled plasma mass spectrometry HR-ICP-MS was used to analyze dissolved trace element and REE concentrations in the laboratory of Isotope and Trace Element Research (LITER) at Old Dominion University, Virginia, without further treatment. The following isotopes were used to control isobaric interferences on REE concentrations: ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{167}Er, ^{169}Tm, ^{172}Yb and ^{175}Lu. A four-point calibration was used to determine concentrations of trace elements and REE ranging 1–10 ppb for Fe, Mn, Cu, Cd and Zn, 2–200 ppt for Pb and 2–20 ppt for Th, Y and REE. ^{115}In was used as an internal standard to mitigate instrument drift and analyte loss during the analysis (Graham et al., 1996). A blank (i.e., 1% HNO_3) and control standard was run every eight samples, and the blank data were used to calculate instrument detection limits (Vandecasteel and Block, 1993). Relative standard deviations (RSD), based on triplicate analysis, were better than 10% for most elements except for Fe (RSD = 17.49%) and Yb (RSD = 15.52%).

HR-ICP-MS was also successfully used to analyze dissolved riverine and lacustrine Na (RSD = 3.08%), Ca (5.12%) and Mg (4.63%) concentrations. DO, temperature, pH, conductivity and nutrient profiles, measured in the Kigoma Sub-basin in the dry season in 2002 (Sako, unpublished data), were also used in the present study to illustrate their decreasing behavior with depth.

7.3.3. Multivariate analysis

Factor analysis, one of the multivariate methods used in hydrogeochemical studies to investigate inter-relationships between several variables (elements), is a useful technique for reducing a dataset that contains several variables to a few interpretable factors (Reeder et al., 1972; Ruiz et al., 1990; Simeonov et al., 2000). To gain insight into the horizontal distribution of trace elements across the lake, samples collected from the Bujumbura and Kigoma sub-basins during the two sampling periods were categorized as the Northern Basin samples ($n = 10$), whereas those from Moba and Mpulungu sub-basins were treated as the Southern Basin ($n = 10$). Log_e-transformed concentrations of nine trace elements (Cu, Rb, Ba, V, Sr, Zn, Pb, Cd and U) were normally distributed, and consequently these elements were used in the factor analysis test. The test was performed using Minitab version 12.21 (Minitab Inc, 1998).

Varimax rotation, which maximizes the variance of the squared factor loadings, increased the data interpretability (Kaiser, 1958), and was selected to rotate the data; principle component analysis was chosen as the extraction method. The initial extraction yielded nine possible factors, which proved difficult to interpret. However, 96–97% of the total variability for both basins was explained by the first four factors. Although Eigen values for factors 3 and 4 were relatively low (<1.0), each of these factors accounted for about 12% of the total variance, and were therefore used for further analysis. Furthermore, the communality for factors 1, 2, 3 and 4 was close to 100%, suggesting that the variance of each element is well described by these factors, and the elimination of the five factors did not cause a significant loss of information (Drever, 1997).

7.4. Results

7.4.1. Riverine trace elements and REE abundance

The Lufubu River represented the highest average dissolved Fe and the lowest Mn concentrations among the three rivers followed by the

Table 7.1. Dissolved major, trace element and REE concentrations in the Ruzizi River

Elements	DL	R1-R	R2-R	Mean	R1-D	R2-D	Mean
Na (ppm)	0.01	55.18	53.23	54.21	79.70	82.79	81.24
Mg (ppm)	0.00	40.41	40.27	40.34	57.27	62.35	40.34
Ca (ppm)	0.00	7.50	5.23	6.36	7.00	7.50	7.29
Cd (ppb)	0.00	0.02	0.02	0.02	0.01	0.01	0.01
V (ppt)	0.34	2470.96	685.96	1578.46	678.11	2743.18	1710.65
Mn (ppb)	0.00	1.94	6.69	4.31	9.68	0.52	5.10
Fe (ppb)	0.00	10.21	116.00	63.10	2.04	1.05	1.54
Cu (ppb)	0.00	14.94	1.21	8.07	1.07	1.05	1.06
Zn (ppb)	0.01	23.72	4.49	14.11	0.66	0.21	0.44
La (ppt)	0.00	117.32	24.40	70.86	34.39	43.48	38.94
Ce (ppt)	0.00	210.74	30.81	120.78	32.58	43.55	38.06
Pr (ppt)	0.01	16.87	4.09	10.48	5.71	7.19	6.45
Nd (ppt)	0.01	6.31	36.01	21.16	15.00	18.74	16.87
Sm (ppt)	0.09	5.42	6.02	5.72	4.23	5.34	4.78
Gd (ppt)	0.22	3.27	4.29	3.78	4.95	6.28	5.61
Tb (ppt)	0.02	1.52	1.64	1.58	2.37	2.88	2.62
Dy (ppt)	0.15	8.27	7.24	7.75	13.74	16.17	14.95
Ho (ppt)	0.01	2.21	1.59	1.90	3.76	5.00	4.38
Er (ppt)	0.15	7.30	4.37	5.83	12.59	14.39	13.49
Tm (ppt)	0.03	1.20	0.70	0.95	1.83	2.19	13.49
Yb (ppt)	0.25	8.32	3.69	6.01	10.74	12.81	11.77
Lu (ppt)	0.03	1.15	0.67	0.91	1.74	2.11	1.92
ΣREE		423.81	129.72	276.77	143.61	180.13	161.87
Y (ppt)	0.01	64.31	41.52	52.91	66.01	76.31	71.16
Ce/Ce*		1.05	0.69	0.87	0.52	0.55	0.54
(La/Yb)$_{UCC}$		1.03	0.48	0.87	0.52	0.55	0.54
(La/Sm)$_{UCC}$		2.06	0.29	1.18	0.40	0.40	0.40
(Gd/Yb)$_{UCC}$		0.23	0.67	0.45	0.27	0.28	0.27
(Er/Nd)$_{UCC}$		2.05	4.81	3.34	9.48	8.67	9.07
(Sm/Yb)$_{UCC}$		0.50	1.65	1.08	0.59	0.62	0.60

Note: DL, Detection limit.

R1 and R2 are samples collected at the Ruzizi River mouth and upstream, respectively. R and D stand for rainy and dry seasons.

Ce/Ce* = $(Ce_{wat}/Ce_{UCC})/[(La_{wat}/La_{UCC})^{0.5} X (Pr_{wat}/Pr_{UCC})^{0.5}]$.

REE ratios (e.g., (La/Yb) = $(La_{wat}/LaUCC)/(Yb_{wat}/Yb_{UCC})$ are normalized to upper continental crust (UCC, Taylor and McLennan, 1985).

Malagarasi and then the Ruzizi (Tables 7.1–7.3). The highest Mn concentrations were found in the Malagarasi and Ruzizi rivers. The average Cd concentrations were slightly greater in the Malagarasi River (Table 7.2) compared to the Lufubu and Ruzizi rivers. As with the other trace elements, the dissolved V concentrations showed significant variations among the three rivers, with the highest concentrations in the Ruzizi River (Tables 7.1–7.3).

Table 7.2. Dissolved major, trace element and REE concentrations in the Malagarasi River

Elements	M1-R	M2-R	M3-R	Mean	M1-D	M2-D	M3-D	Mean
Na (ppm)	24.80	8.67	8.41	13.96	8.41	12.75	12.93	11.336
Mg (ppm)	18.52	7.11	6.52	10.72	6.52	10.11	9.92	8.85
Ca (ppm)	7.26	10.27	9.08	8.87	9.08	11.95	12.65	11.23
Cd (ppb)	7.05	0.22	0.18	2.48	0.01	0.01	0.40	0.14
V (ppt)	571.48	602.21	631.18	601.62	2854.36	747.00	690.79	1430.72
Mn (ppb)	3.40	9.39	7.74	6.84	0.95	9.83	10.77	7.18
Fe (ppb)	62.56	86.07	123.31	90.65	1.37	2.00	1.52	1.63
Cu (ppb)	1.91	4.06	2.64	2.87	1.37	0.82	0.61	0.93
Zn (ppb)	16.43	39.53	29.56	28.51	0.25	1.07	0.23	0.52
SiO_2 (ppm)	7.02	6.97	6.89	6.96	n.d	n.d	n.d	n.d
T (°C)	26.90	27.70	27.20	27.27	n.d	n.d	n.d	n.d
pH	8.36	8.35	8.30	8.34	n.d	n.d	n.d	n.d
DO (ppm)	7.48	6.80	7.18	7.15	n.d	n.d	n.d	n.d
La (ppt)	22.87	39.65	50.16	37.56	10.19	9.86	5.96	8.67
Ce (ppt)	31.28	51.94	70.73	51.32	12.92	11.62	5.87	10.14
Pr (ppt)	2.73	5.28	6.53	4.85	1.27	1.23	0.72	1.07
Nd (ppt)	6.41	12.43	15.25	11.36	3.18	3.09	2.00	2.76
Sm (ppt)	1.82	3.07	3.96	2.95	0.84	0.96	0.59	0.80
Gd (ppt)	12.13	3.37	4.45	3.32	0.95	1.18	0.71	0.94
Tb (ppt)	0.77	1.37	1.57	1.24	0.34	0.36	0.27	0.32
Dy (ppt)	3.66	6.30	6.84	5.60	1.77	1.68	1.44	1.63
Ho (ppt)	1.55	1.40	2.30	1.75	0.41	0.36	0.27	0.32
Er (ppt)	6.52	3.94	7.92	6.13	1.20	1.21	1.14	1.19
Tm (ppt)	0.52	0.59	0.68	0.60	0.20	0.16	0.13	0.16
Yb (ppt)	9.11	3.29	9.67	7.36	0.99	1.06	0.85	0.97
Lu (ppt)	0.90	0.55	1.04	0.83	0.16	0.16	0.14	0.15
ΣREE	90.29	133.19	181.11	134.87	34.42	32.97	20.21	29.20
Y (ppt)	16.57	16.20	17.03	16.60	6.14	5.84	5.42	5.80
Ce/Ce*	0.85	0.79	0.85	0.83	0.78	0.72	0.61	0.70
$(La/Yb)_{UCC}$	0.18	0.88	0.38	0.48	0.76	0.68	0.51	0.65
$(La/Sm)_{UCC}$	0.72	0.61	0.64	0.66	0.59	0.54	0.50	0.54
$(Gd/Yb)_{UCC}$	0.14	0.59	0.27	0.33	0.55	0.64	0.48	0.56
$(Er/Nd)_{UCC}$	11.49	3.57	5.87	6.97	4.27	4.44	6.45	5.05
$(Sm/Yb)_{UCC}$	0.26	1.45	0.59	0.77	0.27	1.26	1.03	1.19

Note: M1, M2 and M3 are samples collected at the Malagarsi River mouth, 500m and 1000m upstream, respectively. n.d not determined.

The average total REE concentrations (ΣREE) were higher in the Lufubu River than the two other rivers (Tables 7.1–7.3). Although the Ruzizi and Malagarasi rivers showed the same seasonal variation patterns in their REE concentrations, the average seasonal ΣREE were higher in the Ruzizi River compared to the Malagarasi River. Whereas the average dissolved Y concentrations were comparable between the Ruzizi and

Table 7.3. Dissolved major, trace element and REE concentrations in the Lufubu River

Elements	L1-R	L2-R	Mean	L1-D	L2-D	Mean
Na (ppm)	3.31	3.21	3.26	3.03	2.95	2.99
Mg (ppm)	0.56	0.45	0.50	0.58	0.58	0.58
Ca (ppm)	1.04	1.30	1.17	1.34	1.34	1.34
Cd (ppb)	0.23	0.18	0.20	0.02	0.03	0.02
V (ppt)	238.08	195.41	216.75	158.69	159.52	159.11
Mn (ppb)	1.89	0.87	1.38	3.52	3.47	3.50
Fe (ppb)	129.98	94.75	112.36	100.09	97.74	98.91
Cu (ppb)	3.82	3.09	3.46	1.81	1.71	1.76
Zn (ppb)	44.80	31.82	38.31	7.98	8.56	8.27
SiO_2 (ppm)	6.22	0.95	3.58	1.081	1.53	1.31
pH	7.83	7.35	7.59	8.88	8.93	8.91
T (°C)	28.00	28.00	28.00	24.60	22.90	23.75
La (ppt)	419.12	371.06	395.09	416.41	440.53	428.47
Ce (ppt)	412.98	421.21	417.10	216.76	230.72	223.74
Pr (ppt)	41.22	42.53	41.87	20.70	21.89	21.29
Nd (ppt)	92.08	94.21	93.14	10.07	10.64	10.36
Sm (ppt)	21.04	17.79	19.41	10.07	10.64	10.36
Gd (ppt)	22.07	16.27	19.17	10.47	11.05	10.76
Tb (ppt)	7.47	5.40	6.44	3.54	3.76	3.65
Dy (ppt)	32.61	23.62	28.12	15.58	16.84	16.21
Ho (ppt)	7.46	5.40	6.43	3.42	3.67	3.55
Er (ppt)	21.49	15.53	18.51	9.46	10.03	9.74
Tm (ppt)	3.06	2.29	2.67	1.47	1.50	1.49
Yb (ppt)	17.46	12.71	15.09	8.44	9.05	8.74
Lu (ppt)	2.73	1.95	2.34	1.21	1.31	1.26
Sum REE	1100.79	1029.98	1065.39	762.26	808.31	785.29
Y (ppt)	84.10	61.26	72.68	36.07	38.08	37.07
Ce/Ce*	0.65	0.72	0.68	0.40	0.41	0.40
$(La/Yb)_{UCC}$	1.76	2.14	1.95	3.62	3.57	3.59
$(La/Sm)_{UCC}$	1.02	2.89	1.95	2.09	2.11	2.10
$(Gd/Yb)_{UCC}$	0.73	0.74	0.74	0.67	0.71	0.69
$(Er/Nd)_{UCC}$	2.63	1.86	2.24	2.38	2.39	2.38
$(Sm/Yb)_{UCC}$	1.72	1.75	1.74	1.74	1.69	1.71

Note: L1 and L2 are the samples collected at the Ruzizi mouth and 500m upstream. R and D stand for rainy and dry seasons, respectively.

Lufubu rivers for both sampling periods, they were considerably lower in the Malagarasi River (Tables 7.1–7.3).

A small positive Ce-anomaly ($Ce/Ce^* = 1.05$) was observed at the Ruzizi River mouth during the rainy season, whereas a substantial negative anomaly occurred upstream ($Ce/Ce^* = 0.69$). The Ce/Ce^* values were similar within the Ruzizi River during the dry season (0.52 and 0.55). The Malagarasi River exhibited the lowest negative Ce-anomalies

($0.60 < Ce/Ce^* < 0.85$), without a significant seasonal variation. The highest negative Ce-anomalies occurred in the Lufubu River, which decreased in the rainy season samples (Table 7.3).

With the exception of its mouth ($La_{UCC}/Yb_{UCC} = 1.05$), the Ruzizi River showed HREE-enrichment (La_{UCC}/Yb_{UCC} ratios ranged from 0.23 to 0.48). Likewise, the Malagarasi River samples were HREE-enriched relative to LREE (La_{UCC}/Yb_{UCC} ratios ranged from 0.18 to 0.88; Figs. 7.2 and 7.3). In contrast to the two northern rivers, the Lufubu River showed LREE-enrichment (La_{UCC}/Yb_{UCC} ratios ranged from 1.76 to 3.62). However, Er_{UCC}/Nd_{UCC} values for the three rivers were greater than unity, suggesting that La concentrations were exceptionally high in certain samples (particularly in the Lufubu River samples). All samples showed HREE-enrichment relative to the middle REE (MREE; Sm to Dy) with $Gd_{UCC}/Yb_{UCC} < 1$.

7.4.2. *Surface trace elements and REE distribution in the Lake*

Surface trace elements and REE concentrations of Lake Tanganyika are presented in Tables 7.4–7.7. Elements such as Fe, Mn, Th, Ba, Cd, Zn and Pb fluctuated widely across the lake, whereas Sr, Rb, to a lesser extent, U and V were constant. Finally, the average U/Sr values for different the sub-basins were: $3.18 \pm 0.21 \times 10^{-3}$ (Bujumbura), $2.93 \pm 0.19 \times 10^{-3}$ (Kigoma), $2.87 \pm 0.23 \times 10^{-3}$ (Moba) and $2.69 \pm 0.16 \times 10^{-3}$ (Mpulungu).

7.4.2.1. Factors controlling horizontal distribution of trace elements in the lake

The factor analysis test, performed on surface waters, identified four dominant factors that may explain the distribution and behavior of Cu, Rb, Ba, V, Sr, Zn, Pb, Cd and U across the lake (Tables 7.8 and 7.9). Factor 1, which accounted for 44% and 54% of the total variability in the Northern and Southern basins, respectively, was characterized by high-positive loading coefficients for Ba, V, Sr and U and a moderate negative loading for Zn (55%) in the Northern Basin, and high-positive loading coefficients for Rb, Ba, V, Sr and U in the Southern Basin. Factor 1 also showed moderate positive loadings for Pb (47%) in the Northern Basin and Cd (35%) in the Southern Basin. Factor 2 accounted for 26% and 19% of the total variability in the Northern and Southern basins, respectively, with high-negative loading coefficients for Cu, Rb and Zn in the Northern Basin and high-positive loading coefficients for Cu and Pb in the Southern Basin. Factor 3 had a significant influence on Pb concentrations in the Northern Basin, whereas Cd was most affected by factor 3 in the Southern Basin. Factor 4, which only accounted for 12%

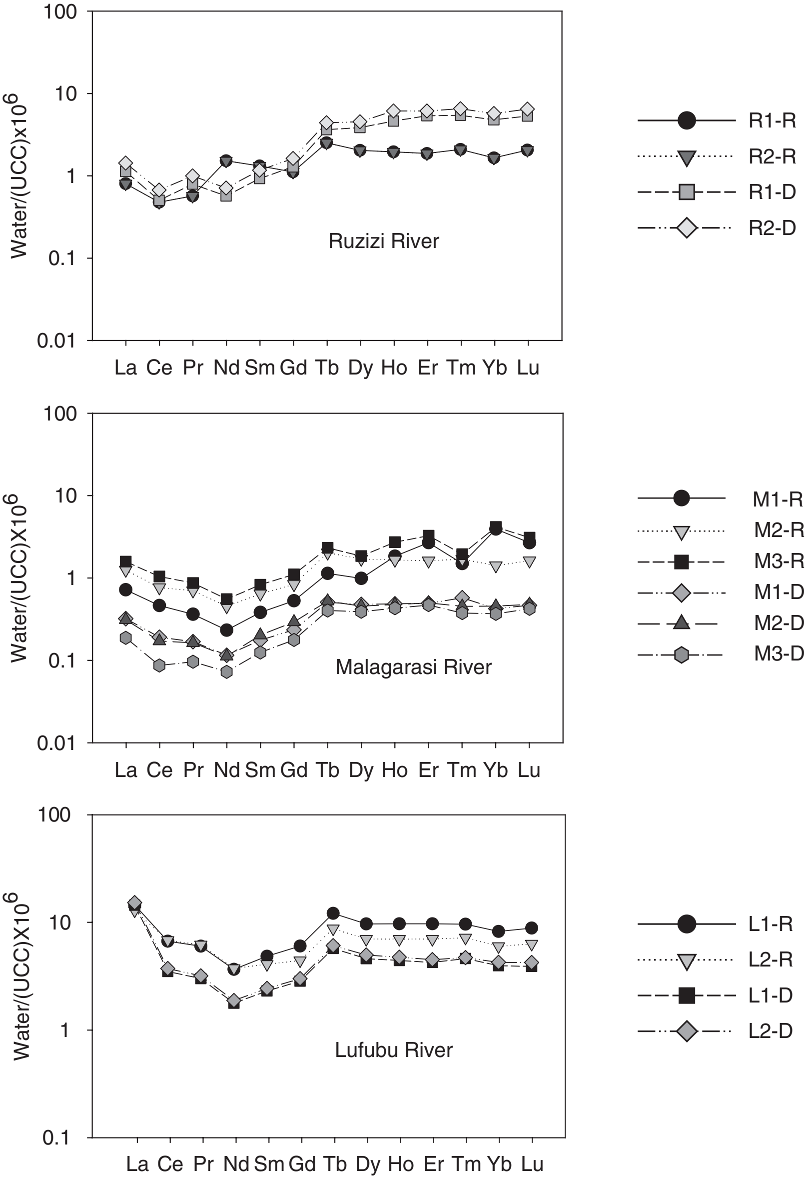

Figure 7.2. UCC-normalized riverine REE patterns. 1, 2 and 3 stand for river mouth, at 500 m and 1000 m upstream, respectively. R&D represents the rainy and dry seasons.

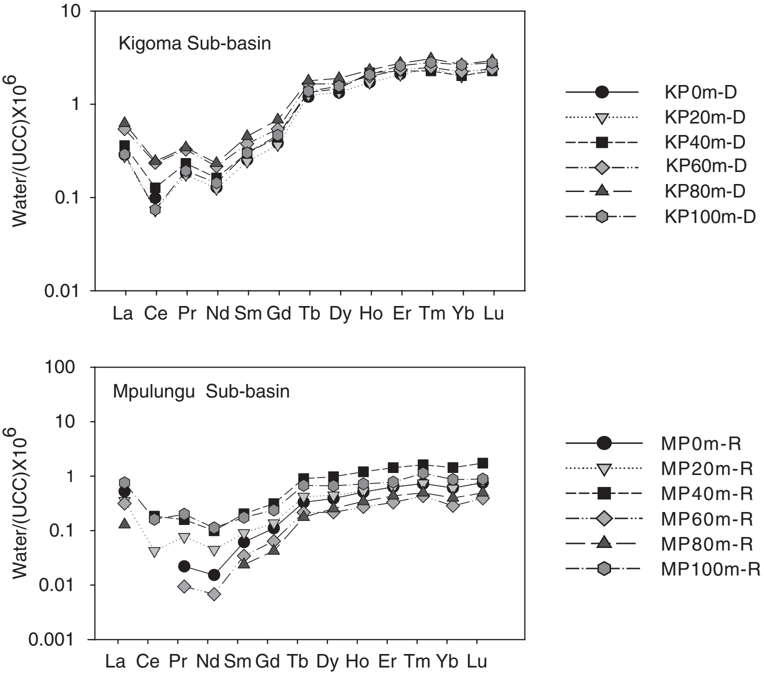

Figure 7.3. Representative UCC-normalized lacustrine REE patterns of the rainy and dry season profile samples from the Kigoma and Mpulungu sub-basins, respectively.

(Northern Basin) and 11% (Southern Basin) of the total variability, was characterized by high-negative loadings for Cd in the Northern Basin and Zn in the Southern Basin.

7.4.2.2. REE distribution and patterns

Average ΣREE concentrations showed large spatial and temporal variations across the lake with the highest values in the Mpulungu Sub-basin followed by the Bujumbura, Kigoma and Moba sub-basins (Tables 7.4–7.7). As with Fe and Mn, most of the LREE concentrations were below detection limits in the Kigoma and Moba sub-basins during the rainy season. The Mpulungu Sub-basin exhibited the highest negative Ce-anomalies, whereas the lowest negative values were recorded in the Bujumbura Sub-basin (Tables 7.4–7.6). The UCC-normalized REE patterns (Fig. 7.4) showed a predominantly HREE-enrichment over LREE with La_{UCC}/Yb_{UCC} ratios lower than unity, except for samples PM1-R

Table 7.4. Dissolved major, trace element and REE in Bujumbura Sub-basin (Littoral zone)

Elements	BL-R	BL-D	Mean	UP-R	UP-D	Mean
Na (ppm)	64.77	56.83	60.80	53.99	55.54	54.77
Mg (ppm)	15.32	41.08	28.20	38.62	39.66	39.14
Ca (ppm)	10.78	10.50	10.64	10.49	10.29	10.39
Rb (ppb)	8.82	24.40	16.61	22.70	22.74	22.72
Cd (ppb)	0.01	0.05	0.03	0.02	2.20	1.11
Ba (ppb)	50.04	73.75	61.90	124.06	70.25	97.16
Pb (ppt)	136.05	193.00	164.56	77.91	28.80	53.35
Th (ppt)	5.34	0.31	2.83	<DL	1.01	1.01
U (ppt)	33.38	352.47	192.93	325.47	345.82	335.65
V (ppt)	551.23	907.39	729.31	963.19	835.17	899.18
Mn (ppb)	58.46	1.65	30.05	5.5	0.21	2.85
Fe (ppb)	<DL	0.71	0.71	24.76	0.85	12.81
Cu (ppb)	9.55	0.68	5.12	3.04	0.41	1.72
Zn (ppb)	27.52	0.70	14.11	8.84	0.8	4.82
Sr (ppb)	98.06	119.64	108.85	99.69	103.40	101.54
DO (ppm)	n.d	7.50	7.50	8.00	n.d	8.00
pH	9.00	9.10	9.05	9.81	n.d	9.81
Y (ppt)	17.65	8.83	13.24	37.71	1.94	19.83
La (ppt)	54.02	7.33	30.67	23.29	27.93	25.61
Ce (ppt)	72.85	5.76	39.31	30.16	24.84	27.50
Pr (ppt)	6.26	1.13	3.67	8.36	10.66	9.51
Nd (ppt)	14.24	3.11	8.67	8.36	10.66	3.87
Sm (ppt)	3.50	0.98	2.24	2.59	5.14	3.87
Gd (ppt)	3.84	1.21	2.52	3.16	3.56	3.36
Tb (ppt)	1.26	0.66	0.96	1.31	1.48	1.39
Dy (ppt)	5.45	4.43	4.94	7.13	8.15	7.64
Ho (ppt)	1.31	1.62	1.47	2.11	2.36	2.23
Er (ppt)	3.24	4.59	3.92	6.11	6.82	6.46
Tm (ppt)	0.59	0.70	0.64	0.98	1.00	0.95
Yb (ppt)	3.35	3.91	3.63	6.93	5.85	6.39
Lu (ppt)	0.49	0.70	0.60	0.94	0.96	0.95
Sum REE	170.41	36.12	103.27	96.41	102.96	99.68
Ce/Ce*	0.85	0.45	0.65	0.76	0.51	0.63
$(La/Yb)_{UCC}$	1.18	0.14	0.66	0.25	0.35	0.30
$(La/Sm)_{UCC}$	0.79	0.37	0.58	0.48	0.47	0.48
$(Gd/Yb)_{UCC}$	0.66	0.18	0.42	0.26	0.35	0.31
$(Er/Nd)_{UCC}$	2.57	16.70	9.63	8.25	7.23	7.74
$(Sm/Yb)_{UCC}$	1.49	0.38	0.93	0.51	0.74	0.63

Note: BL, sample collected in the littoral zone in the Bujumbura area (Bujumbura Sub-basin); UP, sample collected in the pelagic zone in the Uvira area (Bujumbura Sub-basin); R and D stand for rainy and dry seasons, respectively.

Table 7.5. Dissolved major, trace element and REE concentrations in the Kigoma Sub-basin (littoral zone)

Elements	KG1-R	KG2-R	KG3-R	Mean	KG1-D	KG2-D	KG3-D	Mean
Na (ppm)	n.d	n.d	n.d	n.d	57.76	54.23	58.53	56.84
Mg (ppm)	n.d	n.d	n.d	n.d	43.01	38.34	41.22	40.86
Ca (ppm)	n.d	n.d	n.d	n.d	10.50	9.97	10.68	10.38
Rb (ppb)	5.93	1.38	3.39	3.57	22.39	21.56	22.56	22.17
Cd (ppb)	0.03	0.00	0.01	0.01	0.01	0.03	0.08	0.04
Ba (ppb)	35.90	7.38	18.14	20.47	70.70	68.93	70.37	70.00
Pb (ppt)	44.13	2.61	18.22	21.65	24.15	54.10	n.d	26.09
Th (ppt)	<DL	<DL	<DL		0.55	0.52	0.85	0.64
U (ppt)	103.59	24.77	45.47	57.95	309.27	296.89	308.49	304.88
V (ppt)	295.14	79.24	116.73	163.75	893.20	750.23	872.19	838.54
Mn (ppb)	0.01	<DL	<DL	0.01	0.06	0.20	0.29	0.18
Fe (ppb)	0.04	<DL	<DL	0.04	0.37	0.90	2.97	1.41
Cu (ppb)	0.23	0.08	0.07	0.13	0.08	0.23	0.37	0.23
Zn (ppb)	4.06	2.57	3.54	3.39	0.10	0.57	7.77	2.81
Sr (ppb)	35.77	7.60	16.15	19.84	108.37	96.54	113.02	105.98
SiO_2 (ppm)	0.24	0.24	0.20	0.23	n.d	n.d	n.d	n.d
NO_3^- (ppm)	0.15	0.10	0.03	0.23	n.d	n.d	n.d	n.d
PO_4^{-3} (ppm)	0.00	0.02	5.69	1.90	n.d	n.d	n.d	n.d
DO (ppm)	8.50	8.60	7.90	8.33	n.d	n.d	n.d	n.d
pH	9.17	9.09	9.23	9.16	n.d	n.d	n.d	n.d
Y (ppt)	3.70	23.66	28.27	18.54	2.78	45.61	34.26	27.55
La (ppt)	4.04	0.47	<DL	1.50	16.61	19.84		12.15
Ce (ppt)	1.80	<DL	<DL	0.60	6.63	8.84	19.36	11.61
Pr (ppt)	0.50	<DL	<DL	0.17	1.69	1.67	3.00	2.12
Nd (ppt)	1.36	<DL	<DL	0.45	4.60	4.47	8.54	5.87
Sm (ppt)	0.14	0.00	<DL	0.05	1.56	1.41	2.42	1.80
Gd (ppt)	0.23	<DL	<DL	0.08	1.96	1.73	2.85	2.18
Tb (ppt)	0.29	0.04	0.03	0.12	0.90	0.87	1.12	0.96
Dy (ppt)	1.58	0.34	0.52	0.81	5.61	5.29	6.70	5.87
Ho (ppt)	0.41	0.19	0.52	0.37	1.59	1.49	1.83	1.64
Er (ppt)	1.33	0.22	1.28	0.94	5.45	5.08	6.15	5.56
Tm (ppt)	0.20	0.04	0.06	0.10	0.88	0.83	0.93	0.88
Yb (ppt)	1.13	0.21	0.26	0.53	5.27	4.71	5.70	5.23
Lu (ppt)	0.16	0.01	0.05	0.07	0.86	0.82	0.91	0.86
ΣREE	13.17	1.52	2.72	5.80	53.60	57.06	59.51	56.72
Ce/Ce*	0.28			0.28	0.26	0.31		0.29
$(La/Yb)_{UCC}$	0.26	0.17		0.21	0.23	0.31		0.27
$(La/Sm)_{UCC}$	0.26	0.17		0.21	0.23	0.31		0.27
$(Gd/Yb)_{UCC}$	0.12			0.26	0.23	0.31		0.21
$(Er/Nd)_{UCC}$	10.99			10.99	13.39	12.84	8.13	11.45
$(Sm/Yb)_{UCC}$	0.58			0.58	0.14	0.15		0.15

Table 7.6. Dissolved major, trace element and REE concentrations in the Moba Sub-basin (littoral zone)

Elements	MB1-R	MB2-R	MB3-R	Mean	MB1-D	MB2-D	MB3-D	Mean
Na (ppm)	n.d	n.d	n.d	n.d	60.35	57.13	55.55	57.68
Mg (ppm)	n.d	n.d	n.d	n.d	42.14	40.89	40.22	41.08
Ca (ppm)	n.d	n.d	n.d	n.d	10.96	10.74	10.63	10.78
Rb (ppb)	11.02	1.42	6.83	6.42	22.73	22.47	22.82	22.67
Cd (ppb)	0.02	0.00	0.02	0.01	0.02	0.00	0.07	0.03
Ba (ppb)	33.41	5.11	18.62	19.05	72.04	71.02	70.63	71.10
Pb (ppt)	5324.48	37.16	85.11	1815.58	92.96	12.17	477.63	194.25
Th (ppt)	<DL	<DL	<DL		1.07	0.39	0.72	0.73
U (ppt)	168.13	22.59	95.20	95.30	301.43	306.69	315.28	307.80
V (ppt)	449.42	48.06	270.50	255.99	861.04	877.88	876.41	871.78
Mn (ppb)	0.05	<DL	<DL	0.05	0.17	0.11	0.44	0.24
Fe (ppb)	4.03	<DL	<DL	4.03	1.21	0.85	5.13	2.39
Cu (ppb)	4.34	0.10	0.44	1.63	0.46	0.12	1.56	0.71
Zn (ppb)	7.01	1.85	6.74	5.20	0.50	0.13	0.93	0.52
Sr (ppb)	57.39	6.96	31.98	32.11	116.15	115.24	110.49	113.96
Y (ppt)	10.20	1.89	2.78	4.96	29.54	31.92	33.17	24.90
La (ppt)	7.50	<DL	<DL	7.50	11.21	12.27	13.36	11.09
Ce (ppt)	9.14	<DL	<DL	9.14	8.33	8.93	9.92	9.08
Pr (ppt)	0.94	<DL	<DL	0.94	1.68	1.95	2.02	1.65
Nd (ppt)	2.24	<DL	<DL	2.24	4.40	5.20	5.34	4.29
Sm (ppt)	1.71	<DL	<DL	1.71	4.21	4.88	5.34	4.29
Gd (ppt)	0.55	<DL	<DL	0.55	1.58	1.94	2.21	1.57
Tb (ppt)	0.28	<DL	<DL	0.28	0.87	0.94	1.01	0.78
Dy (ppt)	1.94	0.12	0.26	0.77	5.35	5.87	6.01	4.50
Ho (ppt)	0.90	0.23	0.47	0.53	1.76	1.85	2.09	1.56
Er (ppt)	1.73	0.24	1.01	0.99	5.24	5.72	5.98	4.48
Tm (ppt)	0.26	0.02	0.07	0.12	0.87	0.92	0.90	0.70
Yb (ppt)	1.84	0.15	0.46	0.81	4.97	5.17	5.69	4.16
Lu (ppt)	0.30	0.01	0.09	0.13	0.85	0.86	0.95	0.70
Sum REE	29.34	0.76	2.36	10.82	51.31	56.50	60.83	48.59
Ce/Ce*	0.75				0.43	0.41	0.42	0.42
$(La/Yb)_{UCC}$					0.17	0.15	0.70	0.34
$(La/Sm)_{UCC}$					1.28	0.50	0.84	0.87
$(Gd/Yb)_{UCC}$					0.18	0.33	0.85	0.87
$(Er/Nd)_{UCC}$					13.47	12.42	12.99	12.96
$(Sm/Yb)_{UCC}$					0.13	0.30	0.83	0.42

and PM1-D in the Mpulungu Sub-basin and BL-R in the Bujumbura Sub-basin (Figs. 7.2 and 7.3). Er_{UCC}/Nd_{UCC} values also indicated HREE-enrichment relative to LREE. As was the case with the rivers, the lake waters showed HREE-enrichment relative to MREE with Gd_{UCC}/Yb_{UCC} ratios less than unity.

Table 7.7. Dissolved major, trace element and REE concentrations Mpulungu Sub-basin (littoral zone)

Elements	MP1-R	MP2-R	Mean	MP1-D	MP2-D	Mean
Na (ppm)	56.84	56.04	56.44	57.25	54.74	56.00
Mg (ppm)	41.19	40.85	41.02	42.70	41.64	42.17
Ca (ppm)	10.55	10.16	10.35	11.04	10.64	10.84
Rb (ppb)	22.93	22.73	22.83	23.29	22.86	23.07
Cd (ppb)	0.03	0.02	0.03	0.04	0.00	0.02
Ba (ppb)	74.29	73.27	73.78	101.22	75.65	88.43
Pb (ppt)	485.01	180.45	332.73	1879.12	1181.85	1530.48
Th (ppt)	2.92	1.57	2.25	0.58	0.34	0.46
U (ppt)	296.38	292.64	294.51	291.49	294.05	292.77
V (ppt)	792.36	755.72	774.04	840.76	773.72	807.24
Mn (ppb)	1.11	0.19	0.65	0.59	0.18	0.38
Fe (ppb)	8.77	0.90	4.84	2.79	1.41	2.10
Cu (ppb)	2.23	0.67	1.45	2.23	0.67	1.45
Zn (ppb)	10.18	0.99	5.58	12.98	2.67	7.82
Sr (ppb)	106.81	99.81	103.31	116.31	108.30	112.31
pH	8.71	8.72	8.71	9.02	9.02	9.02
Y (ppt)	45.61	34.26	39.93	42.02	33.82	37.92
La (ppt)	116.63	40.71	78.67	113.28	78.10	37.92
Ce (ppt)	84.88	20.11	52.49	47.73	21.00	34.37
Pr (ppt)	9.49	3.26	6.37	7.11	3.36	5.23
Nd (ppt)	21.45	8.22	14.83	15.76	7.84	11.80
Sm (ppt)	15.79	6.78	11.29	10.69	6.19	8.44
Gd (ppt)	6.17	2.87	4.52	4.46	2.89	3.67
Tb (ppt)	2.30	1.19	1.75	1.80	1.18	1.49
Dy (ppt)	11.38	6.85	9.11	9.33	6.67	8.00
Ho (ppt)	4.44	2.62	3.53	2.71	2.00	2.35
Er (ppt)	8.83	6.38	7.60	7.86	6.38	7.12
Tm (ppt)	1.39	0.97	1.18	1.19	0.94	1.07
Yb (ppt)	8.12	5.92	7.02	6.82	5.80	6.31
Lu (ppt)	1.35	1.01	1.18	1.10	0.94	1.02
ΣREE	337.82	141.13	239.47	271.86	177.12	224.49
Ce/Ce*	0.51	0.35	0.43	0.31	0.21	0.26
$(\mathrm{La/Yb})_{\mathrm{UCC}}$	1.05	0.50	0.78	0.99	1.22	1.10
$(\mathrm{La/Sm})_{\mathrm{UCC}}$	3.18	2.53	2.85	4.90	4.25	4.57
$(\mathrm{Gd/Yb})_{\mathrm{UCC}}$	0.44	0.28	0.36	0.29	0.38	0.33
$(\mathrm{Er/Nd})_{\mathrm{UCC}}$	8.77	9.19	8.98	31.96	5.63	18.79
$(\mathrm{Sm/Yb})_{\mathrm{UCC}}$	0.33	0.20	0.27	0.20	0.29	0.24

7.4.2.3. Trace elements and REE distributions in the water column

Vertical distribution of trace elements in lakes is mainly a function of physico-chemical parameters such as temperature, DO, pH and nutrients (Webster, 1993; De Carlo and Green, 2002). The average Sr and Ba concentrations showed slight seasonal variations in the Kigoma

Table 7.8. Four factors, controlling trace element loading into the Northern Basin of Lake Tanganyika

Elements	Factor 1	Factor 2	Factor 3	Factor 4	Communality
Cu	0.177	**−0.911**	−0.222	−0.098	0.921
Rb	0.294	**−0.905**	−0.06	0.059	0.913
Ba	**0.884**	−0.0353	−0.178	−0.178	0.97
V	**0.909**	−0.285	−0.165	−0.227	0.986
Sr	**0.874**	−0.353	−0.178	−0.178	0.97
Zn	−0.557	**−0.612**	−0.534	0.015	0.97
Pb	0.472	−0.233	**−0.837**	−0.101	0.987
Cd	0.371	−0.011	−0.067	**−0.924**	0.996
U	**0.916**	0.118	−0.062	−0.269	0.928
Variance	3.999	2.412	1.147	1.08	8.64
% of variability	0.444	0.268	0.127	0.12	0.96

Note: Significant loading coefficients are in bold.

Table 7.9. Four factor, controlling trace element loading into the Southern Basin of Lake Tanganyika

Elements	Factor 1	Factor 2	Factor 3	Factor 4	Communality
Cu	0.22	**0.922**	0.058	–0.197	0.94
Rb	**0.965**	0.154	0.174	–0.111	0.998
Ba	**0.949**	0.188	0.139	–0.201	0.995
V	**0.963**	0.133	0.221	–0.038	0.995
Sr	**0.969**	0.174	0.153	–0.081	0.999
Zn	0.162	0.354	0.038	**–0.918**	0.996
Pb	0.161	**0.764**	0.413	–0.296	0.868
Cd	0.355	0.235	**0.889**	–0.027	0.972
U	**0.966**	0.155	0.183	–0.08	0.998
Variance	4.859	1.745	1.121	1.036	8.763
% of variability	0.54	0.194	0.125	0.115	0.974

Note: Significant loading coefficients are in bold.

Sub-basin (Table 7.10), whereas the Ba profile coincided with those of NO_3^- and PO_4^{3-} in the Mpulungu Sub-basin at 20 m (maxima) and 60 m (minima; Fig. 7.4). Additionally, Th, U, V, Mn and Fe exhibited relatively high concentrations in the dry season compared to the rainy season, whereas the opposite was observed for Pb, Zn and Cu (Tables 7.10 and 7.11). In contrast to Fe, Mn, Th, Ba and nutrient profiles, which showed non-conservative behavior in the two sub-basins, Sr (Fig. 7.4) and Rb (Tables 7.10 and 7.11) concentrations appeared to be less affected by changes in pH, DO, or biological uptake.

A striking similarity was found between the Fe and Mn distributions in the two locations, which is probably to be expected. Dissolved concentrations

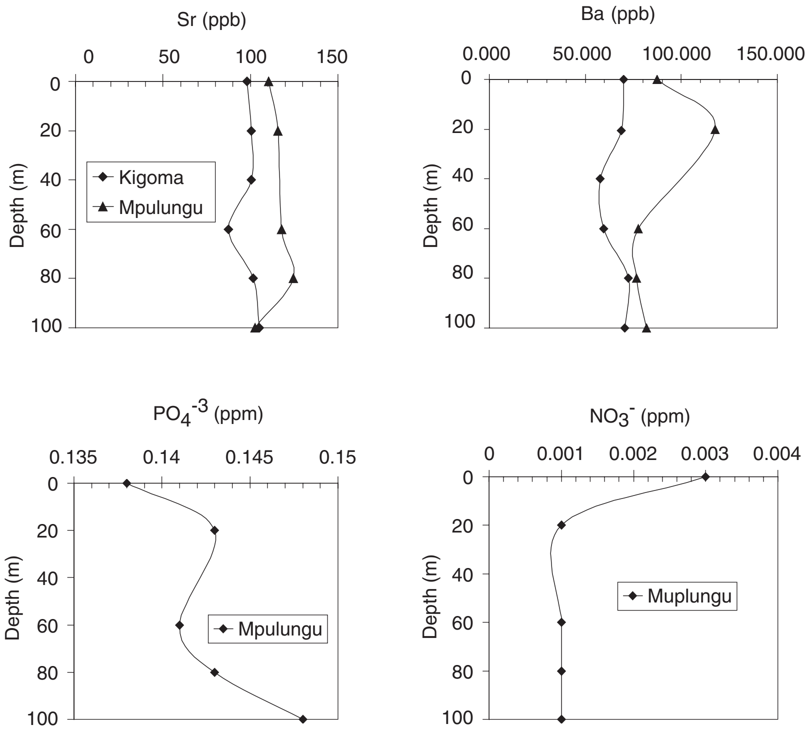

Figure 7.4. Sr, Ba, PO_4^{3-} and NO_3^- profiles in the Kigoma and Mpulungu sub-basins (dry season in 2003).

of these two elements reached their maxima at 60 m (Fig. 7.5). The maximum concentrations of Th were also observed at this depth.

REE showed decreasing concentrations from the surface to 60 m, where they reached their maxima, dropped at 80 m and increased at 100 m. The local REE maxima were observed at 40 m in the Mpulungu Sub-basin with a similar fluctuation across the profile, as seen in the Kigoma Sub-basin. The absolute concentrations of REE, in the water column, were higher in the dry season than the rainy season for the two sub-basins (Table 7.12).

7.4.2.4. Inter-element relationships

The PO_4^{-3} and Cd profiles collected in the Mpulungu Sub-basin during the dry season showed a substantial negative correlation ($r = -0.823$; $P = 0.087$). A strong positive correlation was also found between V and U ($r = 0.976$; $P < 0.001$; Fig. 7.6a) and between V and Rb ($r = 0.959$;

Table 7.10. Dissolved major and trace element profiles from the Kigoma Sub-basin

	Sample						Mean
	KP1-R	KP2-R	KP3-R	KP4-R	KP5-R	KP6-R	
	(0 m)	(20 m)	(40 m)	(60 m)	(80 m)	(100 m)	
Na (ppm)	43.47	53.33	28.33	54.01	27.51	55.36	43.67
Mg (ppm)	32.25	37.86	21.48	39.82	20.08	36.79	31.38
Ca (ppm)	n.d	n.d	n.d	9.67	4.97	9.62	8.09
Rb (ppb)	16.13	21.25	11.33	21.55	10.34	20.83	16.90
Cd (ppb)	0.03	0.24	0.01	0.03	0.02	0.02	0.06
Ba (ppb)	52.50	66.85	36.79	66.54	34.73	67.100	54.080
Pb (ppt)	51.43	207.20	15.84	125.53	29.08	104.81	88.98
Th (ppt)	<DL	<DL	<DL	1.54	0.58	2.24	0.73
U (ppt)	232.38	281.6	162.46	269.12	153.75	264.57	227.31
V (ppt)	639.24	775.96	437.05	700.74	323.39	575.24	575.27
Mn (ppb)	<DL	0.07	<DL	0.21	<DL	<DL	0.04
Fe (ppb)	2.03	<DL	<DL	0.27	<DL	<DL	0.38
Cu (ppb)	0.58	0.93	0.030	1.39	0.19	0.33	0.62
Zn (ppb)	1.59	9.94	0.56	1.67	0.57	1.16	2.56
Sr (ppb)	88.85	91.26	54.49	95.37	51.99	94.89	79.47
NO_3^- (ppm)	0.07	0.03	0.06	0.24	0.09	0.28	0.13
PO_4-^{3} (ppm)	0.00	0.08	0.006	0.006	0.01	0.08	0.03
Ω(mv)	657	657	668	676	677	678	668
DO (ppm)	5.60	5.32	5.20	5.32	5.42	2.50	4.89
T (°C)	27.40	27.30	26.20	24.90	24.60	24.40	25.80
pH	9.50	9.50	9.40	9.30	9.20	9.20	9.35
	KP-D	KP2-D	KP3-D	KP4-D	KP5-D	KP6-D	Mean
Na (ppm)	52.83	53.32	45.79	45.52	54.82	54.88	51.19
Mg (ppm)	37.2	38.39	34.83	33.20	41.10	40.57	37.55
Ca (ppm)	10.45	9.89	8.88	8.61	10.27	10.31	9.73
Rb (ppb)	22.32	21.90	18.37	18.76	22.97	22.21	21.09
Cd (ppb)	0.03	0.002	0.003	0.004	0.04	0.003	0.007
Ba (ppb)	69.96	68.68	57.85	59.46	72.32	70.43	66.45
Pb (ppt)	44.66	15.92	20.77	35.54	46.18	54.30	36.23
Th (ppt)	0.24	0.22	0.41	1.66	1.62	0.60	0.79
U (ppt)	294.63	297.25	256.48	256.46	312.01	297.25	285.69
V (ppt)	769.88	798.62	756.44	675.32	778.43	701.35	746.67
Mn (ppb)	0.20	0.08	0.12	0.30	0.14	0.17	0.17
Fe (ppb)	0.34	0.22	0.94	5.40	2.74	0.17	1.64
Cu (ppb)	0.59	0.20	0.20	0.23	0.30	0.18	0.28
Zn (ppb)	0.58	0.16	0.32	0.56	0.63	0.66	0.49
Sr (ppb)	98.00	100.46	100.59	87.24	101.49	104.90	98.78

Note: KP1, KP2, KP3, KP4, KP5 and KP6 correspond to depth 0 m, 20 m, 40 m, 60 m, 80 m and 100 m, respectively. R and D stand for rainy and dry seasons.

Table 7.11. Dissolved major and trace element profiles from the Mpulungu Sub-basin

	Samples						Mean
	MP1-R	MP2-R	MP3-R	MP4-R	MP5-R	MP6-P	
	(0 m)	(20 m)	(40 m)	(60 m)	(80 m)	(100 m)	
Rb (ppb)	6.37	5.22	12.88	3.25	4.21	7.03	6.49
Cd (ppb)	0.00	0.00	0.03	0.00	0.00	0.00	0.01
Ba (ppb)	21.69	19.09	43.25	13.87	14.66	29.51	23.68
Pb (ppt)	44.040	38.420	236.380	8.060	16.320	33.930	62.860
Th (ppt)	<DL	<DL	<DL	<DL	<DL	2.34	2.34
U (ppt)	95.59	86.45	169.56	49.33	60.91	98.90	93.46
V (ppt)	225.28	222.82	378.81	127.00	135.66	275.22	227.47
Mn (ppb)	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Fe (ppb)	<DL	<DL	<DL	<DL	<DL	0.96	0.96
Cu (ppb)	7.65	0.35	0.37	0.04	0.10	0.24	1.46
Zn (ppb)	1.13	1.13	2.60	0.99	0.44	1.66	1.33
Sr (ppb)	35.10	29.02	55.92	15.88	22.13	35.85	32.31
SiO_2 (ppm)	1.57	1.63	1.65	1.71	1.88	2.02	1.74
NO_3^- (ppm)	0.04	0.01	0.19	0.35	0.36	0.58	0.25
PO_4^{-3} (ppm)	0.00	0.00	0.03	0.04	0.07	0.09	0.04
Ω(mv)	688	683	694	696	698	700	694
DO (ppm)	7.66	7.75	5.35	4.80	4.50	3.86	5.65
T (°C)	28.52	27.27	26.08	25.51	24.64	26.26	26.05
pH	9.38	13.78	13.70	13.67	13.63	13.58	12.96
	MP1-D	MP2-D	MP3-D	MP4-D	MP5-D	MP6-D	Mean
Na (ppm)	56.02	55.10		58.35	62.06	52.85	56.87
Mg (ppm)	40.30	41.69		42.60	43.96	39.63	41.66
Ca (ppm)	10.86	10.49		10.80	11.19	10.42	10.75
Rb (ppb)	23.44	21.94		22.95	22.89	22.05	13.23
Cd (ppb)	0.01	0.01		0.01	0.0	0.0	0.01
Ba (ppb)	87.24	117.61		77.68	76.62	82.02	50.58
Pb (ppt)	635.24	343.32		628.00	141.80	167.01	196.28
Th (ppt)	1.49	0.75		1.79	0.63	0.27	1.37
U (ppt)	276.55	266.47		277.68	278.67	266.48	168.34
V (ppt)	634.03	597.26		685.81	667.36	565.97	395.23
Mn (ppb)	1.04	1.19		1.42	0.55	0.63	0.97
Fe (ppb)	8.81	2.80		46.83	3.80	2.59	9.54
Cu (ppb)	7.49	10.93		9.18	2.46	8.67	4.08
Zn (ppb)	4.39	11.86		7.89	2.57	5.81	3.48
Sr (ppb)	110.27	115.84		117.75	124.48	102.53	66.42
SiO_2 (ppm)	1.57	1.72		1.70	1.73	1.77	1.72
NO_3^- (ppm)	0.00	0.00		0.00	0.15	0.15	0.15
PO_4^{-3} (ppm)	0.14	0.14		0.14	0.14	0.15	0.08
PH	8.80	8.37		8.95	8.96	8.92	8.80

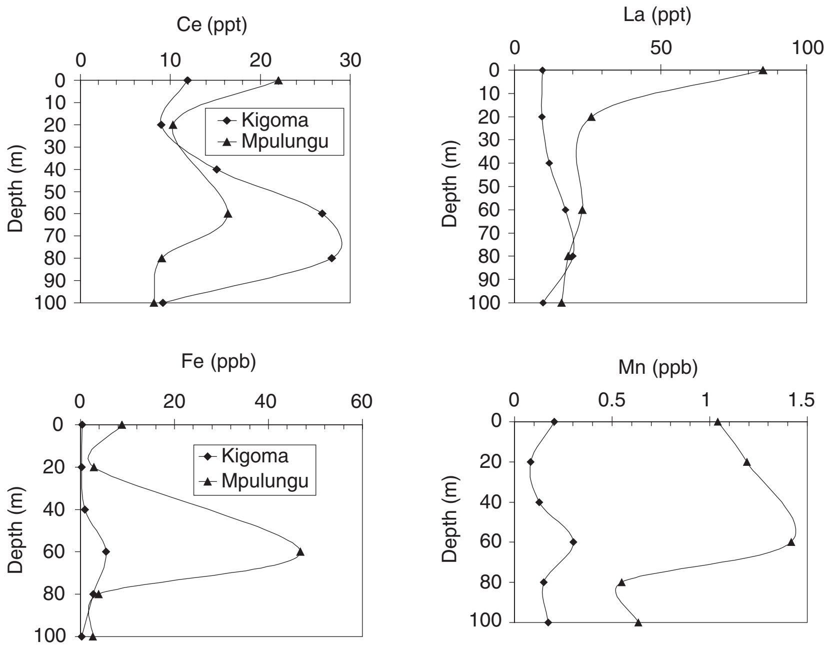

Figure 7.5. Dry season profiles of Ce, La, Fe and Mn from the Kigoma and Mpulungu sub-basins. Both Fe and Mn maxima were found at 60 m in the two sub-basins. Ce and La reached their maxima at the surface in the Mpulungu Sub-basin and at 80 m in the Kigoma Sub-basin.

$P = 0.02$; Fig. 7.6c) in the two sub-basins. Fe and Th profiles, collected during the dry season in the Kigoma Sub-basin, showed a strong positive correlation ($r = 0.89$; $P = 0.016$), whereas the relationship between the two elements was weak in the Mpulungu Sub-basin ($r = 0.79$; $P = 0.110$). The Ba and Sr profiles, however, showed strong positive correlations in the two sub-basins ($r = 0.965$; $P = 0.002$). There were no apparent relationships between Fe and U, Ba, Sr and V.

7.4.2.5. The relationships between REE, Fe and Mn profiles

The UCC-normalized REE of the two dry season profiles, collected from the Kigoma and Mpulungu sub-basins, resembled a typical seawater pattern, which is characterized by HREE-enrichment over LREE (Fig. 7.3). However, the absolute REE concentrations were substantially higher in the Southern Sub-basin compared to the Northern Sub-basin (Table 7.9). The higher REE concentrations were particularly for pronounced LREE (e.g., La and Nd).

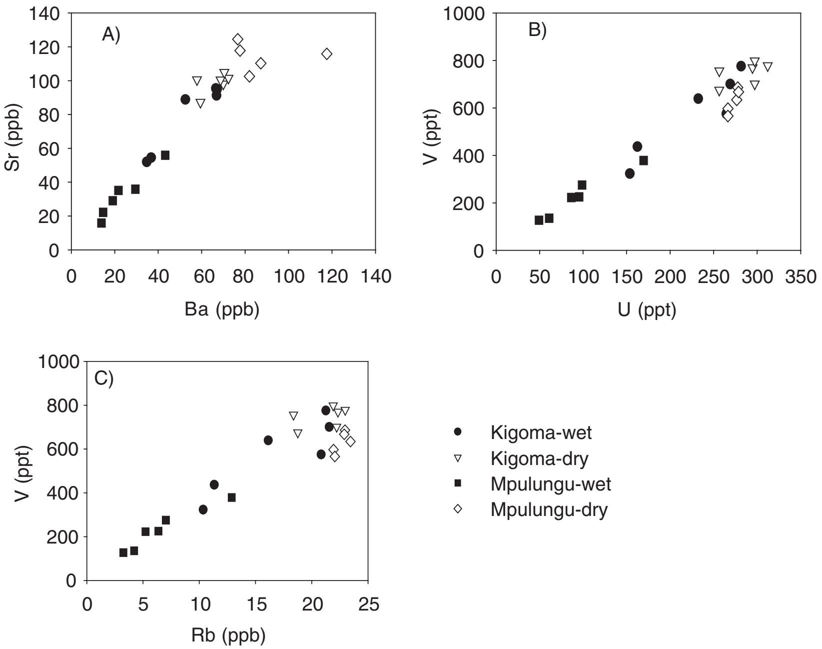

Figure 7.6. A–C relationship between Ba and Sr vertical profiles from the Kigoma and Mpulungu sub-basins.

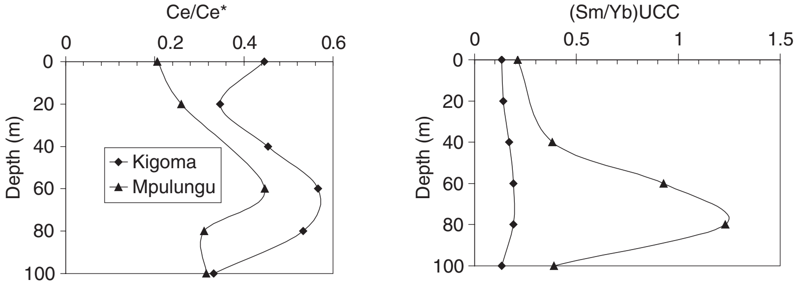

Figure 7.7. Profile samples from the Kigoma and Mpulungu sub-basins, showing LREE/HREE fractionation. According to these plots, the lowest deviation of Ce from the other trivalent species and the maximum Sm release into the water column were found at 60 m depth.

The release of LREE in the water column was similar in the two sub-basins (Fig. 7.7). However, the extent of LREE release was higher in the Mpulungu Sub-basin (Sm_{UCC}/Yb_{UCC} ranged from 0.21 to 1.23) compared to the Kigoma Sub-basin (Sm_{UCC}/Yb_{UCC} ranged from 0.13 to

Table 7.12. Seasonal Y and REE concentration profiles (ppt) from the Kigoma Sub-basin

	Samples						Total
	KP1-R	KP2-R	KP3-R	KP4-R	KP5-R	KP6-R	
	(0 m)	(20 m)	(40 m)	(60 m)	(80 m)	(100 m)	
Y	16.16	30.99	15.26	26.78	10.20	1.89	101.29
La	11.41	9.90	4.47	11.68	4.76	6.81	49.03
Ce	10.30	3.80	1.41	13.74	2.13	3.87	35.24
Pr	1.59	1.16	0.83	1.89	0.69	1.07	7.24
Nd	3.87	3.34	2.18	4.88	2.20	2.99	19.47
Sm	1.27	1.03	0.87	1.61	0.63	1.00	6.39
Gd	1.57	1.25	0.83	2.00	0.74	1.25	7.63
Tb	0.76	0.77	0.46	0.96	0.46	0.76	4.16
Dy	4.45	4.83	2.75	5.25	2.72	4.48	24.48
Ho	1.26	1.41	0.53	1.57	0.79	1.35	6.91
Er	4.33	4.94	2.81	5.57	2.70	4.83	25.17
Tm	0.66	0.80	0.43	0.84	0.40	0.72	3.83
Yb	3.95	4.50	2.43	4.87	2.40	4.00	22.15
Lu	0.65	0.78	0.42	0.87	0.42	0.77	3.90
ΣREE	46.08	38.48	20.41	55.72	21.04	33.89	
Ce/Ce*	0.53	0.24	0.17	0.65	0.26	0.32	
	KP1-D	KP2-D	KP3-D	KP4-D	KP5-D	KP6-D	
Y	9.80	9.48	18.87	5.60	6.39	12.12	62.25
La	9.65	9.36	11.96	17.45	19.91	9.75	78.08
Ce	7.61	5.72	9.65	17.14	17.82	5.83	63.77
Pr	1.50	1.45	1.88	2.58	2.50	1.58	11.68
Nd	3.93	3.83	4.93	6.42	6.91	4.37	30.39
Sm	1.29	1.24	1.51	1.86	2.22	1.52	9.63
Gd	1.60	1.53	1.83	2.21	2.74	1.92	11.83
Tb	0.78	0.81	0.87	1.05	1.13	0.89	5.53
Dy	4.70	4.74	5.14	5.76	6.55	5.47	32.33
Ho	1.36	1.35	1.70	1.57	1.81	1.62	9.41
Er	4.71	4.68	5.07	5.23	8.08	5.74	31.54
Tm	0.77	0.78	0.73	0.79	0.97	0.89	4.942
Yb	4.71	4.31	4.35	4.79	5.67	5.61	29.42
Lu	0.76	0.74	0.71	0.74	0.90	0.86	4.71
ΣREE	43.39	40.53	50.32	67.58	75.38	46.05	
Ce/Ce*	0.45	0.35	0.45	0.57	0.53	0.33	

0.191). Ce-anomalies (Ce/Ce*) were relatively lower in the Kigoma Sub-basin (Ce/Ce$^* = 0.45$–0.57) compared to the Mpulungu Sub-basin (Ce/Ce$^* = 0.21$–0.45). Although the La and Ce maxima did not coincide with Fe and Mn, Ce/Ce* maxima coincide with Fe and Mn at 60 m. Ce and La reached their maxima at 80 m in the Kigoma Sub-basin for the

Table 7.13. Seasonal Y and REE profiles (ppt) from the Mpulungu Sub-basin

	Samples						Total
	MP1-R	MP2-R	MP3-R	MP4-R	MP5-R	MP6-R	
	(0 m)	(20 m)	(40 m)	(60 m)	(80 m)	(100 m)	
Y	9.80	9.48	18.90	5.60	6.40	12.10	62.25
La	16.96	11.69	168.10	10.60	4.60	23.80	235.73
Ce		3.47	13.66	<DL	<DL	12.11	29.24
Pr	0.21	0.67	1.33	0.10	<DL	1.64	3.95
Nd	0.55	1.48	3.12	0.24	0.24	3.51	9.15
Sm	0.63	1.47	2.79	0.36	0.35	2.96	8.56
Gd	0.50	0.62	1.33	0.30	0.21	1.03	3.99
Tb	0.24	0.30	0.60	0.16	0.13	0.48	1.88
Dy	1.50	1.69	3.53	0.87	1.01	2.47	11.07
Ho	0.70	0.92	1.75	0.50	0.53	1.30	5.70
Er	1.55	1.51	3.30	0.84	1.09	1.88	10.17
Tm	0.25	0.26	0.53	0.16	0.18	0.38	1.76
Yb	1.43	1.40	3.18	0.71	0.96	1.99	9.66
Lu	0.25	0.26	0.55	0.14	0.17	0.29	1.67
ΣREE	24.77	25.74	203.73	14.96	9.46	53.85	
Ce/Ce*		0.22	0.07			0.37	
	MP1-D	MP2-D	MP3-D	MP4-D	MP5-D	MP6-D	
Y	33.63	30.55		33.16	31.27	29.25	157.86
La	85.00	26.26		23.29	18.50	16.03	169.08
Ce	22.04	10.32		16.38	9.07	8.19	65.96
Pr	3.66	2.27		2.61	2.07	1.96	12.58
Nd	8.55	5.79		6.50	4.88	4.33	27.63
Sm	7.97	4.98		5.47	4.88	4.33	27.69
Gd	3.14	2.44		2.35	1.90	2.20	12.03
Tb	1.22	1.02		1.04	0.93	0.97	5.17
Dy	6.98	6.09		6.32	5.94	5.60	30.94
Ho	2.39	1.85		1.99	1.82	1.73	9.77
Er	6.29	5.61		6.09	5.63	5.45	29.06
Tm	0.95	0.88		0.95	0.87	0.82	4.47
Yb	5.99	4.89		5.63	5.13	5.05	26.70
Lu	0.94	0.79		0.91	0.87	0.81	4.32
ΣREE	155.13	73.29		79.54	62.94	58.09	
Ce/Ce*	0.21	0.26		0.45	0.31	0.32	

dry season samples, whereas they reached their maxima at the surface in the Mpulungu Sub-basin (Tables 7.10 and 7.11). Ce/Ce^* and Sm_{UCC}/Yb_{UCC} maxima (Fig. 7.5), however, coincided with those of Fe and Mn at 60 m in the two sub-basins, which also corresponded to the nutrient minima in the Mpulungu Sub-basin (Table 7.13).

7.5. Discussion

7.5.1. Rivers–lake interface

The relatively high concentrations of dissolved Fe, Mn and LREE in the rivers compared to the lake indicated that the epilimnion waters of the lake may contain more DO than those of the rivers. The high average ΣREE observed in the Ruzizi River compared to the Malagarasi River, despite the relatively high pH value in Ruzizi River, suggested that, in addition to pH, other factors may control REE behavior in the Ruzizi River. The lower average ΣREE (particularly LREE) in the Bujumbura, Kigoma and Mpulungu sub-basins compared to the Ruzizi, Malagarasi and Lufubu rivers may reflect their co-precipitation and scavenging by Fe-oxyhydroxides at river–lake interface. This observation is consistent with REE behavior at river–ocean interface (Hoyle et al., 1984; Elderfield et al., 1990; Sholkovitz, 1995).

The absolute HREE (0.5–6.32 ppt) concentrations in the lake were consistent with those reported by Barrat et al. (2000). However, LREE concentrations (particularly, Nd and Sm) were lower than those reported by Barrat et al. (2000), which may be due to the preferential removal of these two elements by Fe colloids (Protano and Riccobono, 2002). HREE concentrations in aquatic systems are generally associated with high-dissolved organic carbon and/or low pH (Dupré et al., 1996; Braun et al., 1997; Gaillardet et al., 1997). Thus, the relatively low-dissolved organic carbon contents (2.2–2.9 $\mathrm{mg\,l^{-1}}$, Degens et al., 1971; Hecky et al., 1978; Jârvinen et al., 1996) and high pH (*ca.* 9) of Lake Tanganyika may explain the low-dissolved REE in the lake.

Following the removal of Fe through precipitation, the UCC-normalized patterns of lacustrine REE were more similar to seawater patterns with pronounced HREE-enrichment and LREE-depletion (e.g., Balistrieri et al., 1981; Elderfield and Greaves, 1982). This was clearly noticeable when comparing the UCC-normalized REE patterns of Lake Tanganyika and its three major tributaries. As a result of complexation with carbonate and other ligands, HREE are chiefly found in the dissolved phase, whereas LREE are more likely to be scavenged by Fe-oxyhydroxides (e.g., Sholkovitz and Elderfield, 1988; Elderfield et al., 1990; Sholkovitz and Szymczak, 2000; Quinn et al., 2004). The UCC-normalized REE patterns of the lake waters were more similar to those of the Ruzizi River than the Malagarasi and Lufubu rivers. The similar pattern between the lake and the Ruzizi River may be attributed to their identical pH values (*ca.* 9), or perhaps because this river is the dominant source of REEs for the lake. For example, HREE-enrichment in alkaline waters such as the

Tanganyika system is due to the complexation of REEs with bicarbonate ions (e.g., Johannesson and Lyons, 1994).

Ce-anomalies in the rivers were in the range of the world rivers (Elderfield et al., 1990). However, seasonal variations of Ce/Ce* and their lower values in the Lufubu Rivers with a relatively lower average annual pH of 7.8 compared to 8.7 and 9.0 for the Malagarasi and Ruzizi rivers (Langenberg et al., 2003) suggested that Ce-anomalies in these rivers were chiefly controlled by DO fluctuations and probably microbial reduction rather than pH (Moffett, 1990). Additionally, the spatial variations in Ce-anomalies may be attributed to hydrodynamics and seasonal changes in DO across the lake.

7.5.2. Geochemical control of trace element distribution

In oxic water systems, such as Lake Tanganyika and its tributaries, dissolved Fe and Mn concentrations are found at very low concentrations (Morel et al., 1991). Owing to its relatively low redox potential, the concentration of dissolved Mn tends to be higher than that of Fe in oxic waters (Hutchinson, 1957; Delfino and Otto, 1986). However, Mn is generally found as an inorganic free-ion, whereas Fe is associated with organically stable colloids, which can pass through filter pore of 0.45 μm (Nordstrom and Ball, 1989; Pokrovsky and Schott, 2002). Consequently, water samples filtered through 0.45 μm filter pore size may represent a mixture of dissolved and colloidal Fe phases. The filtration technique used in the present study may therefore explain the high-dissolved Fe contents compared to Mn. According to Sokolowiski et al. (2001), the relatively low Mn concentrations with respect to Fe in freshwater systems can also be attributed to the oxidation of dissolved Mn into less-soluble species, whereas under low DO conditions, Fe(III) may be rapidly reduced to Fe(II). This mechanism may also provide an additional explanation of the relatively low-dissolved Mn concentrations in the Tanganyika system.

High V concentrations in freshwater systems are generally attributed to silicate weathering in catchment basins, whereas high U concentrations are associated with carbonate or garanite bedrock (Shiller and Boyle, 1987). This geochemical process was supported by relatively high concentrations of dissolved V compared to U in Lake Tanganyika and its tributaries, as the lithology of the lake catchment basin is predominantly made of alumino-silicate minerals (Bellon and Pouclet, 1980; Cohen and Palacios-Fest, 1999).

Sr concentrations are consistent with those reported by Barrat et al. (2000), with narrow spatial and temporal variations across the lake. Furthermore, Sr appeared to be less affected by scavenging and biogenic activity (Broecker and Peng, 1982). In contrast to Sr, Ba and Rb, which are normally found in true dissolved phase, U and V can be transported in freshwater systems in various colloidal phases (Riotte et al., 2003). However, the high-loading coefficients for Sr, Ba, Rb, V and U suggested that these elements were less affected by colloidal complexes (organic and inorganic phases) in Lake Tanganyika, and thus Factor 1 may represent the soluble state. In dilute waters, low Fe and organic carbon concentrations (e.g., Lake Tanganyika), U is also thought to be in soluble form with low U/Sr values (1.9×10^{-3} to 6×10^{-3}; Riotte et al., 2003). In contrast to Sr and Rb, U may be associated with organic and inorganic colloids, and thus U/Sr and U/Rb ratios can be used as indices to assess U behavior in freshwater systems (Riotte et al., 2003). The relatively low U/Sr ratios in Lake Tanganyika suggested that U was chiefly transported in the dissolved phase in this system. The high solubility of U in the Tanganyika system can be attributed to its association with carbonate ions in solution (e.g., Langmuir, 1978; Waite et al., 1994). However, the spatial variations in U/Sr ratios across the lake confirmed the spatial variations in hydrodynamics. Hence, the Mpulungu Sub-basin, with the lowest U/Sr ratio, appeared to be the least affected by colloids (i.e., particulates). The lack of relationship between V, U and Rb, elements characterized by a true-dissolved phase, and Fe supported the suggestion that Factor 1 represents mainly the high degree of solubility, or the differences in concentration (Stetzenbach et al., 2001).

Factor 2, however, can be related to the inverse hydrodynamic variations in the two basins. For example, in oxic waters Cu is mainly present in organic complex forms and rarely in free ionic forms (e.g., $CuCl^{+}$; Calvert and Pedersen, 1993; Xue and Sund, 1997), whereas Pb is likely to exist in soluble carbonate form ($PbCO_3$) under high pH conditions, such as Lake Tanganyika (Drever, 1997). Pb may also be associated with organic ligands (Sokolowski et al., 2001). The discrepancy observed between the Cu and Pb loadings in the two basins may be attributed to the higher concentration of dissolved organic carbon in the Northern Basin compared to the Southern Basin, which may be indirectly linked to fluvial inputs, vertical mixing and primary productivity. For example, the Bujumbura (0.40 NTU) and Mpulungu sub-basins (0.35 NTU) are characterized by high seasonal turbidity compared to the Kigoma Sub-basin (0.25 NTU; Plisnier et al., 1996). However, the high-negative loading for Rb in the Northern Basin suggested that Factor 2 did not represent the same biogeochemical factor in the Southern Basin as was the case in the Northern Basin. In oxic waters, Zn tends to be in free ionic phases (e.g., Zn^{2+} and $ZnCl^{+}$; Calvert and Pedersen, 1993), or form strong organic complexes (e.g., Bruland, 1989; Ellwood and Van den Berg, 2000). However, the common factor that may explain the high-negative loadings of

Rb, Cu and Zn in the Northern Basin is their adsorption onto particulate biogenic material. Filtered water samples through 0.45 to 0.20-μm membrane pore sizes may contain fine-grained particulate fraction (Delfino and Otto, 1986). It can be suggested that the solubility of Cu, Rb and Zn was dramatically reduced in the Northern Basin due to high turbidity. Furthermore, Factor 3 may also represent another type of adsoption/desorption of Zn and Pb in the Northern Basin. Significant correlations between Fe and Th in the Kigoma and Mpulungu sub-basins indicated the impact of dissolved organic matter on Th geochemistry. A similar relationship between Fe and Th has been observed in an organic river system in Eastern Cameroon (Braun et al., 1997).

7.5.3. Biological control of trace element distribution in the lake

On the basis of the differences in their chemical, chlorophyll and bacterial concentrations, Lake Tanganyika waters are classified into Northern, Central and Southern waters (Hecky, 1978, 1981). This biological delimitation of the lake may explain the non-conservative behavior of certain trace elements such as Fe, Mn, Ba, Cd, and Cu and to a lesser extent Sr across Lake Tanganyika. For example, the behavior of Fe, Mn and Ba is generally governed by both geochemical and biogenic processes (e.g., Evans et al., 1977; Finlay et al., 1983; Hunt, 1983). Fe, in addition to its scavenging and desorption role, is also subject to active biological uptake (Kolber et al., 1994).

The coincidence of the Ba profile maximum with that of nutrients in the Mpulungu Sub-basin suggested that Ba might be subject to biological uptake. This was consistent with a previous study, which has demonstrated that the removal of Ba from estuarine surface waters is directly associated with seasonal phytoplankton blooms (Stecher and Kogut, 1999). Moreover, a strong negative correlation between Ba removal and protozoa abundance has also been observed (Finlay et al., 1983).

The spatial distribution of dissolved Cd in the two basins was consistent with biogenic activity, as a high-positive correlation between PO_4^{-3} and Cd profiles in the Mpulungu Sub-basin was observed. This observation was supported by Factor 3 with a high-positive loading for Cd in the Southern Basin and Factor 4 with a high-negative loading score in the Northern Basin. Thus, Factor 3 may reflect the breakdown of organic matter and a subsequent release of Cd into the water column, and Factor 4 may represent the uptake of dissolved Cd by organisms in the Northern Basin, and iron sulfide scavenging of Zn in the Southern Basin. For example, an inverse association between Cd and PO_4^{-3} has been observed in the Tay Estuary (Owens and Balls, 1997). According to Owens and

Balls (1997), the positive correlation between Cd and PO_4^{-3} is due to the breakdown of organic matter, and the release of both Cd and PO_4^{-3} into the water column. Co-precipitation of Zn by Fe sulfide has been reported in another lacustrine environment (Acterberg et al., 1997). The occurrence of hydrogen sulfide near the surface in the Mpulungu Sub-basin during the dry season may explain the high-negative loading of Zn in this sub-basin, which may co-precipitate with Fe as FeS.

In conclusion, Factors 2, 3 and 4 appeared to be the most important biogeochemical factors in Lake Tanganyika, as the scatter plots based on their loading scores grouped the samples into two different categories (Fig. 7.8). Because these factors are indirectly affected by primary productivity, it can be inferred from this study that trace element

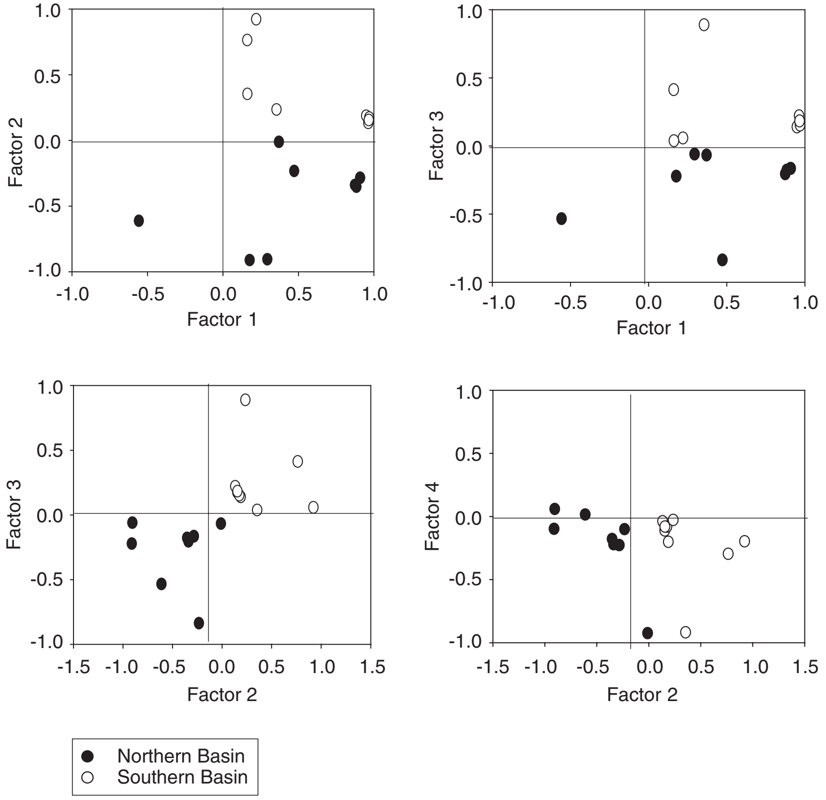

Figure 7.8. Scatter plots of varimax factor loading scores. Factor 2, 3 and 4 appeared to be the most important biogeochemical factors in the lake, as the plots of these three factor loading scores grouped the samples to two distinct categories (North and South).

distribution in Lake Tanganyika was in good agreement with the biological delineation.

7.5.4. Vertical cycling of REE

In permanently stratified lakes such as Lake Tanganyika, pH and DO decrease with depth following organic matter decomposition (Fig. 7.9). As a result, particulate Fe and Mn are broken down from anoxic sediments into the water column, and precipitate at the oxic–anoxic boundary (Haberyan and Hecky, 1987; De Carlo and Green, 2002). This phenomenon plays a fundamental role in trace element cycling in the water column (e.g., LREE; Elderfield et al., 1990). Thus, the coincidence of Fe and Mn maxima at 60 m in the two sub-basins may indicate a possible release

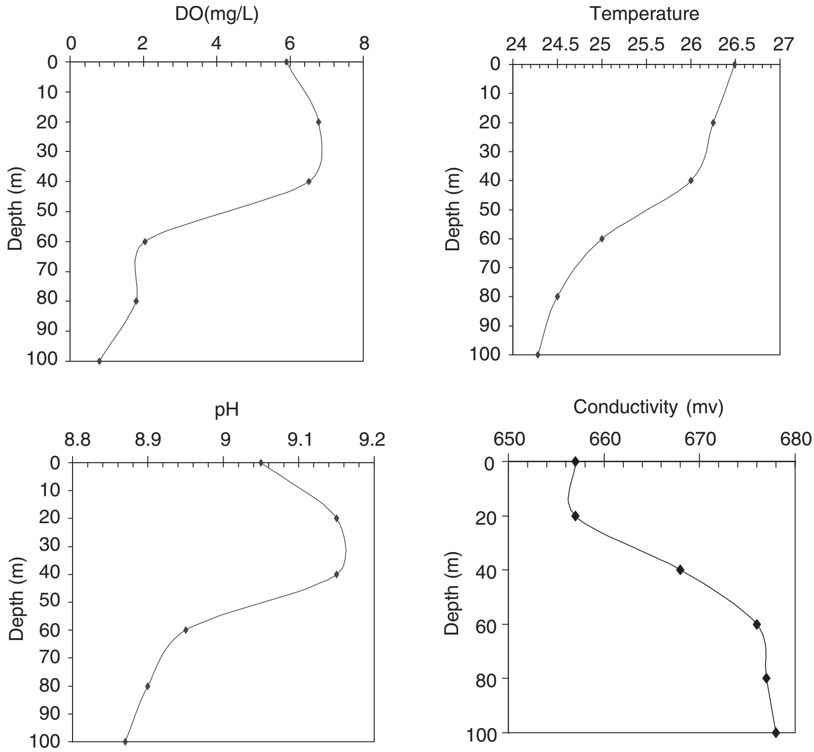

Figure 7.9. A contrast between dissolved oxygen, temperature, pH and conductivity depth in the Kigoma Sub-basin (dry season 2002; Sako, unpublished). A sharp drop of dissolved oxygen content and pH occurred around the thermocline depth (60 m).

of Fe(II) from the monimolimnion and its subsequent removal near mixolimnion through the oxidation process of Mn(IV) (Postma, 1985).

Although the maxima of La and Ce did not coincide with that of Fe, Ce/Ce* and $\mathrm{Sm}_{\mathrm{UCC}}/\mathrm{Yb}_{\mathrm{UCC}}$ for both profiles reached their maxima at 60 m, which corresponded to Fe and Mn maxima in the two sub-basins, suggesting that LREE removal and cycling in the water column can be controlled by Fe and Mn geochemistry.

Another striking difference in trace element patterns between the Northern and Southern basins during the dry season was the relatively high LREE fractionation in the Mpulungu Sub-basin compared to the Kigoma Sub-basin. The high LREE release in the Mpulungu Sub-basin may be a combination of the changes in DO with depth and intensive vertical mixing during this period (Plisnier et al., 1996).

The drop in NO_3^- and PO_4^{3-} minima at 60 m can be attributed to a probable high planktonic density at this depth, resulting in a possible high-nutrient uptake, and a subsequent high bacterial activity may occur. Thus, the occurrence of Fe and Mn maxima at 60 m despite the presence of DO implied that, in addition to changes in pH, trace elements and LREE cycling in Lake Tanganyika was subject to bacteria-mediated reduction. This observation is consistent with previous work (Moffett, 1990; German et al., 1992; Sholkovitz, 1992; Moffett, 1994a, b).

Pronounced high concentrations of most elements at the surface in the Mpulungu Sub-basin compared to the Kigoma Sub-basin supported the influence of seasonal upwelling on water chemistry across the lake. In the Mpulungu Sub-basin, anoxic water is normally found at a depth of 200 m and is rich in hydrogen sulfide and nutrients, which may appear at the surface during the dry season (Coulter, 1963), and sulfide is known to be associated with HREE concentrations (Schijf, 1992; Schijf et al., 1995).

7.6. Conclusions

The three major rivers feeding Lake Tanganyika were Fe- and LREE-enriched compared to the lake, whereas HREE tended to be more conservative. The conservative nature of HREE may be due to the presence of a dominant inorganic ligand such as HCO_3^-. Ce/Ce* values varied between the rivers and within the lake, according to changes in pH and DO. Solubility, biogenic activity, and Fe- and Mn-oxyhydroxides appeared to be the major biogeochemical factors that control trace element behavior in Lake Tanganyika. The coincidence of Ce-anomalies and

Sm_{UCC}/Yb_{UCC} maxima with those of Fe and Mn in the Kigoma and Mpulungu sub-basins implied that LREE were preferentially scavenged from the water column by Fe- and Mn-oxyhydroxides.

The release of LREE into the water column, which seemed to be enhanced by microbial mediated reduction, was greater in the Mpulungu Sub-basin than in the Kigoma Sub-basin. High LREE fraction and trace element abundance at the near surface in the Mpulungu Sub-basin may result from the intensive upwelling in this sub-basin during the dry season. High-trace element concentrations, observed in the depth in the Mpulungu Sub-basin profile compared to the Kigoma Sub-basin, provided insights into understanding the effects of changes in hydrodynamics on trace element behavior in the two extreme basins of Lake Tanganyika.

This study has demonstrated that the spatial distribution of most trace elements in Lake Tanganyika was not conservative, but varied according to riverine input, scavenging by Fe-oxyhydroxides, sedimentation, biological uptake and reduction and remineralization.

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REFERENCES

Aagaard, P., 1974. Rare earth element complexation on clay minerals. Bull. Group France 26, 193–199.

Acterberg, E.P., Van den Berg, C.M.G., Boussemart, M., Davison, W., 1997. Speciation and cycling of trace metals in Estwaite water a productive English Lake with seasonal deep-water anoxia. Geochim. Cosmochim. Acta 54, 971–991.

Atsuyuki, O., Kawabe, I., 2001. REE (III) adsorption onto Mn dioxide (σ-MnO_2) and Fe oxyhydroxides: Ce (III) oxidation by σ-MnO_2. Geochim. Cosmochim. Acta 65(5), 695–703.

Balistrieri, L., Brewer, P.G., Murray, J.W., 1981. Scavenging residence times of trace metals and surface chemistry of sinking particles in Deep Ocean. Deep-Sea Res. 28A, 101–121.

Barrat, J.A., Boulègue, Tiercelin, J.J., Lesoud, M., 2000. Strontium isotopes and rare-earth element geochemistry of hydrothermal carbonate deposits from Lake Tanganyika, East Africa. Geochim. Cosmochim. Acta 64, 287–298.

Bellon, H., Pouclet, A., 1980. Datations K-Ar de quelques laves du rift ouest de l'Afrique Centrale: Implications sur l'évolution magmatique et structurales. Geologishes Rundschau 69(1), 49–62.

Braun, J.J., Viers, J., Dupré, B., Polve, M., Nsill, J., Muller, J.P., 1997. Solid/liquid REE fractionation in the lateritic system of Goyoum, East Cameroon: The implication for the present dynamics of the soil covers of the humid tropical regions. Geochim. Cosmochim. Acta 62(2), 273–299.

Broecker, W.S., Peng, T.-H., 1982. Tracers in the Sea. Eldigo Press, Palisades, NY, p. 690.

Bruland, K.W., 1989. Complexation of zinc by natural organic ligands in the Central North Pacific. Limnol. Oceanogr. 34, 269–285.

Byrne, R.H., Kim, K.-H., 1990. Rare earth scavenging in seawater. Geochim. Cosmochim. Acta 54, 2645–2656.

Calvert, S.E., Pedersen, T.F., 1993. Geochemistry of recent oxic and anoxic marine sediments: Implications for the geological records. Mar. Geol. 113, 67–88.

Cazenave-Piarrot, F., 1981. L'originalité des milieux natureles dans le grand rift occidental africain. L'exemple de l'Imbo au Burundi. Recherches sur les hautes terres d'Afrique centrale. Travaux et documents de géographie tropical, CEGET 42, p. 59.

Coffey, M., Dehairs, F., Collette, O., Luther, G., Church, T., Jickells, T., 1997. The behaviour of dissolved barium in estuaries. Estuar. Coast. Shelf Sci. 45, 113–121.

Cohen, S.A., Palacios-Fest, R.M., 1999. Paleolimnological investigations. Pollution control and other measures to protect biodiversity in Lake Tanganyika (RAF/92/G32).

Coulter, G.W., 1963. Thermal stratification in the deep hypolimnion of Lake Tanganyika. Limnol. Oceanogr. 13(2), 385–387.

Coulter, G.W., Spigel, H.R., 1991. Hydrodynamics. In: Coulter, G.W. (Ed.), Lake Tanganyika and Its Life. Natural History Museum Publication, Oxford University Press, London, pp. 49–75.

De Carlo, E.H., Green, J.W., 2002. Rare earth elements in the water column of Lake Vanda, McMurdo Dry Valleys, Antarctica. Geochim. Cosmochim. Acta 66, 1323–1333.

Degens, E.T., Von Herzen, R.P., Wong, H.-K., 1971. Lake Tanganyika: Water chemistry, sediments, geological structure. Naturwissenschaften 58(5), 229–241.

Delfino, J.J., Otto, G.R., 1986. Trace metal transport in two tributaries of the Upper Chesapeake Bay: The Susquehanna and Bush rivers. Mar. Chem. 20, 29–44.

Devroey, E., 1954. Annuailre hydrologique du C. B. et U. 1953. Public. Com. Hydro. Bass. Congo **7**, p. 326.

Drever, J.I., 1997. The Geochemistry of Natural Waters, third ed. Prentice-Hall, Upper Saddle River, NJ, p. 436.

Dupré, B., Gaillardet, J., Rousseau, D., Allègre, C.J., 1996. Major and trace elements of river-borne material: The Congo basin. Geochim. Cosmochim. Acta 60, 1301–1321.

Elbaz-Poulichet, F., Dupuy, C., 1999. Behaviour of rare earth elements at the freshwater–seawater interface of two acid mine rivers: The Tito and Odiel (Andalucia, Spain). Appl. Geochem. 14, 1063–1072.

Elderfield, H., Greaves, M.J., 1982. The rare earth elements in seawater. Nature 296, 214–219.

Elderfield, H., Upstill-Goddard, R., Sholkovitz, R.E., 1990. The rare earth elements in rivers, estuaries, and coastal seas and their significance to the composition of ocean waters. Geochim. Cosmochim. Acta 54, 971–991.

Ellwood, M.J., Van den Berg, C.M.G., 2000. Zinc speciation in the Northeastern Atlantic Ocean. Mar. Chem. 68, 295–306.

Evans, D.W., Cutshall, N.H., Goss, F.A., Wolfe, D.A., 1977. Manganese cycling in the Newport River estuary, North Carolina. Estuar. Coast. Mar. Sci. 5, 71–80.

Finlay, B.J., Hetherington, N.B., Davison, W., 1983. Active biological participation in lacustrine barium chemistry. Geochim. Cosmochim. Acta 47, 1325–1329.

Gaillardet, J., Dupré, B., Allègre, J.C., Négrel, P., 1997. Chemical and physical denudation in the Amazon River Basin. Chem. Geol. 142, 141–173.

Garrels, R.M., Mackenzie, F.T., 1971. Evolution of Sedimentary Rocks. Norton, New York.

German, C.R., Holliday, B.P., Elderfield, H., 1992. Reply to the comment by E.R. Sholkovitz on "redox cycling on rare earth elements in the suboxic zone of the Black Sea". Geochim. Cosmochim. Acta 56, 4309–4313.

Graham, E.Y., Ramsey, L.A., Lyons, W.B., Welch, K.A., 1996. Determination of rare earth elements in Antarctica lakes and streams of varying ionic strengths. In: Holland, G., Tanner, S.D. (Eds.), Plasma Source Mass Spectrometry: Developments and Applications. The Royal Society of Chemistry, London, pp. 253–262.

Green, W.J., Ferdelman, T.G., Canfield, D.E., 1989. Metal dynamics in Lake Vanda (Wright Valley, Antarctica). Chem. Geol. 76, 85–94.

Haberyan, K., Hecky, E.R., 1987. The late Pleistocene and Holocene stratigraphy and paleolimnology of lakes Kivu and Tanganyika. Palaeogeogr. Palaeoecol. 61, 169–197.

Heaney, S.L., Smyly, W.J.P., Talling, J.F., 1986. Interactions of physical, chemical and biological processes in depth and time within a productive English lake during summer stratification. Intern. Rev. Ges. Hydrol. 71, 441–494.

Hecky, R.E., 1978. The Kivu-Tanganyika basin: The last 14000 years. Polskie Archiwum Hydrobiologii 25(1–2), 159–165.

Hecky, R.E., 1981. East African lakes and their trophic efficiencies. AAAS 1981, Toronto Symposium.

Hecky, R.E., Fee, E.J., Kling, H.J., Rudd, J.W., 1978. Studies on the planktonic ecology of Lake Tanganyika. Can. Dept. Fish. Environm. Fisheries and Marine Services Technical Report 816, 1–51.

Hecky, R.E., Spigel, R.H., Coulter, G.W., 1991. The nutrient regime. In: Coulter, W.G. (Ed.), Lake Tanganyika and Its Life. Natural History Museum Publications, Oxford University Press, London, pp. 75–89.

Hoyle, J., Elderfield, E., Gledhill, A., Greave, M., 1984. The behaviour of rare earth elements during mixing of river and sea waters. Geochim. Cosmochim. Acta 48, 143–149.

Hunt, C.D., 1983. In corporation and deposition of Mn and other trace metals by flocculent organic matter in a controlled marine ecosystem. Limnol. Oceanogr. 28, 913–923.

Hutchinson, G.E., 1957. A treatise on limnology. Geography, Physics and Chemistry, Vol. I, Wiley, New York, p. 1015.

Jârvinen, M., Slonen, K., Sarvala, J., 1996. Experiments on phytoplankton and bacterial production ecology in Lake Tanganyika: The results of the first lake-wide research cruise on R/V Tanganyika Explorer. GCP/RAF/271/FIN–DT/44, p. 33.

Johannesson, K.H., Lyons, W.B., 1994. The rare earth element geochemistry of Mono Lake water and the importance of carbonate complexing. Limnol. Oceanogr. 39, 1141–1154.

Johannesson, K.H., Stetzenbach, K.J., Hodge, V.F., 1997. Rare earth elements as geochemical tracers of regional groundwater mixing. Geochim. Cosmochim. Acta 61, 3605–3618.

Johannesson, K.H., Stetzenbach, K.J., Hodge, V.F., Lyons, W.B., 1996. Rare earth element complexation behavior in circumneutral pH groundwaters: Assessing the role of carbonate and phosphate ions. Earth Planet. Sci. Lett. 139, 305–319.

Kaiser, H.F., 1958. The varimax criterion for analytic rotation in factor analysis. Psychometrika 23, 187–200.

Kolber, Z.S., Barber, R.T., Coale, K.H., Fitzwater, S.Z., Greene, R.M., Johnson, K.S., Lindley, S., Falkowski, P.G., 1994. Iron limitation of phytoplankton photosynthesis in equatorial Ocean. Nature 37, 145–149.

Langenberg, V.T.H., Nyamushahu, S., Roijackers, R., Koelmans, A., 2003. External nutrient sources for Lake Tanganyika. J. Great Lakes Res. 29(2), 169–180.

Langmuir, D., 1978. Uranium solution-mineral equilibria at low temperatures with applications to sedimentary ore deposits. Geochim. Cosmochim. Acta 42, 547–569.

Meybeck, M., 1987. Global chemical weathering of surficial rocks estimated from river dissolved loads. Am. J. Sci. 287, 401–428.

Moffett, J.W., 1990. Microbially mediated cerium oxidation in sean water. Nature 345, 421–423.

Moffett, J.W., 1994a. A radiotracer study of cerium and manganese uptake in Chesapeake Bay. Geochim. Cosmochim. Acta 58, 695–703.

Moffett, J.W., 1994b. The relationship between cerium and manganese oxidation in the marine environment. Limnol. Oceanogr. 39, 1309–1318.

Morel, F.M.M., Rueter, J.G., Price, N.M., 1991. Iron nutrition of phytoplankton and its possible importance in the ecology of ocean regions with high nutrient and low biomass. Oceanography 4(2), 56–61.

Nordstrom, D.K., Ball, J.W., 1989. Mineral saturation states in natural waters and their sensitivity to thermodynamic and analytical errors. Sci. Geol. Bull. 42, 269–280.

Owens, R.E., Balls, P.W., 1997. Dissolved trace metals in the Tay Estuary. Estuar. Coast. Shelf Sci. 44, 421–434.

Patterson, C.C., Settle, D.M., 1976. The reduction of orders of magnitude errors in lead analyses of biological materials and natural waters by evaluating and controlling the extent and source of industrial lead, handling, and analysis. Natl. Bureau Stand. Spec. Publ. 422, 321–351.

Plisnier, P.-D., 1996. Limnological sampling during a second annual cycle (1994–1995) and some comparisons with year one on Lake Tanganyika. FAO/FINNIDA Research for the management of the fisheries of Lake Tanganyika. GCP/RAF/271/FIN–TD/54, p. 48.

Plisnier, P.-D., Langenberg, V., Mwape, L., Chitamwembwa, D., Tshibangu, K., Coenen, E., 1996. Limnological sampling during an annual cycle at three stations on Lake Tanganyika (1993–1994). FAO/FINNIDA Research for the management of the fisheries of Lake Tanganyika. GCP/RAF/271/FIN–TD/46, p. 124.

Pokrovsky, O.S., Schott, J., 2002. Iron colloids/organic matter associated transport of major and trace elements in small boreal rivers and their estuaries (NW Russia). Chem. Geol. 190, 141–179.

Postma, D., 1985. Concentration of Mn and separation from Fe in sediments. I. kinetics and stoichiometry of the reaction between birnessite and dissolved Fe (II) at 10°C. Geochim. Cosmochim. Acta 49, 1023–1033.

Protano, G., Riccobono, F., 2002. High contents of rare earth elements (REEs) in stream waters of Cu–Pb–Zn mining area. Environ. Pollut. 117, 499–414.

Quinn, K.A., Byrne, R.H., Schijf, J., 2004. Comparative scavenging of yttrium and the rare earth elements in seawater: Competitive influences of solution and surface chemistry. Aquat. Geochem. 10(1/2), 59–80.

Reeder, S.W., Hitchon, B., Levinson, A.A., 1972. Hydrogeochemistry of the surface waters of the Mackenzie River drainage basin, Canada-I. Factors controlling inorganic composition. Geochim. Cosmochim. Acta 36(8), 825–865.

Riotte, J., Chabaux, F., Benedetti, M., Dia, A., Gérard, M., Boulègue, J., Etamé, J., 2003. Uranium colloidal transport and origin of the ^{234}U–^{238}U fractionation in surface waters: New insights from Mount Cameroon. Chem. Geol. 202, 365–381.

Ruiz, F., Gomis, V., Blasco, P., 1990. Application for factor analysis to the hydrogeochemical study of coastal aquifer. J. Hydrol. 119, 169–177.

Schijf, J., 1992. Aqueous geochemistry of rare earth elements in marine anoxic basins. PhD Dissertation, University of Utrecht, Utrecht (Geol. Utraiectina No. 85).

Schijf, J., de Baar, H.J.W., Millero, F.J., 1995. Vertical distributions and speciation of dissolved rare earth elements in the anoxic brines of the Bannock Basin, eastern Mediterranean Sea. Geochim. Cosmochim. Acta 59, 3285–3299.

Shan, X.-Q., Lian, J., Wen, B., 2002. Effect of organic acids on adsorption and desorption of rare earth elements. Chemosphere 47(7), 701–710.

Shiller, M.A., Boyle, E.A., 1987. Dissolved vanadium in rivers and estuaries. Earth Planet. Sci. Lett. 86, 214–224.

Sholkovitz, R.E., Elderfield, H., 1988. Cycling of dissolved rare earth elements in Chesapeake Bay. Global Biogeochem. Cy. 2(2), 157–176.

Sholkovitz, E.R., 1992. Comment on "Redox cycling of rare earth elements in the suboxic zone of the Black Sea" by C.R. German, B.P., Holliday, Elderfield, H. Geochim. Cosmochim. Acta 56, 4305–4307.

Sholkovitz, R.E., 1993. The geochemistry of rare earth elements in the Amazon River estuary. Geochim. Cosmochim. Acta 57, 2181–2190.

Sholkovitz, R.E., 1995. The aquatic chemistry of rare earth elements in rivers and estuaries. Aquat. Geochem. 1, 1–34.

Sholkovitz, E.R., Szymczak, R., 2000. The estuarine chemistry of rare earth elements: Comparison of the Amazon, Fly, Spik and the Gulf of Papua Systems. Earth Planet. Sci. Lett. 197, 299–309.

Sichingabula, H.M., 1999. Analysis and results of discharge and sediment monitoring activities in the southern Lake Tanganyika basin, Zambia. Special study on sediment discharge and its consequences. Pollution control and other measures to protect biodiversity in Lake Tanganyika (RAF/92/G32).

Simeonov, V., Stefanov, S., Tsakovski, S., 2000. Environmetrical treatment of water quality survey data from Yantra River, Bulgaria. Mikrochim. Acta 134(1/2), 15–21.

Sokolowski, A., Wolowicz, M., Hummel, H., 2001. Distribution of dissolved and labile particulate trace elements in the overlying bottom water in the Vistula River Plume (Southern Baltic Sea). Mar. Pollut. Bull. 42(10), 967–980.

Stecher, H.A., Kogut, M.B., 1999. Episodic barium removal in the Delaware estuary. Geochim. Cosmochim. Acta 63(7–8), 1003–1012.

Taylor, S.R., McLennan, S.M., 1985. The continental Crust: Its composition and evolution. Blackwell, Oxford, p. 312.

Tiercelin, J.J., Mondeguer, A., 1991. The geology of the Tanganyika trough. In: Coulter, G.W. (Ed.), Lake Tanganyika and Its Life. Natural History Museum Publication, Oxford University Press, London, pp. 6–48.

Vandecasteel, C., Block, C.B., 1993. Modern Methods for Trace Element Determination. Willey, Chichester.

Viollier, E., Jézéquel, D., Michard, G., Pèpe, M., Sarazin, G., Albéric, P., 1995. Geochemical study of a crater lake (Pavin Lake, France): Trace-element behaviour in the monimolimnion. Chem. Geol. 125, 61–72.

Waite, T.D., Davis, J.A., Payne, T.E., Waychunas, G.A., Xu, N., 1994. Uranium (VI) adsorption to ferrihydrite: Application of a surface complexation model. Geochim. Cosmochim. Acta 58, 5465–5478.

Webster, G.J., 1993. Trace-metal behaviour in oxic and anoxic Ca–Cl brines of the Wright Valley drainage, Antarctica. Chem. Geol. 112, 255–274.

Xue, H., Sund, W.G., 1997. Comparison of [Cu^{2+}] measurements in lake water determined by ligand exchange and Cathodic stripping voltammetry and by ion-selective electrode. Environ. Sci. Technol. 31, 1902–1909.