

7.7 Trace Elements in River Waters

J Gaillardet, Institut de Physique du Globe de Paris, Paris, France

J Viers and B Dupré, Geosciences and Environment Toulouse OMP, University Paul Sabatier, Toulouse, France

© 2014 Elsevier Ltd. All rights reserved.

7.7.1	Introduction	195
7.7.2	Natural Abundances of Trace Elements in River Water	196
7.7.2.1	Range of Concentrations of Trace Elements in River Waters	207
7.7.2.2	Crustal Concentrations versus Dissolved Concentrations in Rivers	207
7.7.2.3	Correlations between Elements	209
7.7.2.4	Temporal Variability	210
7.7.2.5	Conservative Behavior of Trace Elements in River Systems	211
7.7.2.6	Transport of Elements	211
7.7.3	Sources of Trace Elements in Aquatic Systems	212
7.7.3.1	Rock Weathering	212
7.7.3.2	Atmosphere	214
7.7.3.3	Other Anthropogenic Contributions	214
7.7.4	Aqueous Speciation	215
7.7.5	The “Colloidal World”	217
7.7.5.1	Nature of the Colloids	217
7.7.5.2	Ultrafiltration of Colloids and Speciation of Trace Elements in Organic-rich Rivers	218
7.7.5.3	The Nonorganic Colloidal Pool	220
7.7.5.4	Fractionation of REEs in Rivers	221
7.7.5.5	Colloid Dynamics	223
7.7.6	Interaction of Trace Elements with Solid Phases	224
7.7.6.1	Equilibrium Solubility of Trace Elements	224
7.7.6.2	Reactions on Surfaces	225
7.7.6.3	Experimental Adsorption Studies	225
7.7.6.4	Adsorption on Hydrous Oxides in River Systems	226
7.7.6.5	The Sorption of REEs: Competition between Aqueous and Surface Complexation	227
7.7.6.6	Importance of Adsorption Processes in Large River Systems	228
7.7.6.7	Anion Adsorption in Aquatic Systems	229
7.7.6.8	Adsorption and Organic Matter	229
7.7.6.9	Particle Dynamics	230
7.7.7	Conclusion	231
	Acknowledgments	232
	References	232

7.7.1 Introduction

Trace elements are characterized by concentrations lower than 1 mg L^{-1} in natural waters. This means that trace elements are not considered when “total dissolved solutes” (TDS) are calculated in rivers, lakes, or groundwaters, because their combined mass is not significant compared to the sum of Na^+ , K^+ , Ca^{2+} , Mg^{2+} , H_4SiO_4 , HCO_3^- , CO_3^{2-} , SO_4^{2-} , Cl^- , and NO_3^- . Therefore, most of the elements, except about ten of them, occur at trace levels in natural waters. Being trace elements in natural waters does not necessarily qualify them as trace elements in rocks. For example, aluminum, iron, and titanium are major elements in rocks, but they occur as trace elements in waters, due to their low mobility at the Earth’s surface. Conversely, trace elements in rocks such as chlorine and carbon are major elements in waters.

The geochemistry of trace elements in river waters, like that of groundwater and seawater, is receiving increasing attention. This growing interest is clearly triggered by the technical advances made in the determination of concentrations at

lower levels in water. In particular, the development of inductively coupled plasma mass spectrometry (ICP-MS) has considerably improved our knowledge of trace-element levels in waters since the early 1990s. ICP-MS provides the capability of determining trace elements having isotopes of interest for geochemical dating or tracing, even where their dissolved concentrations are extremely low.

The determination of trace elements in natural waters is motivated by a number of issues. Although rare, trace elements in natural systems can play a major role in hydrosystems. This is particularly evident for toxic elements such as aluminum, whose concentrations are related to the abundance of fish in rivers. Many trace elements have been exploited from natural accumulation sites and used over thousands of years by human activities. Trace elements are therefore highly sensitive indexes of human impact from local to global scale. Pollution impact studies require knowledge of the natural background concentrations and knowledge of pollutant behavior. For example, it is generally accepted that rare earth elements (REEs) in

waters behave as good analogues for the actinides, whose natural levels are quite low and rarely measured. Water quality investigations have clearly been a stimulus for measurement of toxic heavy metals in order to understand their behavior in natural systems.

From a more fundamental point of view, it is crucial to understand the behavior of trace elements in geological processes, in particular during chemical weathering and transport by waters. Trace elements are much more fractionated by weathering and transport processes than major elements, and these fractionations give clues for understanding the nature and intensity of the weathering+transport processes. This has not only applications for weathering studies or for the past mobilization and transport of elements to the ocean (potentially recorded in the sediments), but also for the possibility of better utilization of trace elements in the aqueous environment as an exploration tool.

In this chapter, we have tried to review the recent literature on trace elements in rivers, in particular by incorporating the results derived from recent ICP-MS measurements. We have favored a “field approach” by focusing on studies of natural hydrosystems. The basic questions which we want to address are the following: What are the trace element levels in river waters? What controls their abundance in rivers and fractionation in the weathering+transport system? Are trace elements, like major elements in rivers, essentially controlled by source-rock abundances? What do we know about the chemical speciation of trace elements in water? To what extent do colloids and interaction with solids regulate processes of trace elements in river waters? Can we relate the geochemistry of trace elements in aquatic systems to the periodic table? And finally, are we able to satisfactorily model and predict the behavior of most of the trace elements in hydrosystems?

An impressive literature has dealt with experimental works on aqueous complexation, uptake of trace elements by surface complexation (inorganic and organic), uptake by living organisms (bioaccumulation) that we have not reported here, except when the results of such studies directly explain natural data. As continental waters encompass a greater range of physical and chemical conditions, we focus on river waters and do not discuss trace elements in groundwaters, lakes, and the ocean.

Section 7.7.2 of this chapter reports data. We will review the present-day literature on trace elements in rivers to show that our knowledge is still poor. By comparing with the continental abundances, a global mobility index is calculated for each trace element. The spatial and temporal variability of trace-element concentrations in rivers will be shown to be important. In **Section 7.7.3**, sources of trace elements in river waters are indicated. We will point out the great diversity of sources and the importance of global anthropogenic contamination for a number of elements. The question of inorganic and organic speciation of trace elements in river water will then be addressed in **Section 7.7.4**, considering some general relationships between speciation and placement in the periodic table. In **Section 7.7.5**, we will show that studies on organic-rich rivers have led to an exploration of the “colloidal world” in rivers. Colloids are small particles, passing through the conventional filters used to separate dissolved and suspended loads in rivers.

They appear as major carriers of trace elements in rivers and considerably complicate aqueous speciation calculation. Finally, in **Section 7.7.6**, the significance of interactions between solutes and solid surfaces in river waters will be reviewed. Regulation by surfaces is of major importance for a great range of elements. Although for both colloids and surface interactions, some progress has been made, we are still far from a unified model that can accurately predict trace-element concentrations in natural water systems. This is mainly due to our poor physical description of natural colloids, surface site complexation, and their interaction with solutes.

7.7.2 Natural Abundances of Trace Elements in River Water

Trace-element abundances in the dissolved load of a number of worldwide rivers, classified by continents, are compiled in **Table 1**, along with the corresponding references. These data have been measured after filtration of the river sample using either 0.2 μm or 0.45 μm filters. We have tried to report, as far as possible, “natural” river systems by discarding data from highly polluted systems. For the Amazon and Orinoco rivers, we have reported data for the dissolved load filtered using filters or membranes with smaller pore size. A major feature of trace-element abundances in river waters is that they are strongly dependent upon filtration characteristics. For simplicity, elements have been ranked in alphabetical order. Most often, data for large rivers are a compendium of data derived from different bibliographical sources and therefore have not been measured on the same river sample. However, in the case of the Amazon basin, two different analyses, corresponding to two different sampling dates are reported for the major tributaries. These comparisons show the high degree of variability of trace-element concentrations in river waters through time. When time series are available, a mean value is given in **Table 1**. It is apparent from these data that the Americas and Africa are the places where most of our information on natural levels of trace elements in waters has been obtained. By contrast, rivers of Asia have received relatively little attention, except for a number of key elements of geochemical importance such as osmium, strontium, and uranium.

North America. A substantial literature exists on the trace-element levels in North American rivers. We have focused in **Table 1** on the largest systems. Smaller and pristine watersheds from northern Canada have also been reported for comparison. The St. Lawrence system is represented by the St. Lawrence itself and by the Ottawa River, which, due to its status as an international standard of river water (SLRS 4), appears as the most often measured river. The Mistassini River is a black (high humic acid content) river discharging into St. Jean Lake and represents the North American end-member in terms of trace-element levels. Other large river systems include the Mackenzie and Peel rivers, the Fraser, the Columbia, Mississippi, Connecticut and Hudson rivers. Small rivers from the Mackenzie Basin have been reported, because they drain relatively pristine regions of North America with well-characterized geological substratum. The Indin River drains the Slave Province, dominated by old granites. The Beaton River is a typical black river and suspended sediment-rich

Table 1 Database of trace element concentration in the dissolved load ($<0.2 \mu\text{m}$) of rivers. All concentrations in ppb ($\mu\text{g L}^{-1}$) except for Ra (fg L^{-1}) and Os (pg L^{-1}). DOC, TSS, TDS are Dissolved Organic Carbon (mg L^{-1}), total suspended solid (mg L^{-1}), and total dissolved solutes (mg L^{-1}). Water discharge and surface are in $\text{m}^3 \text{s}^{-1}$ and 10^3km^2 , respectively.

<i>Element</i>	<i>References</i>	<i>pH</i>	<i>DOC</i>	<i>TSS</i>	<i>TDS</i>	<i>Discharge</i>	<i>Surface area</i>	<i>Ag</i>	<i>A</i>	<i>As</i>
Africa										
Oubangui	1	6.81		30	36.1	3,500	475		12	
Zaire	1	5.98		31	48.68	17,000	1,660		46	
Kasai	1	6.35		17		11,000	900		51	
Congo at Brazzaville	1, 2, 3	6.4		21		39,100	3,500		76	
Niger	2,4	7.00	1.5	43	44	907	141		76	
Douna	2,4									
Nyong	5	5.60	23	5	22	340	29		215	
Sanaga	6	7.43	3.82				133		29	0.17
Nyong	6	5.88	14.1			340	29		159	0.11
Mengong	6	4.62	24						480	0.11
Europe										
Seine at Paris, Fr.	7			40	400	260	44		16	2.71
Garonne River Fr.	8, 9			128	400	540	55			
Rhine in Alsace, Fr.	10	8.01	1.95						<50	
Vosges Stream, Fr.	10	7.10	2.03						76	
Harz Mountains, Ger.	11	5.10							1,080	0.37
Kalix River, Sweden, 1991	12, 45	6.95	3.4			296	24		27	
Kalix River, 1977 May	12					296	24			
Idel river	13	6.85	12.3			2	1		44	0.21
N. America										
St. Lawrence	2, 14, 15, 16, 46	8.00		11	183	10,700	1,020		15	0.91
SLRS 4	17								53	0.70
Ottawa	14								67	0.45
Mistassini, Can.	14	5.50	26	5		195	10		174	0.12
Mackenzie	2, 14, 18, 19	8.10	5.8	300	226	9,000	1,680		18	0.50
Peel, Can.	14	8.10	12.9	250	167	690	71		22	0.35
Indin River, Can.	14	6.70			12	8	2		28	0.14
Beatton, Can.	14	7.20		810	68				91	0.80
Upper Yukon, Can.	2, 14	7.70							25	0.62
Skeena, Can.	14	7.50	4.48	60	53	962	42		33	0.21
Fraser River, Can.	19, 20	7.34	3.39	175	93	3630	238		19	0.52
Columbia River	8, 19	7.85		64	115	5941	670			
Californian Streams	21									
Connecticut	22		3.16		70	540	25			
Hudson River	22, 23, 46	7.00			126	621	35	0.004		
Upper Mississippi	24	7.70		462						
Missouri	24, 25			2,332						
Ohio	25	7.70		177						
Illinois	25	8.20		102						
Mississippi at Mouth	3, 15, 19, 22, 25, 46	7.80		860	280	18,400	2,980			

(Continued)

Table 1 (Continued)

<i>Element</i>	<i>References</i>	<i>pH</i>	<i>DOC</i>	<i>TSS</i>	<i>TDS</i>	<i>Discharge</i>	<i>Surface area</i>	<i>Ag</i>	<i>A</i>	<i>As</i>				
S. America														
Amazon, mean value	3, 15, 26, 27, 28, 29, 46, 48	6.89		182	44	205,000	6,100		9.4					
Amazon <0.2 μm	19,30	7.10	5.05	182	44	205,000	6,100		6.2					
Amazon <100 kDa	30		2.96						0.8					
Amazon <5 kDa	30		1.11						0.5					
Negro <0.2 μm	26	4.85							113.9					
Negro <0.2 μm	30	5.87	7.17						97.0					
Solimoes <0.2 μm	26	7.10							171.4					
Solimoes <0.2 μm	30	7.66	2.76						5.8					
Madeira <0.2 μm	26	6.73							2.6					
Madeira <0.2 μm	30	7.54	11.1						4.3					
Trompetas <0.2 μm	26	6.10							39.2					
Trompetas <0.2 μm	30	6.54	1.85						7.9					
Tapajos <0.2 μm	26	6.68							15.2					
Tapajos <0.2 μm	30	7.45	1.48						4.0					
Rio Beni at Riberalta	31					8,262	243							
Mamore	31					8,392	599							
Rio Beni at Rurrenabaque	31					2,025	68							
Orinoco <0.2 μm	19, 27, 29, 30, 46, 48	6.51	5.42	132	25	35,900	1100		61.8					
Orinoco <10 kDa	27, 30		4.3						5.6					
Caroni at Ciudad Bolivar	19, 27, 29, 30, 32	5.58	3.71						16.1					
Asia														
Ob	33		7.4–9.95	40	126	13,500	2,990							
Yenisei	33		4	23	112	19,800	2,500							
Lena	2, 19, 34	7.60		30	112	19,100	1,200			0.15				
Changjiang	2, 3, 9, 19, 27, 35, 36, 37, 3	7.80		520	221	29,400	1,808			0.83				
Huanghe	2, 15, 38, 39, 40, 47	8.30		27,000	460	1300	752			2.00				
Xijiang	2, 15, 47	7.70		190	161	11,500	437							
Ganges	19, 29, 41, 42, 43, 46, 47, 4	7.70		1,100	182	15,600	1,050							
Mekong	2, 15, 47	7.80		321	263	14,800	795							
Brahmaputra	9, 19, 41, 42, 46, 47, 48	7.40		1,060	101	16,100	580							
Indus	9, 41, 44, 47	7.80		2,780	302	2880	960							
Shinano, Jpn.	44, 47	7.11				475	11							
World average									32	0.62				
Riverine flux (kt y ⁻¹)									1,200	23				
<i>Element</i>	<i>B</i>	<i>Be</i>	<i>Ba</i>	<i>Cd</i>	<i>Ce</i>	<i>Co</i>	<i>Cr</i>	<i>Cs</i>	<i>Cu</i>	<i>Dy</i>	<i>Er</i>	<i>Eu</i>	<i>Fe</i>	<i>Ga</i>
Africa														
Oubangui			17		0.4920	0.077	0.533	0.008		0.043	0.029	0.0160	60	
Zaire			24.8		0.6610	0.075	0.386	0.0026		0.053	0.033	0.0220	202	
Kasai					0.4520	0.0580	0.4	0.009		0.038	0.025	0.0140	108	
Congo at Brazzaville	3.1		20		0.6890	0.0594	0.501	0.016		0.006	0.033	0.0170	179	

Niger	3.2		30		0.1710	0.0400	0.450	0.0100	0.630				105	
Douna														
Nyong			18		1.3200	0.3637				0.119	0.071	0.0255	241	
Sanaga			27		0.1780	0.0590			0.952	0.015	0.016		31	
Nyong			19		0.8060	0.2530			2.030	0.086	0.055		174	0.0220
Mengong			24		0.8274	0.4307			1.397	0.059	0.027		614	0.1087
Europe														
Seine at Paris, Fr.	25.0		32	0.0600	0.0600	0.1800	11.46		3.53				302	
Garonne River Fr.					0.0810						0.004	0.0016		
Rhine in Alsace, Fr.					0.0096					0.002	0.001	0.0003		
Vosges Stream, Fr.					0.0930					0.020	0.012	0.0087		
Harz Mountains, Ger.	0.61		13	0.4200		0.2600	<0.85		0.820					
Kalix River, Sweden, 1991					0.2170								525	
Kalix River, 1977 May														
Idel river	39.0		5	0.0200	0.2430	0.0840	1.07	0.0112	0.456	0.013	0.008	0.0039	666	0.0088
N. America														
St. Lawrence	24.8		23	0.0114	0.0600	0.0632		0.0052	0.936	0.005	0.004	0.0030	111	
SLRS 4	6.0	0.008	13	0.0140	0.3600	0.0480	0.37	0.0090	1.930	0.024	0.013	0.0080	108	0.0119
Ottawa	3.3		15	0.0207	0.5599	0.0746		0.0061	1.144	0.040	0.023	0.0112	112	
Mistassini, Can.			8	0.0873	1.1771	0.1221		0.0070	1.578	0.036	0.022	0.0120	170	
Mackenzie	11.8		56	0.1838	0.0266	0.0682	0.375	0.0066	1.609	0.003		0.0023	119	
Peel, Can.			62	0.0347	0.0310	0.1426	0.294	0.0037	1.043	0.001	0.003	0.0019	152	
Indin River, Can.			3		0.1305	0.0158			0.841				50	
Beatton, Can.			47	0.1206	0.4750	0.1515	0.741	0.0028	2.594	0.072	0.056	0.0290	739	
Upper Yukon, Can.			50	0.0906	0.0311	0.0616	0.241	0.0049	1.306	0.009		0.0010	102	
Skeena, Can.			13	0.0194	0.0637	0.0794		0.0006	1.077				52	0.0083
Fraser River, Can.			15		0.0600	0.0800	2.1		1.040	0.009		0.0030	47	
Columbia River					0.0583							0.0016		
Californian Streams														0.001-0.006
Connecticut					0.0258					0.004	0.003	0.0009	10	
Hudson River					0.0621					0.013	0.008	0.0026		
Upper Mississippi			73						1.850					
Missouri			80						2.010					
Ohio			32						1.741					
Illinois			59						1.984					
Mississippi at Mouth	37.8		62		0.0074				1.60-2.24	0.004	0.004	0.0007		
S. America														
Amazon, mean value	6.1	0.0095	21	0.1781	0.2180	0.1766	0.717		1.463	0.033	0.018	0.0104		0.0174
Amazon <0.2 µm			28		0.0680					0.011	0.006	0.0027	43	0.0217
Amazon <100 kDa			26		0.0200					0.004	0.002	0.0007	23	
Amazon <5 kDa			17		0.0067					0.000	0.000		13	
Negro <0.2 µm			6		0.4150	0.1241			0.399	0.023	0.015	0.0088		0.0050
Negro <0.2 µm			7		0.5853					0.030	0.018	0.0078	117	
Solimoës <0.2 µm	3.8		28		0.3630	0.1643			1.542	0.044	0.028	0.0150	351	0.0390
Solimoës <0.2 µm			29		0.0528					0.007	0.004	0.0019	53	
Madeira <0.2 µm	3.4		18		0.1380	0.0176			0.863	0.024	0.013	0.0083	18	0.0025

(Continued)

Table 1 (Continued)

<i>Element</i>	<i>B</i>	<i>Be</i>	<i>Ba</i>	<i>Cd</i>	<i>Ce</i>	<i>Co</i>	<i>Cr</i>	<i>Cs</i>	<i>Cu</i>	<i>Dy</i>	<i>Er</i>	<i>Eu</i>	<i>Fe</i>	<i>Ga</i>
Madeira < 0.2 µm			32		0.0074					0.001	0.001		26	0.0169
Trompetas < 0.2 µm	1.5		14		0.9080	0.1274			0.269	0.044	0.028	0.0105	87	0.0059
Trompetas < 0.2 µm			15		0.1300					0.007	0.005	0.0017	30	
Tapajos < 0.2 µm			21		0.1150	0.0195			0.227	0.012	0.008	0.0033		0.0033
Tapajos < 0.2 µm			18		0.0277					0.003	0.002	0.0007	11	0.0178
Rio Beni at Riberaita			30	0.0081					1.517					
Mamore			4	0.0091					1.997					
Rio Beni at Rurrenabaque			23	0.0011					0.710					
Orinoco < 0.2 µm		0.009	8		0.5207			0.007–0.013		0.056	0.031	0.0140	142	0.1176
Orinoco < 10 kDa			8		0.1703					0.020	0.012	0.0047	15	0.1143
Caroni at Ciudad Bolivar	2.4	0.0135	7		0.1443			0.006		0.012	0.006	0.0032	16	0.1027
Asia														
Ob				0.0006–0.0008					1.8–2.4				24–36	
Yenisei				0.0012–0.0018					1.39–1.91				14–17.8	
Lena	4.7			0.0089					0.755				24.3	
Changjiang	12.5			0.0033	0.1150				1.66			0.0050	31	
Huanghe	150.0			0.0011–0.0055		0.0059–0.0295			0.96–1.6				1.4–25	
Xijiang	6.0													
Ganges	17.8	0.00056												
Mekong	15.0													
Brahmaputra	20.9													
Indus					0.0024					0.001	0.001	0.0002		
Shinano, Jpn.					0.0834					0.012	0.007	0.003		
World average	10.2	0.0089	23	0.08	0.2620	0.148	0.7	0.011	1.48	0.03	0.02	0.0098	66	0.03
Riverine flux (kt yr ⁻¹)	380	0.33	860.2	3	9.8	5.5	26	0.4	55	1.1	0.75	0.37	2470	1.1
<i>Element</i>	<i>Gd</i>	<i>Ge</i>	<i>Hf</i>	<i>Ho</i>	<i>La</i>	<i>Li</i>	<i>Lu</i>	<i>Mn</i>	<i>Mo</i>	<i>Nb</i>	<i>Nd</i>	<i>Ni</i>	<i>Os (pg L⁻¹)</i>	<i>P</i>
Africa														
Oubangui	0.0510		0.0042	0.0090	0.249		0.0040				0.277	1.15		
Zaire	0.0630		0.0057	0.0110	0.349		0.0040				0.360	1.02		
Kasai	0.0470		0.0038	0.0080	0.189		0.0030				0.241	0.41		
Congo at Brazzaville	0.0660	0.0066	0.0067	0.0120	0.319		0.0045				0.350	0.934	6.7	
Niger			0.0030		0.091			0.50			0.085	0.29	5.3	
Douna														
Nyong	0.1343			0.0199	0.538		0.0080	29.72			0.690			
Sanaga	0.0240				0.09			0.44			0.084	0.70		
Nyong	0.0940	0.0065		0.0165	0.349		0.0105	22.61			0.505	1.18		
Mengong	0.0551	0.0799		0.0116	0.348		0.0053	20.02			0.416	5.04		

Europe													
Seine at Paris, Fr.				0.030			3.76			0.030	5.06	41.8	
Garonne River Fr.	0.0088		0.0016	0.047		0.0006				0.038			
Rhine in Alsace, Fr.	0.0025		0.0004	0.005		0.0004				0.005			
Vosges Stream, Fr.	0.0037		0.0041	0.153		0.0014				0.245			
Harz Mountains, Ger.				0.480	2.00		48.00				0.92		
Kalix River, Sweden, 1991				0.155			9.40						
Kalix River, 1977 May													
Idel river	0.0190	0.0082		0.0027	0.151	0.80	0.0015	22.80	0.112		0.141	0.35	2.67
N. America													
St. Lawrence	0.0059	0.0031	0.0031	0.0013	0.029		0.0006	6.28	1.292	0.0021	0.038	1.33	22.8
SLRS 4	0.0342	0.0100		0.0047	0.287	0.54	1.9000	3.37	0.210		0.269	0.82	
Ottawa	0.0593	0.0086	0.0034	0.0078	0.411		0.0037	14.86	0.199	0.0045	0.411	0.83	
Mistassini, Can.	0.0618	0.0058	0.0070	0.0071	0.635		0.0025	11.31	0.039	0.0107	0.547	0.47	
Mackenzie	0.0019			0.0005	0.002	4.60		1.28	1.067	0.0012	0.019	1.83	25.5
Peel, Can.	0.0116			0.0020	0.002		0.0024	4.54	1.078	0.0019	0.004	2.68	
Indin River, Can.					0.099	0.91		1.89			0.091	0.64	1.82
Beaton, Can.	0.1599	0.0049	0.1106	0.0101	0.090			2.98	0.301	0.0069	0.042	5.14	
Upper Yukon, Can.	0.0136	0.0196		0.0010	0.001	0.64	0.0006	2.29	1.055	0.0019	0.007	10.39	24.7
Skeena, Can.		0.0014			0.051	0.35		5.37	0.418		0.081	0.91	
Fraser River, Can.	0.0110				<0.05	1.05		5.40	1.330		0.044	1.86	
Columbia River	0.0065	0.0138		0.0009	0.030	1.46	0.0007				0.023		
Californian Streams													
Connecticut	0.0047				0.021						0.020		
Hudson River	0.0190						0.0007				0.060		
Upper Mississippi								0.41	1.114			1.66	
Missouri								0.44	1.613			1.53	
Ohio								0.46	1.258			1.12	
Illinois								0.7	2.314			2.92	
Mississippi at Mouth	0.0042	0.0219			0.008	10	0.0006	0.66–1.82	1.63–2.69		0.011	1.12–1.77	
S. America													
Amazon, mean value	0.0356	0.0048		0.0064	0.106	0.91	0.0020	50.73	0.175		0.136	0.74	4.6
Amazon <0.2 µm	0.0123	0.0074		0.0021	0.032	2.46	0.0009	3.31			0.042		
Amazon <100 kDa	0.0043	0.0076		0.0007	0.010		0.0003	2.90			0.013		
Amazon <5 kDa	0.0007	0.0061		0.0001	0.006			2.00			0.003		
Negro <0.2 µm	0.0350			0.0050	0.151		0.0016	8.24			0.172	0.21	
Negro <0.2 µm	0.0432	0.0046		0.0061	0.208		0.0023	7.35			0.211		14.45
Solimoes <0.2 µm	0.0490			0.0093	0.166	1.02	0.0037	14.56			0.226	0.92	
Solimoes <0.2 µm	0.0089	0.0093		0.0017	0.050		0.0006	6.54			0.032		
Madeira <0.2 µm	0.0260			0.0053	0.054	1.18	0.0014				0.100	0.57	
Madeira <0.2 µm	0.0018	0.0041		0.0003	0.005		0.0001	3.29			0.005		
Trompetas <0.2 µm	0.0485			0.0093	0.266	0.41	0.0037	8.62			0.309	0.12	
Trompetas <0.2 µm	0.0102	0.0049		0.0016	0.044		0.0008	1.36			0.053		2.57
Tapajos <0.2 µm	0.0114			0.0020	0.228		0.0009	1.34			0.072	0.22	
Tapajos <0.2 µm	0.0037	0.0053		0.0007	0.016		0.0004	0.46			0.018		
Rio Beni at Riberaita								4.13	0.380			0.91	

(Continued)

Table 1 (Continued)

Element	Gd	Ge	Hf	Ho	La	Li	Lu	Mn	Mo	Nb	Nd	Ni	Os (pg L ⁻¹)	P	
Mamore								113.52	0.240			1.11			
Rio Beni at Rurrenabaque								2.37	0.218			0.79			
Orinoco <0.2 μm	0.0737			0.0107	0.177	0.32	0.0043	6.82			0.289			11.09	
Orinoco < 10 kDa	0.0256			0.0040	0.049		0.0018	5.24			0.094			6.10	
Caroni at Ciudad Boliver	0.0147			0.0021	0.067	0.16	0.0009	5.57			0.078		3.3	6.61	
Asia															
Ob												1.24–1.42			
Yenisei												0.52–0.55			
Lena						1.33						0.38	8.2		
Changjiang		0.0122			0.005	3.44	0.0020	1.00			0.070	0.15	13.9		
Huanghe								0.55–2.2				0.30–0.59	42.1		
Xijiang													8.3		
Ganges						3.47							32.0		
Mekong													17.2		
Brahmaputra						2.61							9.9		
Indus					0.003		0.0002				0.003		11.2		
Shinano, Jpn.					0.037		0.0016				0.050				
World average	0.04	0.0068	0.0059	0.0071	0.12	1.84	0.0024	34	0.42	0.0017	0.152	0.801	9.0		
Riverine flux (kt yr ⁻¹)	1.5	0.25	0.22	0.27	4.5	69	0.09	1270	16	0.063	5.7	30	0.33.10–3		
Element	Pb	Pd	Pr	Ra (fg L ⁻¹)	Re	Rb	Sb	Sc	Se	Sm	Sr	Ta	Tb	Th	Ti
Africa															
Oubangui			0.069			2.7		0.055		0.0600	15.0		0.0070	0.042	
Zaire			0.093			3.9		0.067		0.0820	21.0		0.0100	0.056	
Kasai			0.052			2.7		0.062		0.0470	10.5		0.0060	0.023	
Congo at Brazzaville			0.089			3.1		0.087		0.0620	11.5		0.0097	0.065	
Niger	0.039					3.86					26.4			0.013	
Douna															
Nyong			0.179			4.18				0.1362	9.7		0.0178	0.121	
Sanaga			0.024			6.16					30.3			0.012	0.231
Nyong			0.114			3.68				0.1210	12.4			0.111	0.199
Mengong			0.096			0.73				0.0780	17.9			0.137	5.808
Europe															
Seine at Paris, Fr.	0.220					1.40		1.340			227.0			0.010	
Garonne River Fr.			0.005							0.0082			0.0012		
Rhine in Alsace, Fr.			0.001							0.0012			0.0003		
Vosges Stream, Fr.			0.049							0.0500			0.0046		
Harz Mountains, Ger.	3.800					5.90	0.190				20.0				
Kalix River, Sweden, 1991															
Kalix River, 1977 May															
Idel river	0.119		0.037			0.96	0.027			0.0240	16.8		0.0025	0.022	1.070

N. America														
St. Lawrence	0.233		0.009	2		1.04	0.205		0.0067	177.2		0.0010	0.004	0.509
SLRS 4	0.084	0.021	0.069			1.53	0.270	0.230	0.0574	28.2		4.3000		1.460
Ottawa	0.105		0.104			1.55	0.057		0.0705	50.7		0.0073	0.027	1.854
Mistassini, Can.	0.113		0.149	48		1.14	0.023		0.0783	11.4		0.0085	0.041	2.278
Mackenzie	0.771		0.012			0.66	0.121		0.0055	237.8	0.0009		0.634	0.423
Peel, Can.	1.129		0.012			0.36	0.120		0.0149	154	0.0029	0.0025	0.588	0.574
Indin River, Can.		0.001	0.023			1.77	0.005		0.0152	10.5				0.112
Beaton, Can.	0.269		0.132			0.30	0.102		0.1849	62.7	0.1484	0.0289	1.054	1.200
Upper Yukon, Can.	0.818		0.006			0.90	0.150		0.0056	162.2		0.0010	0.988	0.768
Skeena, Can.		0.028	0.015			0.20	0.044		0.0230	78.4				0.372
Fraser River, Can.	0.078		0.011			0.91	0.053	0.141	0.0110	108.0				0.680
Columbia River			0.01						0.0435			0.0012		
Californian Streams														
Connecticut									0.0042					
Hudson River				4–31					0.0119					
Upper Mississippi	0.008					1.24								
Missouri	0.006					0.93								
Ohio	0.007					0.87								
Illinois	0.035					0.94								
Mississippi at Mouth	0.011–0.016		5–30			1.17			0.003					
S. America														
Amazon, mean value	0.064		0.031	9–31	0.00020	1.49	0.061	0.051	0.0349	25.8		0.0043		
Amazon <0.2 μm			0.009			1.89	1.540		0.0100	51.2		0.0017	0.006	
Amazon <100 kDa			0.003			1.79	1.580		0.0041	47.2		0.0007		
Amazon < 5 kDa			0.001			1.29	1.550			31.3				
Negro < 0.2 μm	0.170		0.047			1.13			0.0380	3.6		0.0040		
Negro < 0.2 μm			0.054			1.73	0.900		0.0390	4.2		0.0056	0.053	
Solimoes < 0.2 μm	0.151		0.052			1.59			0.0520	45.7		0.0067	0.010	
Solimoes < 0.2 μm			0.007			1.69	1.770		0.0082	61.5		0.0014	0.002	
Madeira < 0.2 μm	0.005		0.022			1.34			0.0311	19.2		0.0048		
Madeira < 0.2 μm			0.001			1.94	1.510		0.0014	55.5		0.0002	0.001	
Trompetas < 0.2 μm	0.052		0.080			2.95			0.0596	6.7		0.0061	0.121	
Trompetas < 0.2 μm			0.013			4.04	1.260		0.0094	9.6		0.0012	0.016	
Tapajos < 0.2 μm	0.061		0.017			2.75			0.0181	9.9		0.0015		
Tapajos < 0.2 μm			0.004			2.08	1.410		0.0040	6.5		0.0005	0.002	
Rio Beni at Riberaita						1.01				42.9				
Mamore						1.44				31.4				
Rio Beni at Rurrenabaque						0.90				48.3				
Orinoco < 0.2 μm			0.062	12–17	0.00083	1.50	0.560	0.032–0.050	0.0682	8.0		0.0098	0.073	
Orinoco < 10 kDa			0.020			1.43	0.620		0.0234	7.5		0.0035	0.026	
Caroni at Ciudad Bolivar			0.019			1.13	0.530	0.019–0.020	0.0153	2.9		0.0020	0.017	
Asia														
Ob	0.011–0.017													
Yenisei	0.005–0.006													
Lena	0.019													

(Continued)

Table 1 (Continued)

<i>Element</i>	<i>Pb</i>	<i>Pd</i>	<i>Pr</i>	<i>Ra (fg L⁻¹)</i>	<i>Re</i>	<i>Rb</i>	<i>Sb</i>	<i>Sc</i>	<i>Se</i>	<i>Sm</i>	<i>Sr</i>	<i>Ta</i>	<i>Tb</i>	<i>Th</i>	<i>Ti</i>
Changjiang	0.054			50					0.22–0.23	0.0150	210				
Huanghe	0.010–4.1										1140				
Xijiang											110				
Ganges				45–90	0.00170						90				
Mekong											298				
Brahmaputra				31	0.00011						59				
Indus										0.0007	324				
Shinano, Jpn.										0.0110					
World average	0.079	0.028	0.04	24	0.0004	1.63	0.07	1.2	0.07	0.036	60.0	0.0011	0.0055	0.041	0.489
Riverine flux (kt yr ⁻¹)	3	1.05	1.5	0.9.10–6	0.015	60.962	2.6	45	2.6	1.3	2240	0.04	0.2	1.5	18
<i>Element</i>	<i>Tl</i>	<i>Tm</i>	<i>U</i>	<i>V</i>	<i>W</i>	<i>Y</i>	<i>Yb</i>	<i>Zn</i>	<i>Zr</i>						
Africa															
Oubangui		0.0040	0.055				0.0240								
Zaire		0.0050	0.071				0.0270								
Kasai		0.0030	0.027				0.0190								
Congo at Brazzaville		0.0035	0.049				0.0290								
Niger			0.020	0.590				0.89	0.120						
Douna															
Nyong		0.0085	0.029	0.645			0.0597		0.395						
Sanaga			0.028			0.0870		1.02	0.038						
Nyong		0.0085	0.022			0.4610	0.0530	1.81	0.355						
Mengong		0.0051	0.022			0.2821	0.0311	3.12	0.592						
Europe															
Seine at Paris, Fr.			0.820	2.850		0.0500		4.98							
Garonne River Fr.		0.0006	0.750				0.0036								
Rhine in Alsace, Fr.							0.0018								
Vosges Stream, Fr.							0.0120								
Harz Mountains, Ger.	0.0400		0.060	0.400		1.4000		27.00							
Kalix River, Sweden, 1991			0.090												
Kalix River, 1977 May															
Idel river		0.0015	0.038	0.442		0.0920	0.0079	6.30	0.130						
N. America															
St. Lawrence		0.0006	0.373	0.439		0.0320	0.0029	2.58	0.022						
SLRS 4	0.0076	0.0002	0.050	0.350		0.1460	0.0120	1.24	0.120						
Ottawa		0.0035	0.072	0.341		0.2173	0.0201	3.53	0.086						
Mistassini, Can.		0.0025	0.022	0.324		0.2033	0.0191	3.79	0.047						
Mackenzie		0.0016	0.730	0.253		0.0313	0.0073	0.50	0.054						
Peel, Can.		0.0011		0.236		0.0574		0.88	0.038						
Indin River, Can.				0.009		0.0533		1.52	0.037						

Beaton, Can.	0.0087		0.398		0.8936		1.34	0.710
Upper Yukon, Can.			0.347		0.0283	0.0040	2.29	0.041
Skeena, Can.			0.106		0.1412			0.048
Fraser River, Can.		0.330	0.390		0.0690			
Columbia River						0.0045		
Californian Streams				0.1–180				
Connecticut						0.0047		
Hudson River						0.0091		
Upper Mississippi		1.285	2.055				0.21	
Missouri		1.142	0.638				0.12	
Ohio		0.333	0.581				0.17	
Illinois		1.404	1.770				0.98	
Mississippi at Mouth		0.62–1.3	0.82–1.84			0.0044	0.18–0.35	
S. America								
Amazon, mean value	0.0033	0.052	0.703		0.0159	0.45		
Amazon <0.2 μm	0.0009	0.055			0.0051	0.76		0.027
Amazon, <100 kDa	0.0003	0.022			0.0016			0.004
Amazon, <5 kDa		0.004				0.80		
<i>Negro</i> , <0.2 μ m	<i>0.0024</i>	<i>0.019</i>			<i>0.0100</i>	<i>1.80</i>		
Negro, <0.2 μ m	0.0025	0.034			0.0169	1.21		0.068
<i>Solimoes</i> , <0.2 μ m	<i>0.0045</i>	<i>0.040</i>			<i>0.0214</i>	<i>2.35</i>		
Solimoes, <0.2 μ m	0.0006	0.050			0.0037	3.01		0.008
<i>Madeira</i> , <0.2 μ m	<i>0.0025</i>	<i>0.023</i>			<i>0.0092</i>	<i>0.67</i>		
Madeira, <0.2 μ m	0.0001	0.026			0.0007	0.67		0.001
<i>Trompetas</i> , <0.2 μ m	<i>0.0041</i>	<i>0.044</i>			<i>0.0264</i>	<i>1.15</i>		
Trompetas, <0.2 μ m	0.0006	0.024			0.0043	1.16		0.026
<i>Tapajos</i> , <0.2 μ m	<i>0.0013</i>	<i>0.019</i>			<i>0.0055</i>	<i>1.02</i>		
Tapajos, <0.2 μ m	0.0003	0.015			0.0019	0.75		0.003
Rio Beni at Riberalta		0.033				0.46		
Mamore		0.042				0.27		
Rio Beni at Rurrenabaque		0.060				0.40		
Orinoco, <0.2 μ m	0.0043	0.049				1.75		0.105
Orinoco, <10 kDa	0.0018	0.023				2.42		0.029
Caroni at Ciudad Bolivar	0.0009	0.012				1.53		0.070
Asia								
Ob								
Yenisei								
Lena						0.36		
Changjiang		1.100			0.0080	0.039–0.078		
Huanghe		7.500				0.065–0.32		
Xijiang								
Ganges		2.000						

(Continued)

Table 1 (Continued)

<i>Element</i>	<i>Tl</i>	<i>Tm</i>	<i>U</i>	<i>V</i>	<i>W</i>	<i>Y</i>	<i>Yb</i>	<i>Zn</i>	<i>Zr</i>
Mekong									
Brahmaputra			1.000						
Indus			4.940			0.0009			
Shinano, Jpn.						0.0071			
World average		0.0033	0.372	0.71	0.1	0.0400	0.0170	0.60	0.039
Riverine flux (kt yr ⁻¹)		0.12	14	27	3.7	1.5	0.6	23	1.5

(1) Dupré et al. (1996), (2) Levasseur et al. (1999), (3) Froelich et al. (1985), (4) Picouet et al. (2001), (5) Viers et al. (2000), (6) Viers et al. (1997), (7) Roy (1996), (8) Keasler and Loveland (1982), (9) Chabaux et al. (2001), (10) Tricca et al. (1999), (11) Frei et al. (1998), (12) Ingri et al. (2000), (13) Pokrovski and Schot (2002), (14) Gaillardet et al. (2003), (15) Lemarchand et al. (2000), (16) Andrae and Froelich (1985), (17) Yeghicheyan et al. (2000), (18) Vigier et al. (2001), (19) Huh et al. (1998), (20) Cameron et al. (1995), (21) Johannesson et al. (1999), (22) Sholkovitz (1995), (23) Benoit (1995), (24) Shiller (1997), (25) Shiller and Mao (2000), (26) Gaillardet et al. (1997), (27) Yee et al. (1987), (28) Seyler and Boaventura (2002), (29) Brown et al. (1992a), (30) Deberdt et al. (2002), (31) Elbaz-Poulichet et al. (1999), (32) Edmond et al. (1995), (33) Dai and Martin (1995), (34) Martin et al. (1993), (35) Zhang et al. (1998), (36) Shiller and Boyle (1985), (37) Edmond et al. (1985), (38) Huang et al. (1988), (39) Zhang (1994), (40) Zhang et al. (1993), (41) Sharma et al. (1999), (42) Sarin et al. (1990), (43) Dalai et al. (2001), (44) Goldstein and Jacobsen (1988), (45) Porcelli et al. (1997), (46) Chabaux et al. (2003), (47) Gaillardet et al. (1999a), (48) Colodner et al. (1993).

river draining the interior sedimentary platform. Other rivers drain the western Cordillera, composed of volcanic and volcanoclastic rocks (Upper Yukon and Skeena rivers) or sedimentary rocks (Peel river).

Europe. Situation is far less favorable in Europe. Fewer data are available in the standard scientific literature and most of the rivers are strongly impacted by pollution. Only the rivers from the northern part of Europe (Kola peninsula) reported by Pokrovski and Schott (2002) are probably close to the natural background. The enhancement of dissolved concentrations for a number of elements due to human activities is apparent from the data on the Seine River. Data for REEs in the Rhine River and streams from the Vosges mountains in Alsace and central Europe have been reported for comparison. All these locations are known to have suffered from acid deposition in the very recent past.

Africa. Recently published studies have considerably improved our knowledge of trace-element concentrations in the rivers of central Africa. We have reported in Table 1 data for the Congo–Zaire River (the second largest river in the world in terms of discharge) and its main tributaries (Ubangui, Kasai, and Zaire), data from the upper Niger and Douna (the main tributary of the Niger river) and from smaller rivers in Cameroon. The Mengong River is a small stream that has been shown to have extreme concentrations of certain trace elements. All the rivers reported for Africa drain the humid and forested part of the continent.

South America. Due to its importance in terms of water discharge and to generally high trace-element levels, the Amazon river system has been well documented for a number of elements, including their seasonal variations. In Table 1, we have reported different analyses of the Amazon River and its major tributaries to show their temporal variability at a given location. Results of ultrafiltration experiments for the Amazon and Orinoco rivers demonstrate that the concentration of a number of elements in waters depends on filtration pore size. Finally, data for some Andean tributaries of the Madeira River have been reported. They show remarkably similar levels to those of the Amazon. Trace-element data for rubidium caesium barium and uranium have been measured for the Guyana shield.

Asia. Large rivers of Asia are clearly the less well documented in terms of trace-element concentrations. This is mainly due to their low abundances of trace elements, probably related to their high pH character. A couple of studies have focused on the riverine input of metals to the Arctic and Pacific oceans. Himalayan rivers have not been documented for REEs (except the Indus river?), but have been analyzed for particular elements such as strontium uranium osmium and radium. There is clearly a need for data on trace elements in the rivers of Asia, particularly in the highly turbid peri-Himalayan rivers.

7.7.2.1 Range of Concentrations of Trace Elements in River Waters

Based on the compilation of Table 1, an attempt has been made to compute the mean value of trace-element input to the estuaries and ocean by selecting the largest rivers (Congo, Niger, Sanaga, Seine, Garonne, Kalix, Idel, St. Lawrence, Mackenzie, Peel, Fraser, Columbia, Connecticut, Hudson, Mississippi, Amazon, Orinoco, Ob, Yenisei, Lena, Changjiang, Huanghe,

Xijiang, Ganges, Mekong, Brahmaputra, and Indus). This calculation is based on the assumption that our database is representative of most of the rivers and a total water discharge of $3.74 \times 10^4 \text{ km}^3 \text{ yr}^{-1}$ (Berner and Berner, 2012).

This mean value should be considered as a firstorder approximation, because for the majority of elements, the number of analyses is small. Because our best information on trace concentrations is from humid tropical areas, the mean values proposed here are dominated by rivers such as the Amazon, Orinoco, and Congo, and may therefore be overestimates for a number of elements (such as REEs). For trace metals, the role of global pollution is an unresolved issue that may also contribute to enhancing the mean value proposed in Table 1 (especially for trace metals). These values compare relatively well with the previous estimates of Martin and Meybeck (1979) for selected trace elements, with the exception of lower concentrations for some metals in the present study.

The results of Table 1 are summarized in Figure 1, in which elements are ranked according to the order of magnitude of their concentration in river water. Trace-element concentrations in river waters span 10 orders of magnitude, from elements present in extremely low concentrations such as radium (on the order of fg L^{-1}) to elements present in relatively high concentrations such as iron, aluminum, and barium whose concentration range exceeds $10 \mu\text{g L}^{-1}$. In between, the vast majority of trace elements have dissolved concentrations between 1 ng L^{-1} and $1 \mu\text{g L}^{-1}$ (heavy REEs (HREEs), transition metals). The platinum group elements (PGEs) are represented by osmium and show very low concentrations, $\sim 10 \text{ pg L}^{-1}$. Very few data exist for PGEs in river waters.

7.7.2.2 Crustal Concentrations versus Dissolved Concentrations in Rivers

The abundances of trace elements in rivers depends both on their abundances in the continental crust and their mobility during weathering and transport. In order to depict a global “solubility” trend of trace elements, dissolved concentrations (C_w) must be normalized to those of the upper continental crust (C_c) (Figure 2). Data from the continental crust are from Li (2000). In this figure, major elements in river waters are also shown and all normalized concentrations are compared to the value for sodium. It is important to note that the C_w/C_c ratio is a global mobility index rather than a solubility index because, as will be shown below, a number of very different processes contribute to the occurrence of trace elements in river dissolved load. In addition, for a number of rarely measured elements, the concentrations in the upper continental crust may well not be correct. The graph of Figure 2 is therefore a first-order approach.

A rough classification of trace-element mobility in river waters can be drawn. The first group comprises the highly mobile elements, having mobility close to or greater than that of sodium. It consists of chlorine, carbon, sulfur, rhenium, cadmium, boron, selenium, arsenic, antimony, molybdenum, calcium, magnesium, and strontium. The case of palladium is uncertain because few data are available, and its enrichment in Figure 2 could well be a result of an incorrect continental crust concentration. The following group of moderately mobile elements includes uranium, osmium, silicon, lithium, tungsten, potassium, manganese, barium, copper, radium, rubidium,

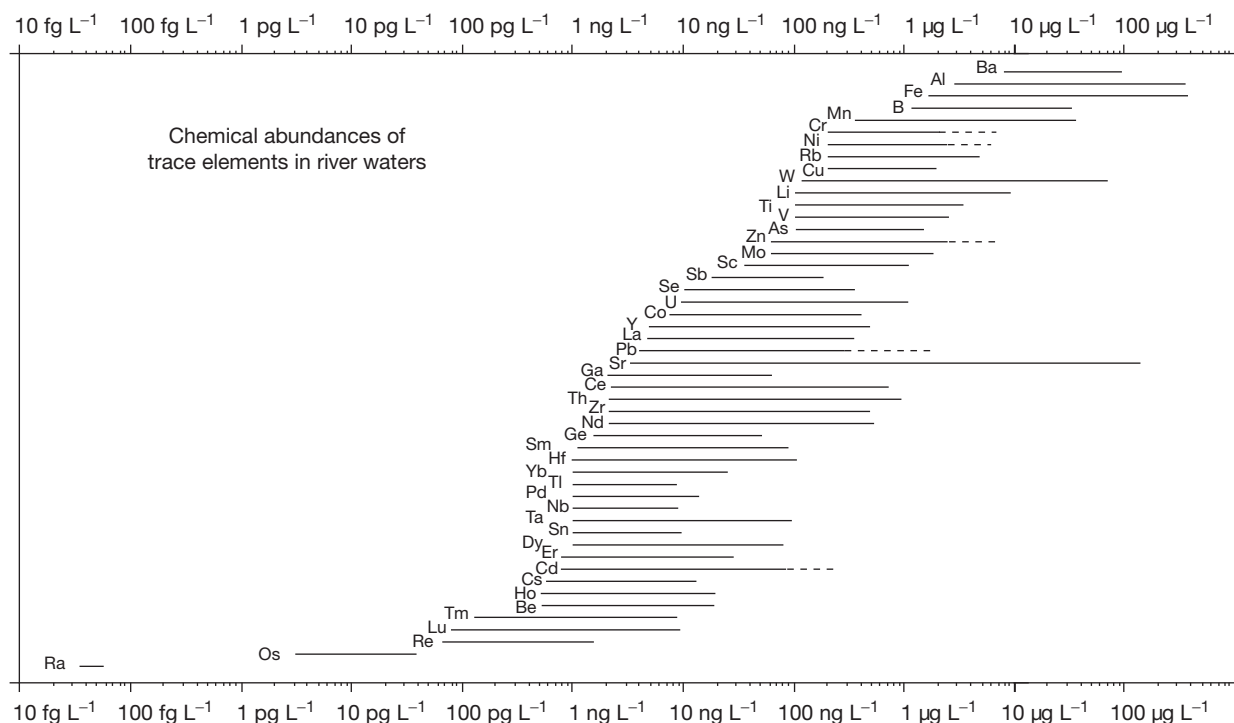


Figure 1 Graphical representation of the order of magnitude of natural trace-element concentrations in the river dissolved load. World average values derived from [Table 1](#).

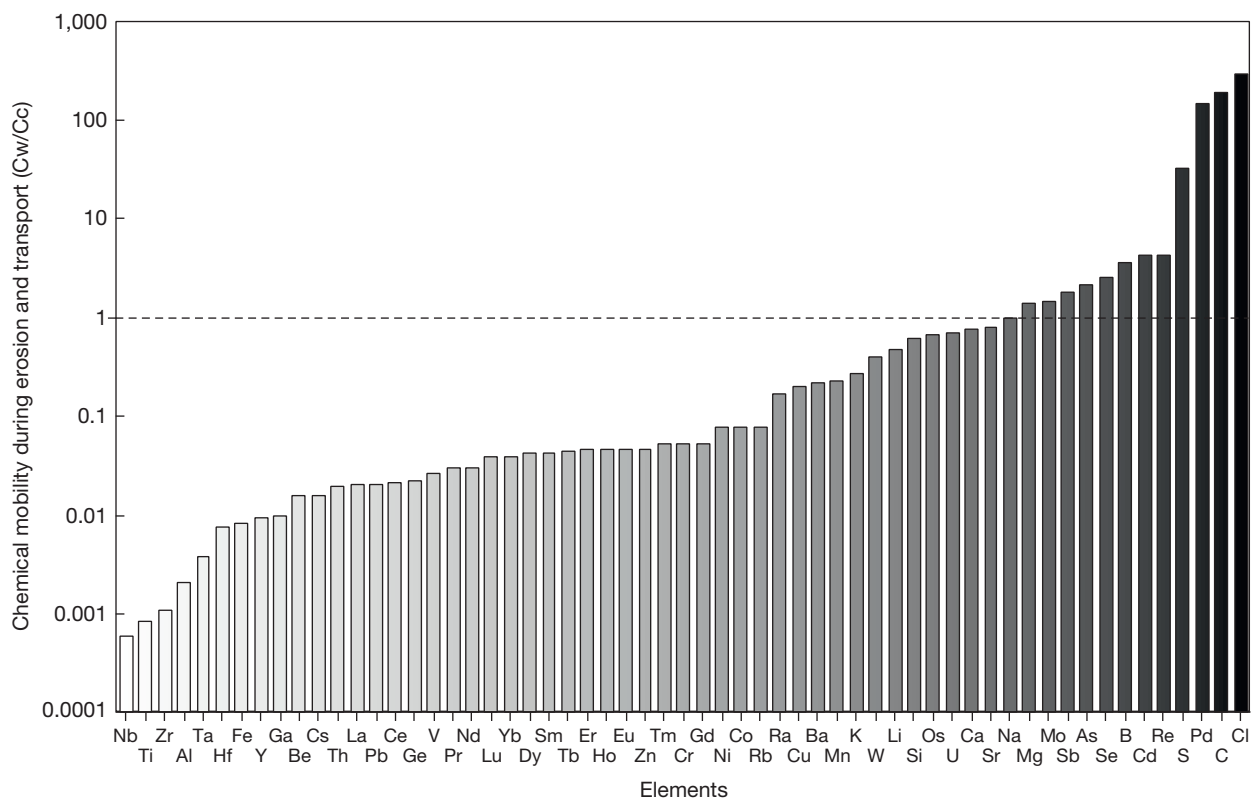


Figure 2 Normalization diagram of dissolved concentrations in rivers (C_w , [Table 1](#)) to continental abundances (C_c , [Li, 2000](#)). All values are compared to that of Na. This graph shows the increasing mobility of the elements in the weathering + transport processes, from the left to the right.

cobalt, and nickel. Their mobility is ~ 10 times less than that of sodium. The third group of elements contains the REEs, zinc, chromium, yttrium, vanadium, germanium, thorium, lead, caesium, beryllium, gallium, iron, and hafnium. Their mobility is 10–100 times less than that of sodium. We will call them the nonmobile elements. Finally, the last category, the most immobile elements, includes niobium, titanium, zirconium, aluminum, and tantalum, with mobility indexes more than 100 times lower than that of sodium. Depending on weathering, soil and river conditions, it is clear that some elements of these groups can pass to another group (e.g., for highly variable elements such as aluminum, iron, rubidium, lithium, and manganese), but the picture described here should be considered as an average global trend. At present, the database of trace elements in river waters is too incomplete, but there is probably much information on the processes that control the distribution of trace elements in river waters to be gained by addressing the variability of trace-element concentrations in rivers. Part of this variability corresponds to seasonal variability (see below).

7.7.2.3 Correlations between Elements

Generally, trace-element variations are not independent, and a number of authors have reported good correlations among trace elements or between trace elements and major elements. These correlations allow us to isolate groups of elements that present similar behavior during weathering and transport.

Interrelationships between trace elements and major elements or within the group of trace elements give information not only on their origin, but also about the mechanisms controlling the transport of the elements in rivers.

A clear distinction exists between trace elements whose abundance follows the abundance of major elements or TDS, and those whose concentrations are decoupled from the variations of major ions. This is illustrated by the dendrogram (Figure 3) deduced from a cluster analysis of trace-element concentration in the river waters of the Congo Basin (from Dupré et al., 1996). In the Congo waters, three categories are revealed by a cluster analysis. In the first set of elements, uranium, rubidium, barium, and strontium are closely related to variations of major elements. By contrast, REE variations are not correlated with those of the previous set but rather co-vary with thorium, scandium, and chromium (elements of the second set). A third set of elements showing good intercorrelation consists of caesium, cobalt, iron, and aluminum. The behavior of the latter elements is decoupled from that of the major elements but close to that of the REE group. Elements from both second and third sets show decreasing concentrations with increasing pH, in contrast to elements of the first set.

On a global scale, alkali and alkaline earth trace elements are strongly correlated to either sodium, calcium, or TDS in rivers (Edmond et al., 1995, 1996). Beryllium is an alkaline-earth element with a peculiar behavior. As shown by Brown et al. (1992a,b) and Willenbring and Von Blanckenburg (2010), it is easily adsorbed by particle surfaces. Like beryllium, caesium has a behavior that contrasts with that of the other alkali elements. In the Upper Beni river (Bolivia) good correlations between molybdenum, zinc, cadmium, rubidium, strontium, barium and major solutes have been reported, indicating that under those conditions, trace metals can also co-vary with major

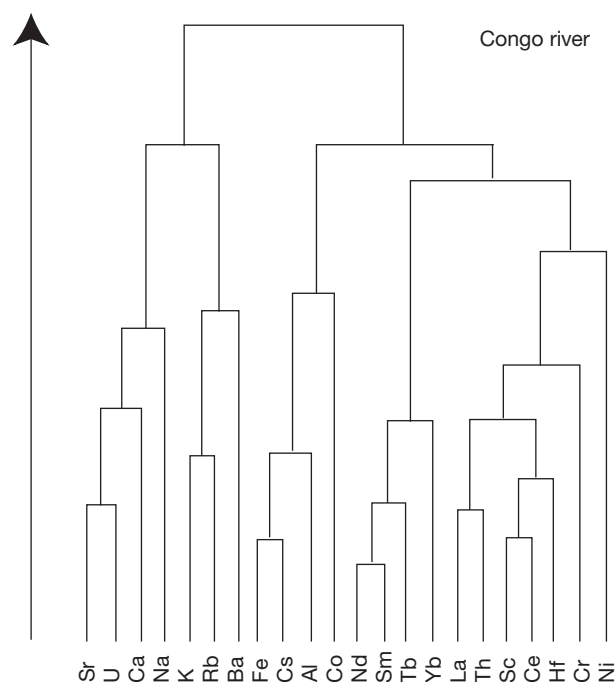


Figure 3 Dendrograms of cluster analysis of the trace-element concentrations in the dissolved load of the Congo rivers (Dupré et al., 1996) showing affinity groupings of elements.

elements (Elbaz-Poulitchet et al., 1999). From the largest tributaries of the Amazon basin, Seyler and Boaventura (2001) reported that vanadium, copper, arsenic, barium, and uranium concentrations are strongly positively correlated with major elements and pH. A correlation of vanadium with HCO_3^- has also been reported by Shiller and Mao (2000) in Californian streams. Other trace metals, in nonorganic contexts, have been shown to follow major elements, e.g., the correlation between copper and silica concentrations reported by Zhang and Huang (1992) for the Huanghe River.

Selenium concentrations correlate with those of calcium and sulfate in the Orinoco river system (Yee et al., 1987). Similarly, co-variations of tin or antimony with sulfate are documented by Cameron et al. (1995) in the Fraser river system. Little information is available on the behavior of the platinum group elements. Osmium and rhenium appear to correlate with the variations of major elements (Dalai et al., 2001; Levasseur et al., 1999). A good correlation between rhenium concentration and the sum of major cations is reported by Dalai et al. (2001) for the rivers of Yamuna and Ganga river systems in India. More generally, elements known to be present as oxyanions in oxidized waters also exhibit some coherence with major solute variations. A good correlation between tungsten or boron concentrations and chlorine has been reported by Johannesson et al. (1999) in rivers from California and Nevada, suggesting an essentially conservative behavior for these elements in the watershed and a strong contribution from evaporite weathering. Correlation between boron and major solutes is also reported by Lemarchand et al. (2000) at a global scale. In California and Nevada, the correlation between molybdenum or vanadium with chlorine is poor compared to tungsten or boron, suggesting that secondary processes operate for the

regulation of these elements. From the 56 rivers analyzed for germanium by Froelich et al. (1985), a relatively good correlation between germanium and silicon on a global scale is observed, provided contaminated rivers are disregarded.

The behavior of uranium varies considerably across samples studied. Palmer and Edmond (1993) have reported increasing trends of uranium concentration with river alkalinity in the Orinoco, Amazon and Ganga river basins, showing the importance of limestone and black shale dissolution for the control of uranium concentrations in river waters. The association of uranium and major soluble elements is also reported by Elbaz-Poulichet et al. (1999) for the upper Amazonian basins of Bolivia. However, under the organic-rich conditions of Scandinavian rivers (Porcelli et al., 1997) or African rivers (Viers et al., 1997), uranium concentrations can be decoupled from those of major elements, due to the existence of a colloidal fraction of uranium.

The best examples of decoupling between major solutes and trace elements in river waters come from the REEs. In most cases, dissolved REE concentrations are insensitive to major solute concentrations or even increase when solute concentrations are low. Parameters such as dissolved organic carbon (DOC) and pH appear to control the REE concentrations, and those of a number of associated elements, in river waters. Figure 4 is from Deberdt et al. (2002) and shows the extensive database of neodymium concentrations in river water ($<0.2 \mu\text{m}$ or $0.45 \mu\text{m}$) as a function of pH. Given the very good correlation coefficients between the different REE elements, this correlation indicates that the lowest concentrations of REEs in river waters are found in the rivers having the highest pH. This graph explains why the majority of dissolved REE concentrations published so far are for African or Northern rivers of low pH. The rivers of Asia, being much influenced by carbonate dissolution, have high pH and alkalinity values and therefore present very low REE concentrations.

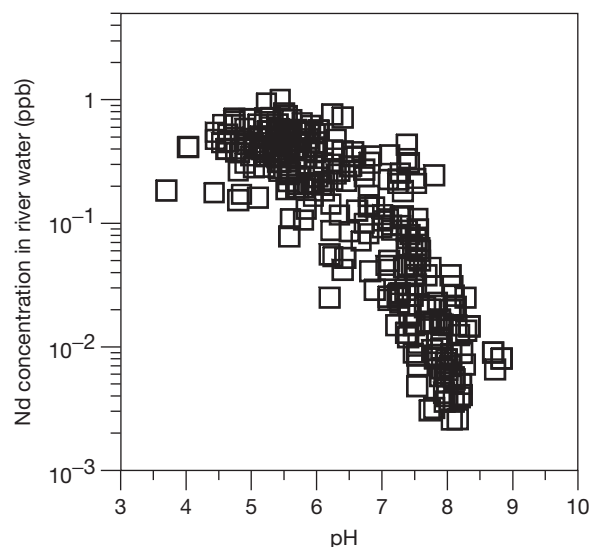


Figure 4 Nd concentrations measured in the dissolved phase ($<0.2 \mu\text{m}$) of a great variety of rivers draining different regions of the world. This graph is based on the compilation of Deberdt et al. (2002) and shows the global control of dissolved REE concentrations by pH.

Correlated with REE concentrations in river waters are elements such as thorium, yttrium, and, to a lesser extent, iron, aluminum, gallium, zirconium, manganese, and zinc (Dupré et al., 1996; Laxen et al., 1984; Pokrovski and Schott, 2002; Shiller and Boyle, 1985; Viers et al., 1997). The close association of these elements in river waters with DOC has been shown by several authors (Bagard et al., 2011; Deberdt et al., 2002; Elderfield et al., 1990; Ingri et al., 2000; Perdue et al., 1976; Pokrovsky et al., 2010; Pourret et al., 2010, 2012; Sholkovitz, 1978; Sholkovitz et al., 1978; Tricca et al., 1999; Vasyukova et al., 2010; Viers et al., 1997).

7.7.2.4 Temporal Variability

The temporal variability of trace-element concentrations has been poorly addressed in the literature. The variability of trace-element concentration may be important even on a diel basis. Brick and Moore (1996) have reported diel variations, for example, in the Upper Clark Fork river, Montana. This river is a high-gradient river rich in metals because of mining. Correlating with pH variations between day and night, dissolved manganese and zinc concentrations increase two- and three-fold at night, while major solutes and water discharge show no evidence of variations.

Tenfold daily to weekly variations of manganese have been described in the Kalix River (Ponter et al., 1992) between winter (minimum concentrations) and snow-melt in May. These variations are attributed to the input of manganese-rich mire waters (due to rapid oxidation–reduction processes) and are shown to be associated with significant variations of dissolved REEs, aluminum, and iron. A sevenfold increase of lanthanum is observed and is associated with the increase of water discharge and DOC concentrations and the decrease of pH occurring at spring flood (Figure 18; Ingri et al., 2000). It is important to note that even the REE patterns are affected, changing from a relatively flat to an LREE-enriched pattern when water discharge increases. In the Kalix River, these variations in the dissolved load are associated with variations in particulate concentrations. A similar cycling of manganese and iron concentrations has been reported for the St. Lawrence system by Cossa et al. (1990).

A similar seasonal variability is observed in the organic-rich rivers of Africa. Viers et al. (2000) have classified the trace elements as a function of their variability (standard deviation/mean value) during the period 1994–1997. While major elements show the lowest variability (except potassium), trace elements show high variability, ranging from 80% for rubidium and manganese to 40–50% for DOC, REEs, thorium, aluminum, and iron. The temporal evolution of elements such as thorium or REEs strictly mimics that of DOC and shows the highest concentrations during the high-water stage period. Major elements follow the reverse tendency.

The variability of very large river systems has been addressed for the Mississippi (Shiller, 1997, 2002; Shiller and Boyle, 1987) and the Amazon (Seyler and Boaventura, 2002). In the Mississippi, the largest amplitude of dissolved concentrations is observed for manganese (50 times increase with water discharge increase) and iron (eightfold variation). All other trace elements analyzed show lower concentration variability (from 1.5-fold for barium and rubidium to fourfold for lead and molybdenum). Certain trace elements vary in phase

with manganese and iron, being maximum at high-water stages, e.g., zinc and lead, some others show an opposite seasonal behavior, such as vanadium, molybdenum, uranium and, to a lesser extent, copper, nickel, and cadmium. REEs (Shiller, 2002) co-vary with manganese or zinc, the LREEs showing much more variability than the HREEs. These seasonal trends for the lower Mississippi are remarkably similar to those observed for the Kalix River. In the Amazon system, a time series of trace-element concentrations at Obidos (800 km upstream from the mouth of the Amazon) shows (Seyler and Boaventura, 2002) that several patterns of variation exist. As in the Mississippi river, manganese shows the largest variations (10-fold) and exhibits maximum concentrations at high-water stage (but one month after the water peak). Elements such as cadmium ($\times 8$) and cobalt ($\times 4$) show similar patterns. The opposite trend is observed for antimony, molybdenum, copper, strontium, barium, vanadium, and major elements, with maximum concentrations at low-water stage and less variability. The elements uranium, rubidium, nickel, and chromium do not show significant or systematic variations during the hydrological cycle. So far, variations of REEs, aluminum, and iron have not been documented in the Amazon.

The conclusion of this rapid review of the literature on temporal variations of trace-element abundances in river waters is that the range of variation can be very large. Temporal series are thus necessary not only to compute riverine budgets to the oceans but also to understand the processes controlling trace-element concentrations. Manganese and iron appear to be the most variable elements in rivers, as well as a number of elements whose chemistries seem to be associated with those of manganese and iron. As will be discussed later, manganese and iron variations are consistent with redox changes within the river system. We would stress that, in order to understand controls on trace-element concentrations in watersheds and to refine load budgets of elements to the ocean, future studies will have to take into account temporal variations.

7.7.2.5 Conservative Behavior of Trace Elements in River Systems

The question of seasonal variability of trace elements in river systems raises the question of their conservative or nonconservative behavior during the mixing of tributaries. Major elements and trace elements of high mobility indexes generally have conservative behavior during the mixing of tributaries. This is apparent for the Amazon River (Seyler and Boaventura, 2002). Conversely, if redox cycling and associated exchange with solid phases, related to temperature or biological activity within the river system, control the temporal variations of manganese, iron, and associated elements, it is highly probable that their behavior will not be conservative. In the Mississippi River, seasonal changes in trace-element concentrations are not explained by the hydrological mixing of tributaries, except for barium and uranium (Shiller, 1997; Shiller and Boyle, 1987). The same conclusion is reached from times-series comparison in the Amazon basin by Seyler and Boaventura (2002). The downstream evolution of major and trace elements along the Solimoes and Amazon rivers (from 3,000 km upstream to the river mouth) illustrates conservative and nonconservative behavior in the Amazon system. The patterns of manganese,

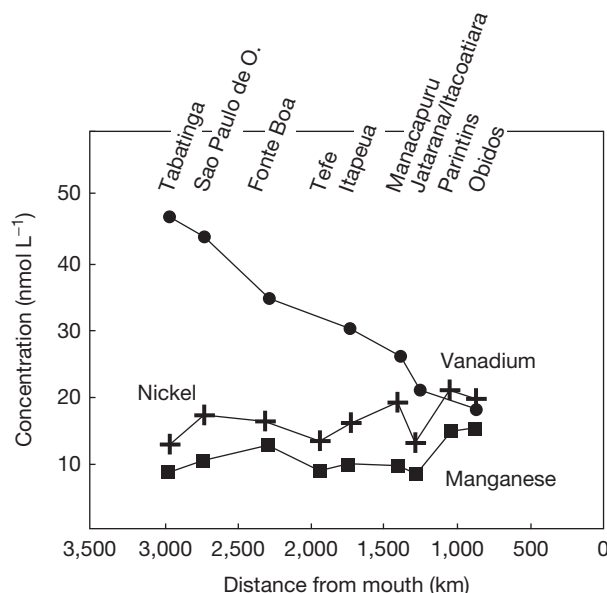


Figure 5 Downstream evolution of vanadium, nickel, and manganese concentrations measured in the dissolved load of the Amazon river showing different possible behaviors of trace elements in river systems. Major solutes and TDS follow the similar pattern to that of vanadium and correspond to a dilution of Andean waters by waters from the Amazonian lowlands (source Seyler and Boaventura, 2002).

vanadium, and nickel are shown on Figure 5. While vanadium, like the major elements, shows a downstream decrease of concentration, consistent with the inputs of the dilute lowland rivers, manganese and nickel show increasing and constant concentrations, respectively. In the case of manganese and nickel, a substantial source is necessary that cannot be represented by the minor input of lowland tributaries, but rather by processes releasing these elements into the dissolved load.

7.7.2.6 Transport of Elements

Rivers transport material both in dissolved form and as solid load (suspended matter and bottom sands). The dominant form of transport of trace elements per liter of river water depends on both the mobility of the element in the weathering + transport process and on the amount of solids transported annually by the river. Two contrasted examples of big rivers from the Amazon basin are shown on Figure 6. The Solimoes River is characterized by relatively high concentrations of suspended sediments (230 mg L^{-1}), whereas the Rio Negro is characterized by very low suspended sediment concentrations (less than 10 mg L^{-1}). This discrepancy is related to contrasting erosion regimes in the two basins. In the Solimoes, even the most mobile elements, such as sodium, are transported dominantly in a solid form. This also applies to the highly turbid rivers of Asia. Conversely, rivers from humid tropical regions such as the Rio Negro can show a significant fraction of their trace elements transported in the dissolved load, both because the suspended matter concentration is low (less than 10 mg L^{-1}) and because their dissolved load is generally enriched in the so-called “nonmobile and highly insoluble” elements of Figure 2. In the Rio Negro, half of the REEs, thorium, and aluminum are transported in the dissolved load.

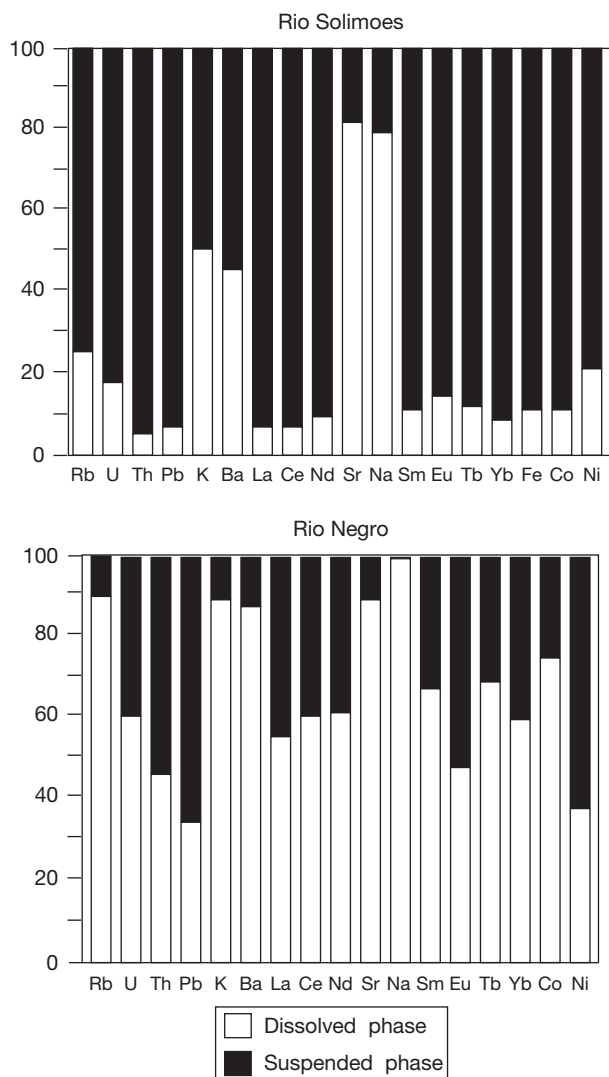


Figure 6 Proportion of elements transported in dissolved ($<0.2 \mu\text{m}$) and particulate forms by contrasted rivers of the Amazon Basin: the Solimoes (a turbid river, mostly influenced by the Andes) and the Rio Negro (a typical lowland, black river with very low suspended sediments yields).

If TSS is total suspended sediment concentration in the river, K_d , the ratio of concentration in the suspended sediments over dissolved concentration, then the proportion D of a given element in the dissolved phase can be expressed as

$$D = \frac{1}{1 + K_d \cdot \text{TSS}}$$

The typical values of K_d can be estimated using Table 1 and average values of concentrations in suspended sediments (Caillardet et al., 1999b). Except for the most mobile elements, K_d values are not very different from the continental crust normalized concentrations shown on Figure 2. We have plotted in Figure 7 the proportion D as a function of TSS for three types of elements: thorium (immobile element), nickel (intermediate), and boron (mobile element), corresponding to the K_d values of 1,000, 100, and 10, respectively. This graph shows that at the world average value of TSS (350 mg L^{-1}), the dominant form of

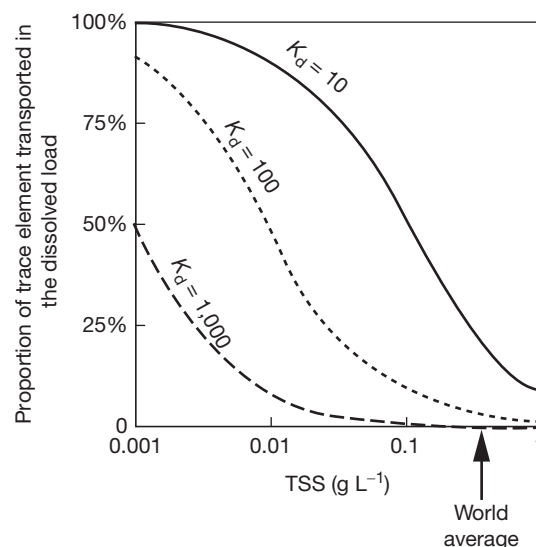


Figure 7 Theoretical proportion of dissolved transport as a function of the concentration of riverine suspended sediments for three values of the ratio of concentration in the suspended load over concentration in the dissolved load. $K_d=10$, 100, and 1,000 correspond to the most mobile elements (Na, B, Re, Se, As, Sb), the intermediate elements (Cu, Ni, Cr, Ra) and highly immobile elements (Th, Al, Ti, Zr) respectively (see Figure 2).

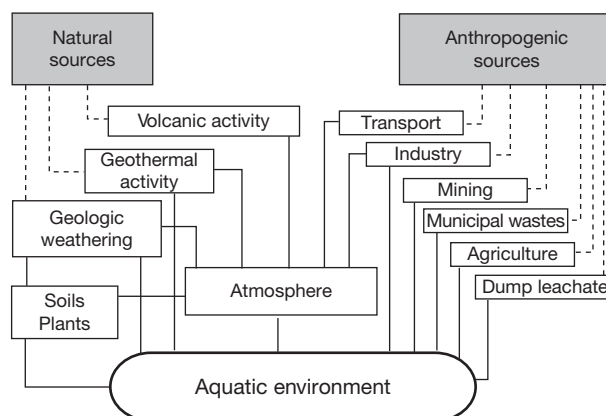


Figure 8 Pathways of trace elements to the aquatic system.

transport is the solid form. Only the most mobile elements can be significantly transported in a dissolved form.

7.7.3 Sources of Trace Elements in Aquatic Systems

Continental crust is the ultimate source of trace elements in hydrologic systems. Trace elements are introduced in the river basin by rock weathering, atmospheric dry and wet deposition and by anthropogenic activities. The sketch diagram of Figure 8 summarizes the natural and anthropogenic sources of elements in aquatic environments (modified after Foster and Charlesworth, 1996).

7.7.3.1 Rock Weathering

The chemical weathering of rocks results in the release of the most soluble elements and, in the case of silicate rocks, leaves a residue,

which, conversely, is enriched in the insoluble elements. The normalization of soil materials or river suspended sediments, taken as a natural average of the finest soil materials, allows a first-order examination of the behavior of trace elements during chemical weathering. For example, the suspended sediments of some large unpolluted rivers have been normalized to the upper-crust concentrations (Gaillardet et al., 1999b) in Figure 9. Elements are classified according to their magmatic compatibility. Most of the trace elements analyzed on those patterns have continental-like abundances. Only a few elements are depleted. They include soluble elements (rubidium, uranium, barium, and major elements) and elements concentrated in heavy minerals (zirconium, hafnium). The complementary reservoirs are, respectively, the dissolved phase and bottom sands. For elements that are not depleted by chemical weathering and transport processes, their ratio in the particles is expected to be similar to that of the source rock from which they are derived. For example, the Sm/Nd ratio of suspended sediments is a good integrated signature of the rocks that have undergone weathering throughout the drainage basin. The Sm/Nd isotopic system is therefore insensitive to the weathering history of sediment, and it records episodes of crustal formation rather than weathering + deposition cycles. This property is the basis of the use of neodymium isotopes as tracers of crustal growth (Allègre, 2008).

In the dissolved load, the preferential dissolution of the different types of lithology or mineral can cause large variations in trace-element abundances in rivers. A classical tracer of rock dissolution is strontium. The isotopic ratio of strontium in river waters is, to a first approximation, explained by mixing between different sources. Rain, evaporite dissolution, and carbonate and silicate weathering are the predominant sources of strontium in rivers (see Chapter 5.12). Examples of the use of Ca/Sr, Na/Sr, and Sr isotopic ratios to quantify the proportion of strontium derived from carbonate weathering in large basins can be found in Nègre et al. (1993) and Gaillardet et al. (1999a). Levasseur (1999) have used isotopic ratios of osmium in river waters to determine the origin of osmium in the largest rivers. As a global average, osmium in river waters is derived from silicates (14%), carbonates (55%), and shales (31%). Uranium in river basins

(Palmer and Edmond, 1993) is associated with carbonate dissolution. A number of trace elements also appear to be good tracers of black shale weathering (Chabaux et al., 2001; Dalai et al., 2001; Peucker-Ehrenbrink and Hannigan, 2002; Pierson-Wickman et al. (2000)). These rocks are enriched in elements that have a strong affinity for organic matter and are stable in reducing conditions (uranium, metals, PGE); their dissolution can lead to substantial enrichments. The correlation between tungsten and chlorine in California streams reflects the importance of evaporite dissolution to the riverine budget of tungsten (Johannesson et al., 2000). An important source of trace metals to rivers is the oxidative weathering of sulfide that occur in sedimentary and magmatic settings. The production of sulfuric acid creates low pH conditions that favor the mobility of trace metals. An extreme case of sulfide oxidation is acid mine drainage (e.g., Fortner et al., 2011).

Geothermal areas may also show high dissolved trace element concentrations in particular due to the acidic character of geothermal waters and high temperature water rock interactions (Kasalainen and Stefansson, 2012; McCleskey et al., 2010; Taran et al., 2008).

Trace-element abundance in rivers depends not only on their abundance in source rocks but also on the weathering style. Some authors have proposed that trace-element ratios involving chemically similar elements might be fractionated during the weathering of silicates and could serve as a proxy for weathering intensity. It has, for example, been shown that significant variations in the Ge/Si or Ga/Al ratios occur in river waters and that these variations are related to the degree of weathering (Murnane and Stallard, 1990; Shiller and Frilot, 1995). A weathering-limited regime would produce high Ga/Al and low Ge/Si in the river dissolved load because of slight differences in solubility between elements. In transport-limited regimes, these ratios should approach those of the source rocks. However, as we will see later, the chemistry of the river, especially organic-matter complexation, can significantly obscure the weathering signal. Shiller and Mao (2000) have shown this for vanadium. Although vanadium in rivers is essentially derived from silicate weathering, variations in the V/Si ratios are observed due to

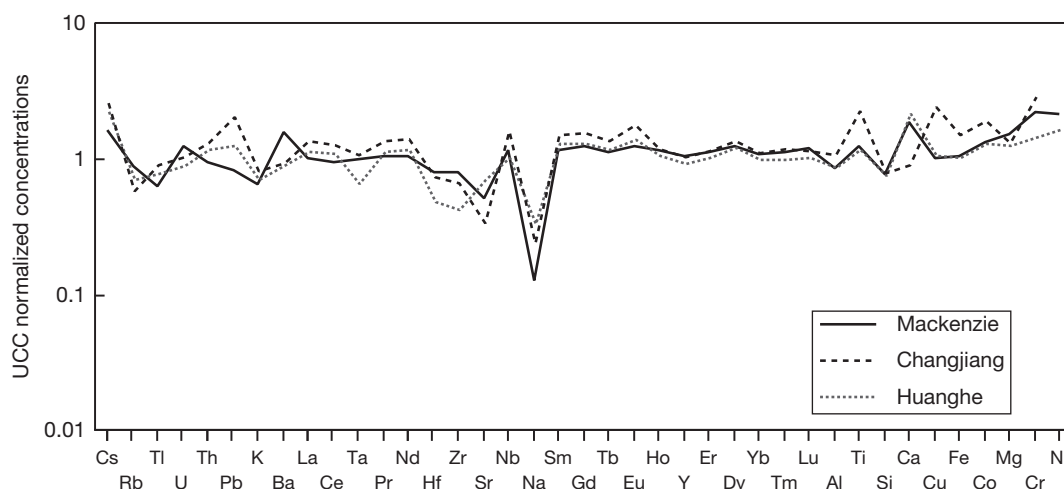


Figure 9 Concentrations measured in the suspended sediments of large river systems normalized to the upper continental crust UCC (Li, 2000). The order of element on the x-axis is an order of magmatic compatibility (source Gaillardet et al., 1999b).

minor inputs from sulfide dissolution, increased solubilization of vanadium by dissolved organic matter, and variations of the vanadium content of source rocks. In spite of these complications, research is needed to evaluate the use of trace element in rivers as tracers of specific types of mineral/rock weathering or as indexes of weathering regimes. A vast majority of dissolved trace elements in natural waters are not provided by rock weathering alone; other sources will be discussed below.

7.7.3.2 Atmosphere

Trace elements are transported in the atmosphere in the form of wind-blown soil particles, fine volcanic products, sea salts, ashes from forest fires, and biogenic aerosols. The atmospheric input of trace elements can be significant, depending on their abundance in rain and aerosol solubility. Due to the ability of aerosols to travel over long distances in the atmosphere, it is difficult, based on present-day sampling, to determine the natural background concentrations of elements in rain water and aerosols. In remote sites of Niger and the Ivory Coast, Freydiser et al. (1998) have shown that the emission of terrigenous particles of crustal composition is the main source of trace elements in atmospheric deposition of this region. Where the amount of crustal particles in the atmosphere is low, the contribution of other sources becomes evident (ocean, vegetation, human activities). In both sites, a 50-fold enrichment of zinc with respect to the continental crust is observed in rainwater, possibly derived from the vegetation or from remote industrial sources. In the Amazon basin (Artaxo et al., 1990), biogenic aerosols are enriched in potassium, phosphorus, sulfur, and zinc, which can explain the enrichment of rain waters. The impact of human activities on rain-water chemistry has been clearly demonstrated in large cities and even in regions far from industrial centers (e.g., Berg et al., 1994). In Western Europe, rain waters in Paris have concentrations more than 100 times those in the mean continental crust for the elements cadmium, zinc, lead, copper, bismuth, nickel, chromium, cobalt, and vanadium (Chen et al., 2008; Roy, 1996). In those samples, arguments based on lead isotopes have shown that 100% of the excess of metals can be attributed to anthropogenic sources. These elements are introduced into the atmosphere by coal-burning or metal smelting that produces fine particles. The atmosphere is therefore extremely sensitive to anthropogenic contamination. Nriagu (1979) has calculated that global atmospheric emissions increased exponentially over the twentieth century.

7.7.3.3 Other Anthropogenic Contributions

The magnitude of a large number of trace element fluxes moved by anthropogenic activities at the surface of the Earth has been estimated by a recent study by Sen and Peuker-Ehrenbring (2012). Apart from the atmosphere, there are a number of potential point and non-point sources of contamination in hydrological systems. The industrial revolution, since the beginning of the twentieth century, has caused a drastic increase in the exploitation and processing of metals, resulting in their release into the environment and the release of associated elements with no economic value (e.g., arsenic). In southwestern France, Schäfer and Blanc (2002) have shown that the geochemistry of suspended sediments of the largest rivers can be related to the occurrence of ore deposits in the upper basins

of the Massif Central and Pyrenees. The release of metals is also associated with the use of metals and other trace elements in paints, cements, pharmaceutical products, wood treatment, water treatment, plastics and electronic items, and fertilizers. These activities can release trace metals directly into the river catchment (De Caritat et al., 1996; Foster and Charlesworth, 1996; Luck and Ben Othman, 1998). For example, positive gadolinium anomalies have been reported in the dissolved load of European rivers and attributed to the use of gadopentetic acid in magnetic resonance imaging (Bau and Dulski, 1996). In the Seine River (Roy, 1996), lead isotope studies have shown that almost half of the lead transported by the river (adsorbed and dissolved) is of anthropogenic origin. In Mediterranean catchments, it has been shown by Luck and Ben Othman (1998) that lead and other metals brought in by rain waters are stored in soils and remobilized during floods as particles. In the Rhine River, the concentration of metals associated with suspended sediments decreases by a factor of 3 between low water discharge and high water discharge (Foster and Charlesworth, 1996). The same effect is observed in the rivers of southwestern France (Schäfer and Blanc, 2002) and is interpreted as a "dilution" of pollution by natural erosion of uncontaminated soil particles at high water discharges. Over longer timescales, there are a few sites where metal pollution has been monitored in rivers. Records from the river Rhine are available in the Netherlands (Foster and Charlesworth, 1996). A steady (between 2 and 20 times) increase in the concentrations of zinc, lead, chromium, copper, arsenic, nickel, cobalt, cadmium, and mercury is observed over the twentieth century and a slight decline after 1975, clearly showing the sensitivity of aquatic systems to human activities. For many trace metals, anthropogenic contributions from all sources far exceeds natural levels. Nriagu and Pacyna (1988) estimated that the man-induced mobilization of arsenic, cadmium, copper, mercury, molybdenum, nickel, lead, antimony, selenium, vanadium, and zinc far exceeds the natural fluxes. For arsenic, cadmium, lead, selenium, and mercury they report enrichment factors due to human activities of 3, 7.6, 24.1, 2.8, and 11.3, respectively, with respect to the natural levels.

Atmospheric acid deposition influences the mobility of trace elements, depending on the source rocks. Central Europe has been strongly affected by acid deposition during the twentieth century. Frei et al. (1998) have shown that the concentrations of trace elements in the Upper Ecker drainage and in the Northern Harz Mountains (Germany) are high and are related to the neutralizing capacity of the source rocks. Acidic waters have the highest trace-element concentrations.

As a conclusion, the origin of trace elements in river waters can be very diverse. Elucidating the sources and quantifying the proportion of elements derived from each of these sources is not an easy task, and it has been addressed by the use of isotopic ratios (strontium, neodymium, lead, metals) and enrichment factors of trace elements with respect to well-characterized reservoirs (upper continental crust, ocean; e.g., Chen et al., 2008). However, we are far from being able to trace the origin of all elements in natural waters, especially when their biogeochemical cycle is complex and involves biomass or an atmospheric subcycle. In addition, human activities have led to a generalized perturbation of element abundances in the atmosphere, soils, and waters; it is very difficult, if not impossible, to assess the natural levels of trace elements in river waters and particles.

The behavior of trace elements in aquatic systems not only depends on the sources but it is also strongly controlled by the soil and in-stream processes, particularly through aqueous (organic and inorganic) complexation and reactions with solids.

7.7.4 Aqueous Speciation

The speciation of a given element is the molecular form under which it is transported in hydrosystems. Like some of the major elements, trace elements are transported in surface waters in complexed forms. Aqueous complexes correspond to the association of a cation and an anion or neutral molecule, called the ligand. Ligands can be inorganic and organic (see Chapter 7.9). It is rarely possible to measure the concentration of an individual complex (Alasonati et al., 2010; Ammann, 2002; Pereiro and Carro Díaz, 2002). Most of the techniques used to measure trace-element concentrations give the total concentration, whatever the speciation. The proportion of elements corresponding to the different chemical forms has therefore to be calculated, depending on the total concentration, pH, Eh conditions, the major element chemical composition of the water, and the complexation constants of the assumed complexes. Knowing the concentrations of the individual species of a given element in waters is of crucial importance in order to predict its toxicity and bioavailability. For example, the toxicity of metals depends more on their chemical form in waters rather than their total concentration (Morel and Hering, 1993), in particular, because complexation may enhance or inhibit adsorption on surfaces.

In river waters, inorganic ligands are essentially H_2O , OH^- , HCO_3^- , CO_3^{2-} and, to a lesser extent, Cl^- , SO_4^{2-} , F^- , and NO_3^- . Organic ligands are small organic weak bases such as Oxalate or acetate and low-molecular-weight humic acids containing phenolate and carboxylate groups.

Speciation calculations are performed according to mass balance equations and mass law equations corresponding to the different complexation reactions. As an example, we show in Figure 10 the calculated speciation of thorium in pure water

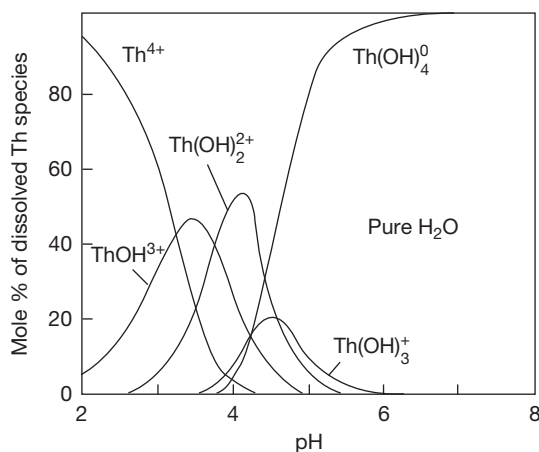
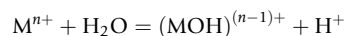


Figure 10 An example of speciation calculation. Distribution of thorium complexes versus pH at 25 °C with $\sum \text{Th} = 0.01 \mu\text{g L}^{-1}$ in pure water (after Langmuir and Herman, 1980).

(Langmuir and Herman, 1980). The situation would be more complex in natural waters, depending on the abundance and nature of the inorganic and organic ligands, but no free thorium is predicted and $\text{Th}(\text{OH})_4^0$ is still the dominant complex at common river water pH.

Complexation constants of trace elements in aqueous solution are determined using a great variety of techniques (including conductimetry, potentiometry, spectrophotometry, solvent extraction, calorimetry, ion exchange) and are reported in numerous publications (see Chapter 7.2). Critical studies reporting complexation constants can be found in Baes and Mesmer (1976), Martell and Smith (1977), or Martell and Hancock (1996). The values for complexation reactions are still a matter of debate, given the high possible number of complexes between trace elements and natural ligands, especially poorly known organic ligands. A number of computer codes have been developed in order to calculate the speciation of trace elements in waters (see Chapter 7.2). These computer codes basically use the mass action laws of the different complexation reactions, activity coefficients and conservation equations (e.g., WATEQF, Plummer et al., 1984).

A number of authors have investigated the interesting issue of relating the aqueous speciation rules of trace elements to the periodic table (Langmuir, 1997; Turner et al., 1981). The classical “Goldschmidt plot” plots the charge of the cation (in the complex) versus the cationic radius. Three groups of elements can be distinguished: those forming oxyanions in solution (carbon, arsenic, boron, nitrogen, . . .), elements forming hydroxycations and hydroxyanions (thorium, aluminum, iron, titanium, lead) and elements forming free cations or aquocations (sodium, potassium, silver). More precisely, following the Born theoretical treatment of ion–water interaction (see Turner et al., 1981), the ability of cations to attract electrons can be approximated by the polarizing power, Z^2/r , where Z is the ion charge and r the ionic radius. Figure 11 is a graph of the intensity of hydrolysis



as a function of the polarizing parameter and allows a classification of trace elements in solution.

A high polarizing power (>1.3) means that the element easily attracts electrons and is fully hydrolyzed. The speciation of such elements is in the form $\text{MOp}(\text{OH})_q$ and depends on pH, via the dissociation constant. Examples of such elements and their associated acid form are arsenic, boron, chromium, germanium, molybdenum, niobium, tantalum, rhenium, antimony, silicon, selenium, uranium, and vanadium. They exist, for example, in the form of $\text{As}(\text{OH})_3$, $\text{B}(\text{OH})_3$, $\text{Ge}(\text{OH})_4$, $\text{Sn}(\text{OH})_4$, CrO_4^{2-} , MoO_4^{2-} , WO_4^{2-} , ReO_4^- , . . ., and behave as strong or weak acids in solution. These elements are known as fully hydrolyzed elements and belong to groups III–VII in the periodic table.

Elements with intermediate and low Z^2/r are capable of producing free cationic forms in solution. Their speciation is a question of competition among the major ligand species (Cl^- , SO_4^{2-} , OH^- , CO_3^{2-}). These elements are the alkalis, alkaline earths, REEs, and metals. They can be classified according to their tendency to form covalent bonds. The concept of hard and soft ions was introduced by Pearson and is equivalent to the concept of (a)- and (b)-type cations introduced by Ahrlund

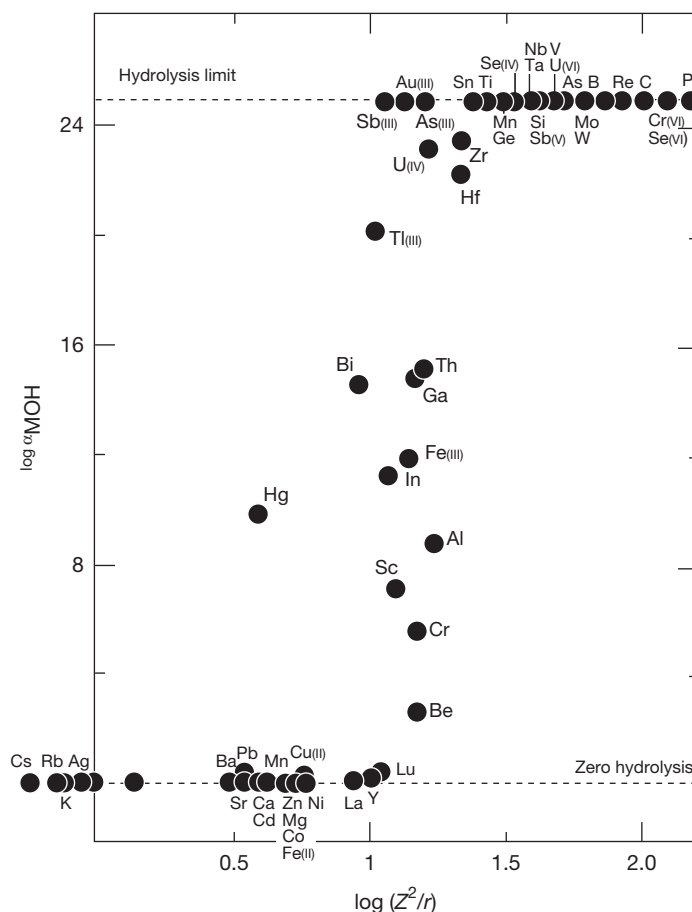


Figure 11 The “Born plot” showing the extent of hydrolysis of a given cation (a_{MOH} quantifies the affinity with OH^-) as a function of the polarizing power (Z^2/r) where r and Z are, respectively, the radius and charge of the cation (after Turner et al., 1981).

(Langmuir, 1997). The cations are Lewis acids (electron acceptor) and the ligands, Lewis bases (electron donor). “Soft” means that the electrons of the species can easily be deformed whereas “hard” means that the species are rigid. Soft species easily form covalent bonds. Hard species prefer electrostatic bonding. Soft cations form strong covalent bonds with soft ligands, and hard acids form strong ionic bonds with hard ligands (Langmuir, 1997). Complexes between hard (soft) acids and soft (hard) bases are weak and rare. Alkaline earths, La , Ti^{4+} , Y^{3+} , Sc^{3+} , Ga^{3+} , In^{3+} , Sn^{4+} , Cr^{3+} , Mn^{3+} , Fe^{3+} , Co^{3+} , U^{4+} , Th^{4+} , and actinides are classified as hard acids and form strong complexes with the major ligands found in natural freshwaters: F^- , OH^- , SO_4^{2-} , CO_3^{2-} , or HCO_3^- (hard bases). Complexes with Cl^- (hard-soft ligands) are weaker. Soft acids comprise Cu^+ , Ag^+ , Au^+ , Au^{3+} , Pd^{2+} , Cd^{2+} , ..., while Zn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Pb^{2+} are classified as borderline acids due to their intermediate behavior. Turner et al. (1981) have reported correlations between the log of complex stability constants for all major freshwater ligands and $Z^2/(r + 0.85)$. Significant linear correlations between the strength of the complex and the electrostatic parameter are observed. Hard ligands (such as F^- , SO_4^{2-}), exhibit a rapid increase of stability constant with polarizing power. Soft ligands, such as Cl^- , show only a slow increase of the affinity constants with $Z^2/(r + 0.85)$.

Intermediate ligands (OH^- , CO_3^{2-}) show a clear increase of association constant with the polarizing parameter. For example, Figure 12 represents the case of carbonate complexes. Such relations are interesting, as they relate the complexation constants of trace elements in solution to relatively simple properties of the periodic table.

The results of cation speciation calculations for freshwaters lead to clear conclusions (Turner et al., 1981). The cations with low polarizing numbers are very weakly complexed in freshwater and exist dominantly as free ions (lithium, strontium, rubidium, caesium, barium). Conversely, elements of high polarizing power (hafnium, thorium, aluminum, scandium, ...) have their speciation dominated by hydrolyzed species and correspond to the elements of the transition zone in the Born graph (Figure 11). A third group of elements corresponds to soft cations (Ag^+ , Au(I) , Tl(I)) in association with soft ligands (essentially Cl^-). The last group of elements consists of the REEs, transition metals, cadmium, which exist both as free ions and carbonate or hydroxyl complexes, depending on the pH. The speciation of REEs in natural waters has been modeled by several authors (Cantrell and Byrne, 1987; Johannesson et al., 1996; Lee and Byrne, 1993; Millero, 1992; Wood, 1990; and references therein, Liu and Byrne, 1997). The dicarbonato ($\text{Ln}(\text{CO}_3)_2^-$) and carbonato (LnCO_3^+) REE

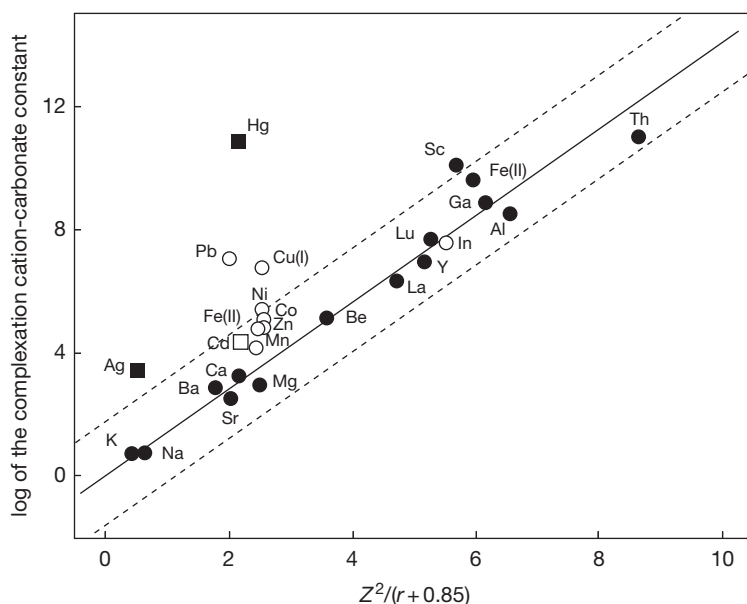


Figure 12 Linear relation between the complexation constant of cations and carbonate in solution as a function of $Z^2/(r + 0.85)$, where 0.85 is an empirical correction of the Born function (after Turner et al., 1981).

carbonate complexes are shown to be the dominant forms of REEs in groundwaters from Nevada and California, having pH values between 7 and 9. Stability constants show that the formation of REE carbonate complexes increases with increasing atomic number across the REE suite. The formation of other complexes such as sulfate, phosphate, or hydroxide is less important but also tends to favor the HREEs. Fractionation of REEs between source rocks and associated groundwaters is not observed in groundwaters from Nevada and California (Johannesson et al., 1996), but HREE enrichments occur in some cases, reflecting the dominance of HREE carbonate complexes, more stable in solution than the LREE carbonate complexes.

Organic speciation has been poorly documented, compared to inorganic speciation. However, as shown by several authors, a good correlation is observed between the first hydrolysis constant and the association of the cation with small organic molecules such as oxalate (Langmuir, 1997). Because humic molecules are large, poorly characterized molecules, they considerably complicate speciation calculations in freshwaters. Most often, these molecules can no longer be considered as dissolved ligands, but rather as “colloids” (see Chapter 7.9).

Finally, it is interesting to note that the relation between the global mobility of trace elements in the aquatic system (Figure 2) and the speciation patterns summarized above is not direct. Although most of the fully hydrolyzed species appear as mobile elements (phosphorus, carbon, rhenium, boron, arsenic, molybdenum), some elements in this family are amongst the least mobile elements (titanium, germanium, niobium, tantalum). Conversely, the elements with zero hydrolysis (Figure 11) are generally mobile elements but exceptions exist such as caesium, rubidium, lead, and lanthanum. This absence of correlation clearly indicates that aqueous complexation is not the only process to control trace-element abundances in aquatic systems.

7.7.5 The “Colloidal World”

It is now well known that trace-element concentrations in continental waters depend on the size of the pore filters used to separate the particulate from the dissolved fraction. This is apparent in Table 1, where results from the Amazon and Orinoco are reported using two filtration sizes: the conventional 0.2 μm filtration and filtration with membranes of smaller cutoff size (ultrafiltration). These results suggest the presence in solution of very small (submicrometric) particles that pass through filters during filtration. The view that trace elements can be separated into “particulate” and “dissolved” fractions can thus no longer be held; this has led authors to operationally define a colloidal fraction (0.20 μm or 0.45 μm to 1 nm) and a truly dissolved fraction (<1 nm) (e.g., Buffle and Van Leeuwen, 1992; Stumm, 1993). The existence of a colloidal phase has a major influence on the speciation calculation schemes presented above (based only on aqueous complexation), as the apparent solubility of trace elements will be enhanced by the presence of colloids. The dynamics of colloids also completely change the way reactive solute transport is modeled and are of importance for water quality standards since the toxicity of trace elements depends not only on their abundance and speciation but also on their bioavailability.

Although, strictly speaking, colloids consist of small particles and could be treated as a particular case of reactive surfaces, we summarize below the recent literature on the nature and reactivity of these phases.

7.7.5.1 Nature of the Colloids

The separation and characterization of submicron-sized and nanophases in water is difficult, in particular because of artifacts from sampling and concentration techniques. Lead et al. (1997) have presented a critical review of the different

techniques for separation and analysis of colloids (filtration, dialysis, centrifugation, but also voltametry, gels (DET/DGT), field-flow fractionation, SPLITT; [Dahlqvist et al., 2004](#)). Ultrafiltration membranes have been developed with nominal cut-off sizes ranging from the thousands of daltons (Da) to hundreds of thousands of daltons, which have been used to separate the colloidal pool into several fractions.

Figure 13 (after [Buffle and Van Leeuwen, 1992](#)) shows an example of the distribution of mineral and organic colloids as a function of size from ångstrom to micrometer scales. This diagram shows that there is no clear boundary between dissolved and colloidal substances or between colloids and particulates.

Colloids can be organic or inorganic. Colloids are finely divided amorphous substances or solids with very high specific surface areas and strong adsorption capacities. It is shown by [Perret et al. \(1994\)](#) for the Rhine River that the colloids contribute less than 2% of the total particle volume and mass, but represent a dominant proportion of the available surface area for adsorption of pollutants. The abundance of colloids, their fate, through coagulation and sedimentation processes in natural waters therefore control the abundance of a number of elements.

The most common mineral colloids are metallic oxyhydroxides (e.g., mainly iron-, aluminum- and manganese-oxyhydroxides), clays, and siliceous phases. The reaction between trace elements in water and surface hydroxyl groups ($=S-OH$) is, to a first order, analogous to the formation of aqueous complexes. Organic colloids are mainly humic and fulvic acid (humic substances) and derive from an incomplete degradation of soil organic matter (see [Chapter 7.9](#)). Humic substances represent 70–90% of DOC in wetland areas ([Thurman, 1985](#)) and are usually responsible for the brown color of water. Despite their heterogeneity and complexity, humic substances are characterized by similar functional groups (carboxyls, quinones, phenolic OH groups) and the presence of aliphatic and aromatic components ([Stevenson, 1994](#)). Metal binding in natural environments is, however, mainly related to carboxylic and phenolic groups ([Perdue et al., 1984](#)).

Inorganic and organic colloids are most often intimately associated. Association of organic colloids, with clays ([Koshinen and Harper, 1990](#)) and with iron oxyhydroxides ([Gu et al., 1995](#); [Herrera Ramos and McBride, 1996](#); [Tipping, 1981](#)) are commonly described in natural waters and have been the subject of laboratory experiments. For example, [Perret et al. \(1994\)](#) have sampled, fractionated, and characterized submicron particles from the Rhine and showed that these colloids consist of a tight association between organic and inorganic material.

7.7.5.2 Ultrafiltration of Colloids and Speciation of Trace Elements in Organic-rich Rivers

Several authors have performed ultrafiltration of natural waters (river, groundwater, estuaries) in order to determine the role of colloids in the transport of major and trace elements. As noted by some authors ([Hoffmann et al., 2000](#); [Horowitz et al., 1996](#); [Sholkovitz, 1995](#)), these experiments require caution; mass balance calculations must be performed to check the ultrafiltration procedure, as some truly dissolved elements can be retained inside the filtration system.

The main advantage of ultrafiltration techniques is that they permit a direct determination of the association constants between colloids and trace elements in natural systems. This is illustrated by a series of papers dedicated to organic-rich tropical rivers of the Nyong River Basin (Cameroon, Africa) ([Dupré et al., 1999](#); [Viers et al., 1997, 2000](#)), to Siberian rivers ([Pokrovsky et al., 2010](#); [Vasyukova et al., 2010](#)) and surficial groundwaters in Western France ([Dia et al., 2000](#); [Pourret et al., 2007](#)). The Nyong basin river waters exhibit low major cation concentrations (i.e., sodium, potassium, calcium, magnesium) but high concentrations of some trace elements (aluminum, iron, thorium, zirconium, REEs), silica, and DOC. **Figure 14** shows the behavior of some trace elements (samarium, aluminum, strontium), silicon, and organic carbon during successive filtrations through decreasing pore size membranes (0.2 μm , 300 kDa, 5 kDa, and 1 kDa) of the Awout River ([Dupré et al., 1999](#)). Concentrations decrease when samples are filtered through progressively finer pore-size

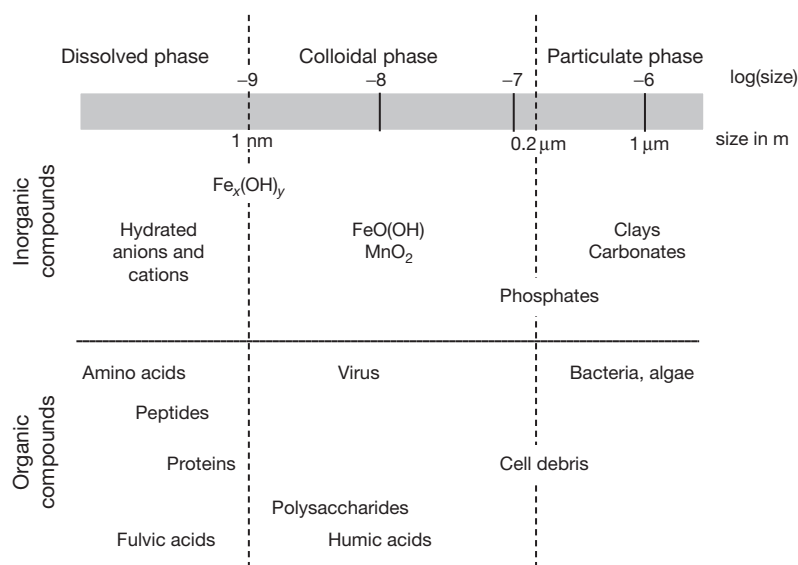


Figure 13 Distribution of mineral and organic colloids as a function of size in aquatic systems (after [Buffle and Van Leeuwen, 1992](#)).

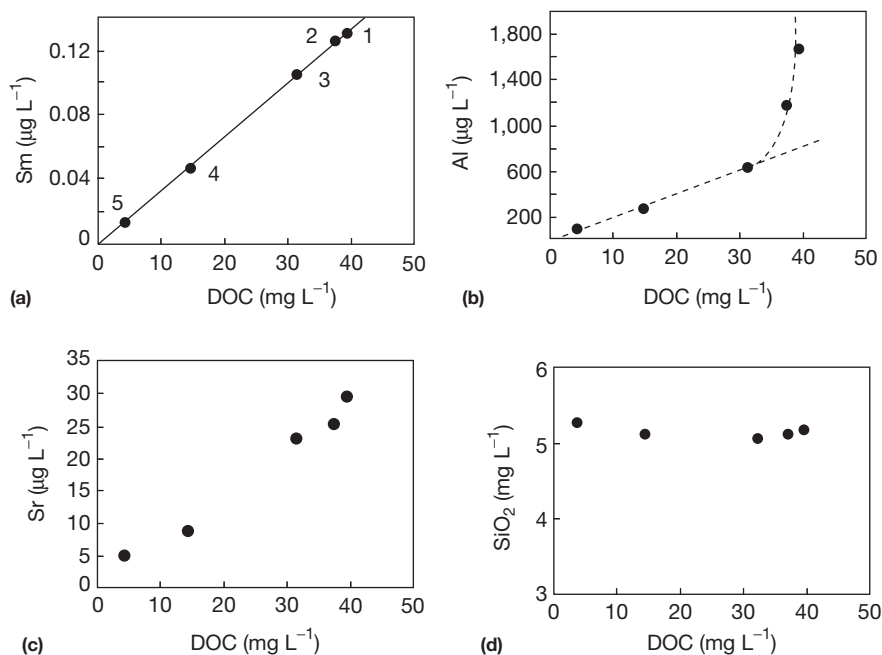


Figure 14 Variation of (a) Sm, (b) Al, (c) Sr, and (d) SiO₂ concentrations as a function of DOC concentrations in the different filtrates of the Awout River. 1: <0.20 µm (FF), 2: <0.20 µm (TF), 3: <300 kDa (TF), 4: <5 kDa (TF), 5: <1 kDa (TF). FF and TF mean frontal filtration and tangential filtration, respectively (source Dupré et al., 1999).

membranes. Three patterns of element concentration as a function of DOC (taken as an index of colloid abundance) are observed. Silica shows no concentration variation as a function of DOC. The second type of behavior is that of yttrium and REEs. The relationship between these elements and DOC defines a straight line going through zero, which means that they are progressively and completely removed from the solution jointly with DOC. A group of elements composed of rubidium, strontium, copper, cobalt, manganese, chromium, vanadium, and major cations presents the same type of relation but a certain amount remains into the solution when all DOC is removed. These linear relationships suggest that the ability of these elements to form complexes with organic colloids remains constant over the whole molecular size range of the colloid materials examined. For some other elements, plots of (aluminum, iron, gallium, thorium, uranium) concentration versus DOC exhibit a nonlinear relationship. This suggests that, for this set of elements, the binding capacities (i.e., the quantity of element bound to organic material per unit mass of carbon) in the organic colloids are a function of the size of colloids. Several authors, with contradictory conclusions, have discussed this hypothesis. Lakshman et al. (1993) separated, by ultrafiltration, three fractions of a fulvic acid extracted from a soil (<500 Da; 500–1,000 Da; 1,000–10,000 Da) and demonstrated that the aluminum binding constant of organic material increases with the molecular weight of the fractions. Conversely, Burba et al. (1995), working on humic substance fractions (<1,000 Da; 1,000–5,000 Da; 5,000–10,000 Da), showed that the lower-molecular-weight fractions exhibit the highest complexing capacity for copper. Eyrolle et al. (1993, 1996) obtained similar results.

One of the major results of ultrafiltration techniques conducted on the Nyong basin rivers is the decrease of major cation (strontium, rubidium, barium) concentrations with

decreasing filter pore size. This result is unexpected, as these cations are known to have a very low affinity for organic matter. Eyrolle et al. (1996) observed the same intriguing concentration decrease of cations (sodium, magnesium, potassium, calcium) during ultrafiltration of organic-rich river waters from South America and proposed that these cations were incorporated in plant debris. Dupré et al. (1999), alternatively, suggested that there are artifacts associated with the ultrafiltration of organic-rich waters. In the pH range of most natural waters (4–8), the surfaces of organic colloids are negatively charged. During the ultrafiltration process, the coating of the membrane by organic colloids disturbs the charge equilibrium of the solution. As a consequence, retention of free cations occurs at the membrane surface in order to maintain charge balance. This view is supported by the results of isotopic tracing (Dupré et al., 1999). The natural isotopic ratio of strontium (⁸⁷Sr/⁸⁶Sr) and the isotopic ratios of strontium (⁸⁶Sr/⁸⁴Sr) and barium (¹³⁸Ba/¹³⁵Ba) in spiked and filtered samples are constant. This shows that there is one pool of strontium and that strontium, barium and by extension, the other cations are present in an exchangeable form at the surface of colloids. In order to avoid the artifact, that would lead to an incorrect determination of complexation constants, Dupré et al. (1999) performed ultrafiltrations at low pH or by adding to the solution a strongly complexing cation such as lanthanum. In both cases, colloids are neutralized and no filtration artifact occurs, allowing Dupré et al. (1999) to calculate metal-humate stability constants by comparing the abundances of elements in the different ultrafiltration fractions with a speciation model (BALANCE, Akinfiev, 1976). Stability constants are determined in order to fit the results from the ultrafiltration. The log *K* values calculated in this way for the metal-humate complexes decrease in the order: Al, Ga, Fe, Th, U, Y, REEs

(more than 7) $>> \text{Cr}$ (5.5) $>> \text{Co}$ (3) $> \text{Rb}$, Ba, Sr, Mn, Mg (≈ 2). As shown in Figure 15, a remarkable relationship is observed between the values calculated for element-humate stability constant and the first hydrolysis constant of the element. The same kind of linear relationship was used by Martell and Hancock (1996), to predict the formation constant for metal ion complexes with unidentate organic ligands. Figure 15 shows, however, that the elements yttrium and REEs appear to lie outside the general trend, having a higher stability constant than metals that have similar first hydrolysis constants. This result is not in agreement with the literature for the complexation of REEs with simple organic acids, which shows that REEs have stability constants comparable to those of copper or zinc (Martell and Hancock, 1996). The filtration experiments performed at low pH and with high lanthanum concentration show that yttrium and the REEs exhibit a very distinct behavior as a function of concentration. This result is in good agreement with a study by Hummel et al. (1995) on the binding of radionuclides (americium, curium, and europium) by humic substances. These authors showed that “complexation at trace-metal concentration on humic acids is rather different than complexation at high metal loading.” They explained this discrepancy by the presence of two different sites having different intrinsic constants. In particular, there is a small amount of strong complexing sites, which raises the overall complexation constant at low concentration levels. The same explanation holds for the experiments of Dupré et al. (1999), who proposed two types of site for REEs: a first site with a large stability constant ($\log K > 7$) and a second site with a small stability constant, comparable to that of copper ($\log K \approx 4.5$). The first kind of site, present in low concentration, plays a role when there is a low REE concentration, whereas the second site, present in higher concentration, operates at high

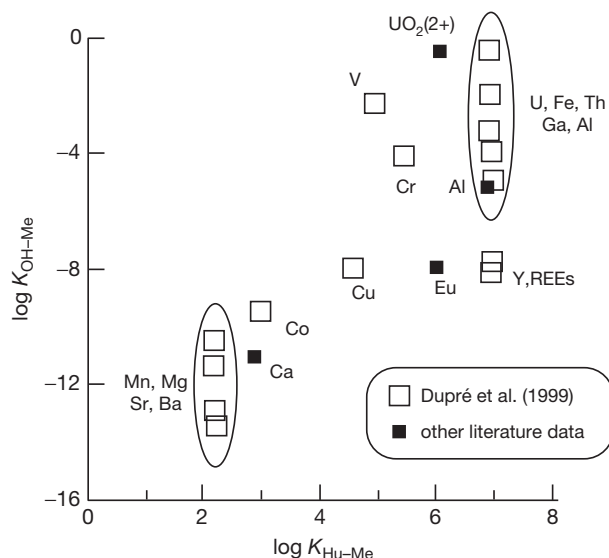


Figure 15 Correlation between metal-humate stability constants ($\log K_{\text{Hu-Me}}$) and the first hydrolysis constant ($\log K_{\text{OH-Me}}$) of the corresponding metal (Dupré et al., 1999). Squares correspond to humic-metal association constants determined by ultrafiltration of organic-rich waters. $K_{\text{Hu-Me}}$ corresponds to the conditional constant of the reaction $\text{Me}^{n+} + \text{Hu}^- \rightarrow \text{MeHu}^{(n-1)+}$.

REE content. The first site has not been characterized, but the second may be related to the carboxylic functional group.

This example illustrates the complexity of colloid-solute interactions in river waters.

7.7.5.3 The Nonorganic Colloidal Pool

In the tropical organic-rich waters of Cameroon, inorganic colloids also explain the behavior of some elements. The relationship between aluminum concentration and DOC, for example, (Figure 14) reflects the combination of two linear relationships with different slopes. The part with the larger slope ($[\text{Al}] > 700 \mu\text{g L}^{-1}$) can be assigned to the retention of kaolinitic particles by the 300 kDa membrane. Using X-ray diffraction (XRD), transmission electron microscopy (TEM), Fourier-transform infrared spectroscopy (FTIR), electron paramagnetic resonance spectroscopy (EPR), and visible diffuse reflectance spectroscopy (DRS) techniques performed on the same samples, Olivé-Lauquet et al. (1999, 2000) showed that iron and manganese in the colloidal fraction were both in the form of hydroxides and organic complexes. They also documented the presence of euhedral particles of kaolinite in the colored waters ($< 0.22 \mu\text{m}$). This result suggests that only the first part of the curve ($[\text{Al}] < 700 \mu\text{g L}^{-1}$) corresponds to aluminum bound to humic substances. Even if organic matter plays a key role in controlling trace-element levels in Cameroon, these results emphasize the difficulty of deciphering the roles of organic and inorganic colloids since metallic oxyhydroxide and organic matter are intimately associated in the solution and in the colloidal phase.

On Earth, organic-rich rivers occur in boreal regions as well as in wet tropical areas. The role of colloids in boreal organic-rich rivers has been addressed by Pokrovski and Schott (2002) and Ingri et al. (2000). For rivers of Karelia (northern Russia) Pokrovski and Schott (2002) reported that, conversely to what has been observed in the tropics (Viers et al., 1997), 90% of the organic matter is concentrated in the smallest filtrate (1–10 kDa) in the form of fulvic acids. Pokrovski and Schott (2002) showed the presence of two types of colloids: one type composed of iron oxyhydroxides and another composed of organic matter. The elements aluminum and iron do not show any significant relation with organic matter, which indicates their control by inorganic colloids (aluminosilicates and/or metallic oxyhydroxides). Three groups of elements are deduced by the authors: (i) those not affected by the ultrafiltration procedure and which are present in the form of true ions (i.e., calcium, magnesium, lithium, sodium, potassium, strontium, barium, rubidium, caesium, silicon, boron, arsenic, antimony, molybdenum); (ii) those present in the fraction smaller than 1–10 kDa under the form of inorganic or organic complexes (manganese, cobalt, nickel, copper, zinc, cadmium and for some rivers lead, chromium, yttrium, HREEs, uranium); and (iii) those strongly associated with large iron colloids (phosphorus, aluminum, gallium, REEs, lead, vanadium, chromium, tungsten, titanium, germanium, zirconium, thorium, uranium). No relation between uranium and iron or DOC was reported by Pokrovski and Schott (2002) for the rivers of Karelia, in contrast to the observations of Porcelli et al. (1997) for the Kalix river in Sweden, where between 30% and 90% of uranium is associated with organic colloids of > 10 kDa molecular weight.

Using a new operational method for testing colloid complexation with metals in rivers from Northern Russia, Vasyukova et al. (2012) confirmed the existence in boreal rivers of two types of colloids: fulvic and humic organic acids (mostly associated with divalent transition metals and alkaline-earth elements) and large-size organo-ferric colloids associated to trivalent and tetravalent elements. The presence and importance of Fe-colloids is also reported in stream waters from the basaltic region of Massif Central, France (Steinmann and Stille, 2008). In these streams, no link is reported between REE dissolved concentrations and organic matter and the precipitation of iron-oxides leads to selective removal of light REE from the dissolved load. These investigations on the role of colloids in high-latitude rivers clearly shows differences compared to rivers from the tropics, even if the total dissolved organic content is similar. This observation shows that there is a potential interesting climatic control on the nature and dynamics of colloids.

7.7.5.4 Fractionation of REEs in Rivers

The geochemistry of REEs has proven to be extremely powerful for the study of the genesis of igneous rocks (Henderson, 1984; Taylor and McLennan, 1985). Several attempts have been made over the last decades to generalize their use to surface water geochemistry (Elderfield et al., 1990; Gaillardet et al.,

1997; Goldstein and Jacobsen, 1988; Martin et al., 1976; Sholkovitz, 1992, 1995). These papers have clearly shown that REEs are among the less mobile elements in weathering and transport by waters. They explained variations in concentrations of REEs in river waters by the existence of colloids that enhance their apparent solubility. REEs are therefore excellent tracers for the dynamics of the colloidal pool in rivers. We have already mentioned that the concentrations of neodymium measured in the $<0.2 \mu\text{m}$ fraction of rivers decrease with pH. This decrease in pH is associated with a fractionation of REEs. High-pH river waters have the most enriched HREE patterns, close to that of seawater (Gaillardet et al., 1997). The REE patterns of seawater have been modeled (see Sholkovitz, 1995 for references); it has been concluded that fractionation for lanthanum to lutetium is a result of gradual differences in affinity of REEs for adsorption to particles and for complexation with ligands in solution. LREEs are preferentially adsorbed on surfaces while HRREs are preferentially complexed with carbonate in solution. The behavior of REEs in river water is far less constrained, due to the diversity of river chemistries and the complexity of solution-colloid interactions. Qualitatively at least, REE concentrations and fractionation in river waters are the result of pH-dependent reactions in solution and at the interface with colloids. Again, ultrafiltration techniques have proved to be extremely useful.

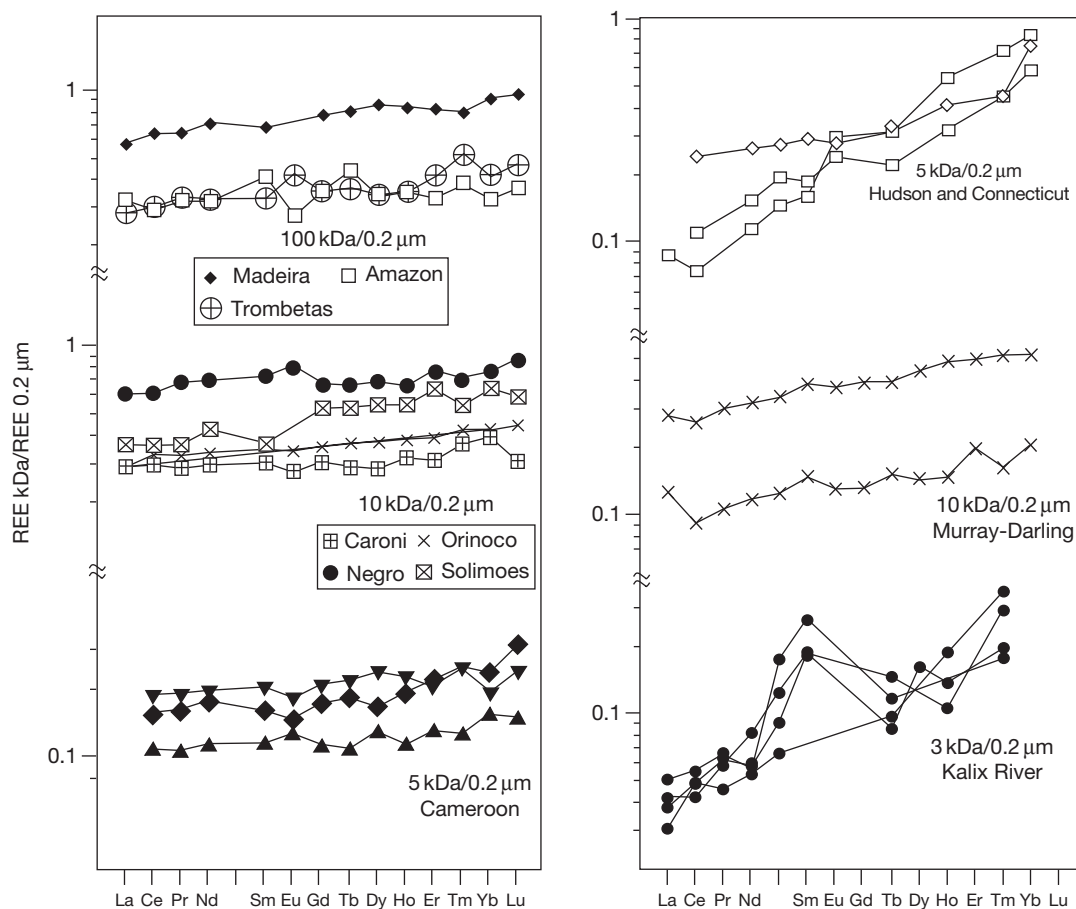


Figure 16 REE concentrations measured in the lower pore size ultrafiltrates (from 3 kDa to 100 kDa) normalized to those found in the solution ($<0.2 \mu\text{m}$) fraction in a panel of world rivers (source Deberdt et al., 2002).

A compilation on REE data in river waters has been made by Deberdt et al. (2002). Figure 16 presents the REE concentrations in the smaller-pore-size ultrafiltrates (from 3 kDa to 100 kDa) normalized to those determined in the corresponding solution fraction ($<0.2 \mu\text{m}$) for different types of rivers. For all these rivers, the concentrations of REEs measured in the solution fraction are strongly to moderately reduced by ultrafiltration. This confirms that REEs are strongly controlled by colloidal matter whatever the pH conditions.

The comparison of REE concentrations for the $<0.2 \mu\text{m}$ fraction with the lower-filter-size fraction shows that there is no unique pattern of colloidal material when rivers of different pH and different environments are compared. Ultrafiltration experiments conducted by Deberdt et al. (2002) on rivers from the Amazon and Orinoco basins as well as on Cameroon Rivers show slightly depleted LREE patterns to flat REE patterns when the colloidal fraction is normalized to the bulk solution. The results obtained by Sholkovitz (1995) and Ingri et al. (2000) for rivers of boreal environments, the Mississippi, Hudson, and Connecticut rivers, and for the Murray river by Douglas et al. (1995) show that the smaller ultrafiltration fractions (e.g., $<5 \text{ kDa}$ or 3 kDa) are more clearly enriched in HREEs compared with the solution fraction ($<0.2 \mu\text{m}$). In these rivers, colloids are therefore LREE enriched and the enrichment of HREEs in the truly dissolved fractions is explained by the authors as the direct consequence of aqueous complexation with common inorganic ions such as carbonate, phosphate, fluoride, nitrate, sulfate, and chloride (Sholkovitz, 1995), which tends to enhance their solubility. Therefore, there is no systematic relationship between LREE

depletion and pH or DOC, although more work is necessary to establish the precise relationship between filtered and ultrafiltered REE patterns and river chemistry on a global scale.

Using the REE concentration obtained in the $<5 \text{ kDa}$ fraction and assuming it to be the free REE concentration (REE^{3+}), Deberdt et al. (2002) deduced the speciation of REE in the whole $<0.20 \mu\text{m}$ fraction using the complexation constants with the most common inorganic ligands in solution and taking into account organic colloidal complexation (carboxylic and phenolic sites). The difference between calculated and observed concentration in the ultrafiltrates is attributed to mineral colloidal material.

The sum of dissolved REE in solution can be described as follows:

$$[\text{REE}]_{\text{colinorg}} = [\text{REE}]_{<0.3 \mu\text{m}} - [\text{REE}]_{\text{free}} \\ \times \left(1 + \sum \frac{K_L a_L^n \gamma_{\text{REE}}}{\gamma_{\text{REE(L)}}} + \sum \frac{K_U a_U^n \gamma_{\text{REE}}}{\gamma_{\text{REE(U)}}} \right)$$

where the subscript *colinorg* refer to inorganic colloids, L and U to solution ligands and humic substances. K are the complexation constants, a and γ are, respectively, the activity and activity coefficients. These calculations demonstrated the general and unexpected predominance of the mineral colloidal fraction in natural river waters (Figure 17). Mineral colloids account for more than 60% of the total neodymium content whatever the pH range (moderately acid to basic) in the rivers studied (Caroni, Orinoco, Amazon, Madeira, Solimoes). Colloidal neodymium can be adsorbed on submicron colloids

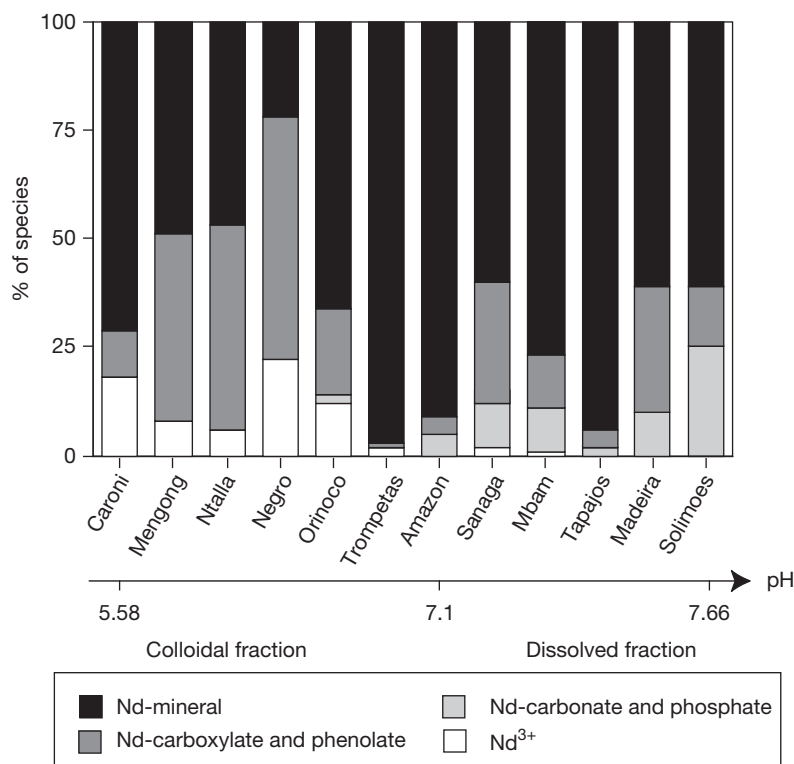


Figure 17 Speciation of Nd in a number of world rivers calculated in the solution fraction ($<0.2 \mu\text{m}$) by considering inorganic complexes (carbonate and phosphate), mineral and organic colloidal Nd species (dicarboxylic and diphenolic acids) (source Deberdt et al., 2002).

such as iron oxyhydroxides or clay minerals (e.g., kaolinite), or can occur as submicron colloids such as REE phosphate or carbonate minerals, which contain structural REEs. Note that the variable origin of neodymium in waters seems to be supported by the nonhomogeneous neodymium isotopic composition measured in the different filtrates of the Mengong (Viers and Wasserburg, 2002). As the physical and chemical properties (e.g., complexation constants) of the hypothetical phases cited above remain poorly documented, it is not possible so far to model the abundances of mineral colloids-related REEs.

This attempt to distinguish between the organic and mineral colloidal pools is still approximate, but it does show that understanding the abundance of REEs and, by extension, other “insoluble” elements requires a better physical characterization of colloidal phases and association constants with individual elements. Experimental work aimed at determining the association constants of elements with surface sites coupled with speciation models (Marsac et al., 2010; Pédrot et al., 2009; Pourret et al., 2007). The diversity of colloids, the diversity of associations between elements and colloids, and the existence of filtration artifacts are intrinsic impediments toward a better description and prediction of trace-element concentration in river waters.

7.7.5.5 Colloid Dynamics

As colloids are a major carrier of trace elements in river waters, their behavior (coagulation, adsorption, and oxidation) as function of pH, increasing solid load, and ionic strength is crucial to predict and model the behavior of trace elements. Ingri et al. (2000) have clearly shown that the strong seasonality of lanthanum abundances in the Kalix River is totally

controlled by the dynamics of organic and inorganic colloids (Figure 18). McKnight and Bencala (1989, 1990) and McKnight et al. (1989) coupled the use of lithium as a conservative tracer and iron, aluminum, and DOC concentrations in acidic mountain streams in the Colorado Rocky Mountains to show that colloid processes (e.g., precipitation of aluminum at stream confluences, sorption of dissolved organic material by hydrous iron and aluminum oxides in a stream confluence) were controlling element concentrations along the river channel. Finally, the importance of colloid dynamics is revealed in estuaries. Siberian rivers (Ob and Yenisei) have low suspended sediment load and the behavior of metals (cadmium, lead, copper, nickel, iron) in the estuary is dominated by the coagulation/sedimentation processes of riverine colloids. Clearly, the input of rivers to the ocean cannot be predicted without paying attention to the behavior of riverine colloids. For example, Dai and Martin (1995) report that copper (or nickel), although associated with colloids, behaves conservatively in the estuarine mixing zone, whereas organic carbon does not. They interpret this unexpected behavior by suggesting that colloidal organic matter is composed of at least two fractions: a refractory fraction and a labile fraction, which is removed during mixing with seawater. It is possible that the refractory fraction may be the degradation products of diatoms, given the good co-variance between silicon and copper in the estuary.

It is interesting to come back to the figure of continental crust-normalized abundances in river waters (Figure 2) in the light of the speciation considerations developed in this section. It seems that the affinity for OH^- and organic-complexation sites decreases from the highly immobile elements (e.g. aluminum, gallium), to the nonmobile elements (REEs, zinc...), moderately mobile elements and mobile elements. The fact

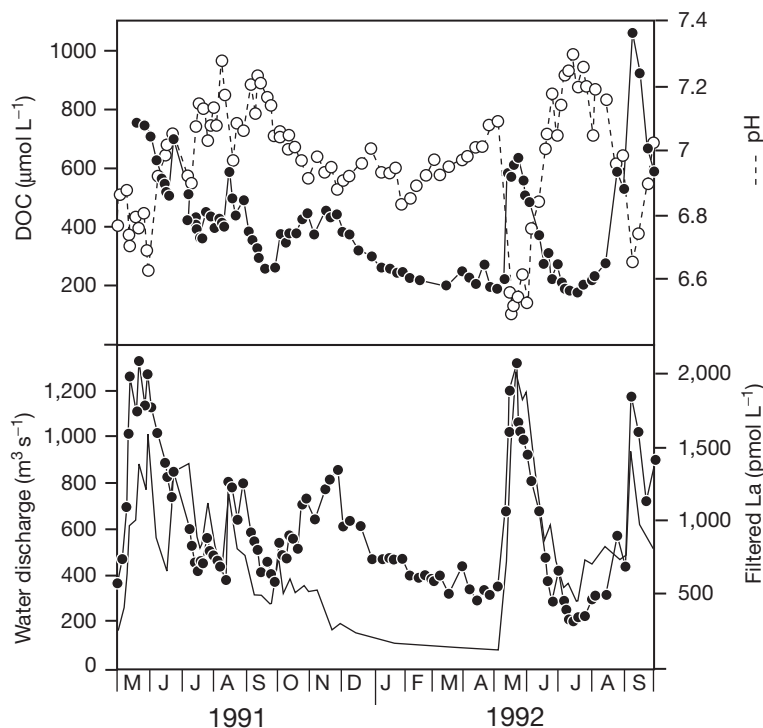


Figure 18 Dissolved organic carbon (DOC; $<0.7 \mu\text{m}$), filtered La ($<0.45 \mu\text{m}$), pH, and water discharge in the Kalix River (after Ingri et al., 2000).

that the elements having the highest affinity for complexation by sites on colloids are the least mobile on a global average indicates that processes other than aqueous complexation control their abundance in aquatic systems.

7.7.6 Interaction of Trace Elements with Solid Phases

7.7.6.1 Equilibrium Solubility of Trace Elements

When a solution equilibrates with a mineral containing a trace element as a major component, the concentration in the solution can be predicted by thermodynamics. In nature, these phases are mostly aluminum, iron, and manganese oxides. A good case study describing solubility of aluminum and iron in the mineral phase is available from the Nsimi-Zoetele watershed in Cameroon (Viers et al., 1997). Aluminum concentrations measured in organic-poor waters have been plotted on a solubility diagram on Figure 19. Ultrafiltered (5000 Da) organic-rich waters similarly plot on the solubility curves of pure well-crystallized kaolinite (observed in the soil profiles). The data suggests that both aluminum and iron concentrations in the waters of the Nsimi watershed are controlled by the solubility of mineral phases produced by rock weathering. Another example is given by Fox (1988), in which dissolved iron concentrations in the Delaware river were determined by dialysis followed by atomic absorption spectroscopy. The concentrations of iron were near saturation with colloidal ferric hydroxides. This is not, however, the case for other rivers such as the Amazon, Zaire, Negro, and Mullica, in which filterable iron concentrations are much higher than values corresponding to equilibrium with ferric hydroxides. The presence of colloids that are not removed by the filtration explains this feature.

For solubility equilibrium to predict the aqueous concentration of a trace element, thermodynamic equilibrium is required and the solid phases must also be identified. In the case of oxyhydroxides and carbonates, it is reasonable to assume a close approach to equilibrium because the

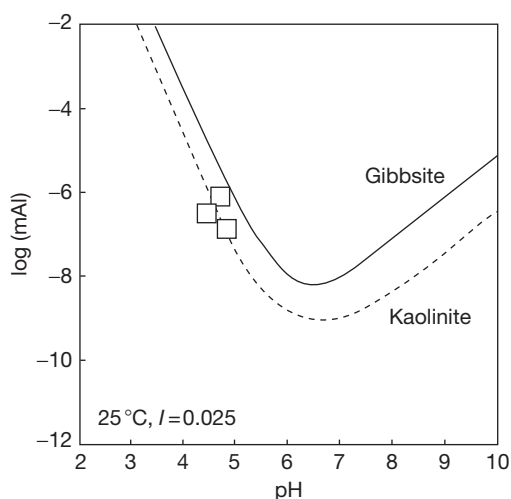


Figure 19 Saturation state of organic-poor waters from the Nsimi-Zoétéle watershed with respect to secondary aluminous phases (i.e., gibbsite, kaolinite). log(mAl) represents the logarithm of the Al concentration measured in the 5 kDa filtrate (source Viers et al., 1997).

characteristic reaction times of dissolution of these minerals are in the range of a few days to a few hundred years (Bruno et al., 2002). For silicate phases the assumption of thermodynamic equilibrium is more problematic due to the low reaction rates compared to the residence time of waters in hydrosystems. Examples of codes and database used by modelers to calculate the speciation and the solubility of a number of trace elements can be found in Bruno et al. (2002).

Iron, like manganese, uranium, and other metals, can exist in nature in more than one oxidation state. The solubility of such elements in aquatic systems depends on the concentration of oxygen, or more generally on the redox state of the fluvial system. Redox processes have been shown to control the behavior of a number of elements in lakes and in the pore waters of sediments where pe–pH diagrams are classically used to calculate the domains of stability of the solids that precipitate (e.g., MnO_2 , $\text{Fe}(\text{OH})_3$, FeS_2). The kinetics of redox reactions in natural systems is generally slow, which makes the use of pe less straightforward than pH (Michard, 1989). Even if pe–pH diagrams are theoretical, they offer a reasonable model for understanding the behavior of a number of redox-sensitive elements such as iron, manganese or uranium. The pe–pH diagram of uranium is shown in Figure 20 for a CO_2 -rich water. The solubility of uranium is sensitive to the presence of vanadium and the diagram of Figure 20 is no longer valid for water with vanadium concentrations above 0.1 mg L^{-1} .

Most often, running waters are oxygenated, but anoxic conditions can prevail locally in watersheds (e.g., in lakes, in mires or anoxic soils) and affect the whole river system. Redox reactions can be abiotic or biologically mediated but, as stated by Morel and Hering (1993), “life is by nature a redox process.”

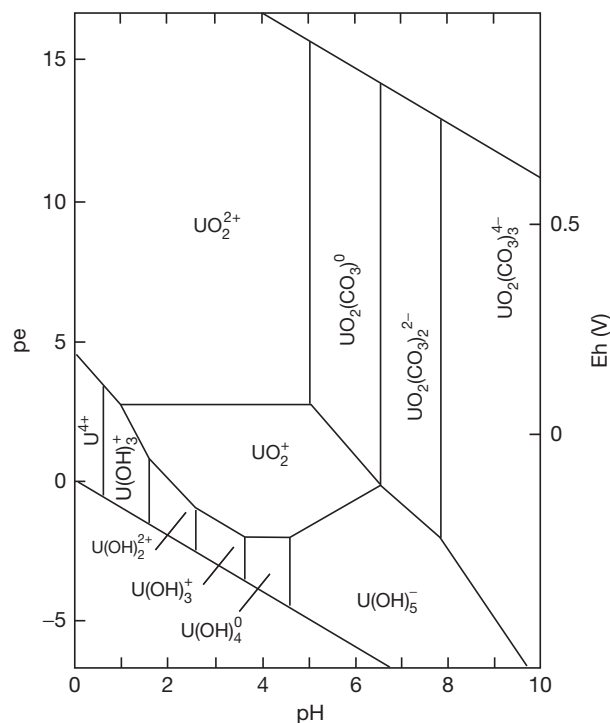


Figure 20 Distribution of dissolved uranium species in the system U–O–H₂O–CO₂ at 25 °C, assuming a P_{CO_2} of 0.01 atm (after Drever, 1997).

The ultimate reductant in nature is organic matter made by photosynthetic organisms, while the ultimate oxidant is molecular oxygen (Morel and Hering, 1993). Light and temperature have a clear impact on the rates of redox reactions: examples of the importance of redox reactions in river systems on the regulation of dissolved trace elements and temporal variations are given below.

Nonphotosynthetic iron photoreduction and oxidation have been shown to control the diel cyclicity of dissolved ferrous ion concentrations in a small acidic mountain stream (McKnight et al., 1989). The cycling of manganese and iron concentrations in the Kalix water-shed has been especially documented by Ponter et al. (1992), Ingri and Widerlund (1994), Ingri et al. (2000), and Porcelli et al. (1997). The Kalix River is an organic-rich Scandinavian river dominated by the coniferous forest. Mires cover 20% of the drainage area. The concentration of suspended matter is very low with peak concentrations of $\sim 10 \text{ mg L}^{-1}$. Tenfold seasonal variations of manganese concentrations in the dissolved load are essentially due to the input of manganese-rich lake waters after breakup of the ice in June. The manganese concentrations are then regulated in the river during summer by precipitation of manganese oxyhydroxide phases in the suspended sediments. This precipitation of manganese-rich oxides occurs when temperature gets higher than 15°C and is probably biologically mediated. The precipitation of iron-rich particles is also reported in the Kalix River during summer and this leads to a depletion of iron in solution.

Similar variations of manganese and iron concentrations are observed in larger river systems and are attributed to similar mechanisms. According to Shiller (1997), the strong seasonality of iron and manganese concentrations in the Mississippi traces a redox cyclicity. Within the drainage basin of the Mississippi, as in the Kalix river system, a number of environments are likely to have variable redox conditions through time, including mires and bogs, stagnant streams, bottom waters of stratified lakes and reservoirs, and river-bed sediments.

7.7.6.2 Reactions on Surfaces

Rather than a clear distinction between colloids and suspended material, separated by a $0.2 \mu\text{m}$ filtration, a continuum of particle radii exists between the smallest and the largest particles in water. Generally, the particle size distribution follows a power-law function in the form

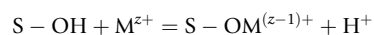
$$N(r) = Ar^{-p}$$

with p close to 4 on the range $1\text{--}100 \mu\text{m}$ in aquatic systems (Morel and Hering, 1993). The chemical reactivity of these particles is inversely correlated to their size, so that the smallest particles play the major role. The amount of suspended sediments in rivers fluctuates widely from a few milligrams per liter (lowland rivers) up to several grams per liter, for example, for the circum-Himalayan rivers. In rivers, particles encompass a wide range of chemical and mineralogical composition (biological debris, organic substances, oxyhydroxides, clays, rock fragments). These sediments are either produced *in situ* or most generally are derived from the erosion of soils.

Like colloidal material, surfaces have complexing sites for trace elements and the same formalism as that described for colloids can be used. Understanding the partitioning of metals and more generally trace elements between water and solids is crucial for fundamental studies on transport, bioavailability, and fate of trace elements in river systems. For example, the spatial and temporal trends of metal or radionuclide partitioning between dissolved and suspended solids is a major issue for understanding and predicting the pathways of pollutants in the environment. As a consequence, an impressive literature focuses on experimental studies of trace-element adsorption/desorption on synthetic surfaces (mostly hydrous oxides). However, field-based studies aimed at assessing the importance of adsorption mechanisms as a regulating process of trace-element concentrations in natural waters are sparse. We will briefly summarize some of the major ideas that emerged from experimental studies before reviewing the few “natural” studies.

7.7.6.3 Experimental Adsorption Studies

The uptake of trace elements by surfaces is due to the presence of complexing sites similar to those complexing ions in solution (e.g., OH, COOH groups). The difficulty of studying the trace-element–surface interaction is the geometry of the sites at the solid surface. The different processes possibly occurring at the surface and influencing the ion complexation are described in Morel and Hering (1993). In particular, the physical proximity of sites and the long-range nature of electrostatic interactions are major differences between reactions in solution and on solid surfaces. There are several types of solids capable of interacting with solutes: oxides surfaces, carbonate and sulfide surfaces, organic surfaces, and clay mineral surfaces. Most of the literature on the experimental determination of adsorption properties is based on metal oxides (iron, manganese, aluminum, silicon). Oxide surfaces are covered with surface hydroxyl groups represented by (S–OH). Following Schindler and Stumm (1987), the adsorption of metals involves one or two surface hydroxyls:



The adsorption of anions is generally by ligand exchange involving one or two hydroxyls:



These reactions can be treated in the same way as equilibria in solution. Equilibrium adsorption constants can thus be defined, which quantify the affinity of the cation/anion for the surface.

For example, in the case of cation sorption, the adsorption constant will be

$$K_{\text{ads}} = \left[\text{S} - \text{OM}^{(z-1)+} \right] \cdot [\text{H}^+] / [\text{S} - \text{OH}] \cdot [\text{M}^{z+}]$$

where the “constant” K_{ads} takes into account electrostatic interactions at the mineral surface (Drever, 1997). It follows that adsorption of cations and anions is strongly dependent upon pH. Cation adsorption increases with increasing pH. The range of pH at which adsorption starts depends on both the acid–base properties of the surface and the metal adsorption

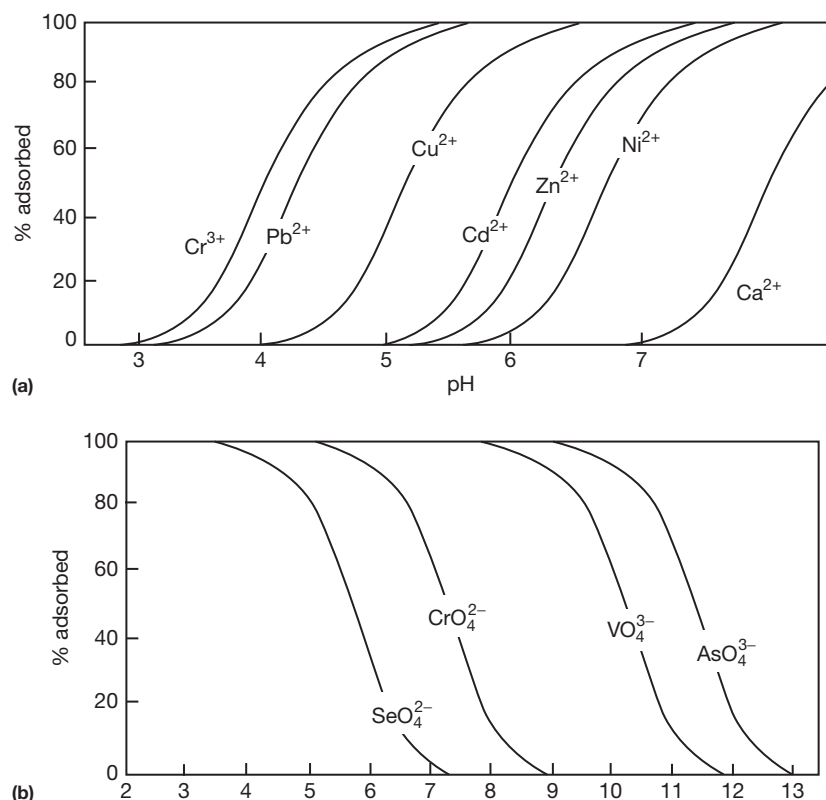


Figure 21 Proportion of cations and anions adsorbed at the surface of hydrous oxides, at high ratio of adsorption sites to adsorbing cations. Adsorption constants are from Dzomback and Morel (1990) (after Sigg et al., 2000).

constant. The percentage of adsorption on FeOOH for selected cations as a function of pH is shown in Figure 21(a) (Sigg et al., 2000). Conversely, the adsorption of anions decreases with increasing pH. Very often, the exchange of ligands is associated with acid–base reactions in solution. Figure 21(b) shows some selected adsorption curves for anions on FeOOH . The association of a ligand in solution, a trace metal in solution and a surface can lead to the formation of ternary surface complexes. In this case, a metal–ligand association is adsorbed on the surface.

Finally, finely divided hydrous oxides of iron, aluminum, manganese, and silicon are the dominant sorbents in nature because they are common in soils and rivers, where they tend to coat other particles. This is the reason why numerous laboratory researchers have been studying the uptake of trace elements by adsorption on hydrous oxides (Dzomback and Morel, 1990). Partition coefficients (concentration in solid/concentration in the solution) for a number of trace elements and a great variety of surfaces have been determined. The comparison of these experimental K_d with natural K_d values should give information on the nature of the material on which trace elements adsorb in natural systems and allow quantitative modeling.

The comparison of experimental adsorption coefficients and measured partition coefficients in natural systems remains difficult because partition coefficients are often defined with respect to bulk solid concentration and not the desorbable element concentration. Except in a few case studies of river systems having very low detrital suspended sediments concentration (e.g., iron in the Kalix River, Ingri et al. (2000)), there is no agreement

between adsorption and experimental partition coefficients. Another difficulty has been pointed out by Benoit (1995) and Benoit and Rozan (1998) and is known as the “particle concentration effect” (PCE). The PCE is a decline in partition coefficient as suspended particulate matter concentration increases in the river, although thermodynamics predicts no variation of K_d with solute or particle concentration. PCE occurs owing to both the increasing contribution of colloidal material as water discharge and particle discharge increase (Morel and Gschwend, 1987) and the contribution of coarser particles (with lower specific surface area and complexing site density) in periods of high suspended sediment concentrations and high water discharge. The PCE illustrates quite well the inherent difficulties in comparing experimental and field approaches.

7.7.6.4 Adsorption on Hydrous Oxides in River Systems

A series of studies have shown that adsorption onto hydrous oxides is a major mechanism regulating the concentration of trace elements in river waters. Several authors have described the formation of freshwater Fe–Mn coatings on gravels in well-oxygenated rivers. The use of the radioactive tracers ^{60}Co , ^{90}Sr , and ^{137}Cs (Cerling and Turner, 1982) clearly demonstrated the rapid and nonreversible (in oxic conditions) adsorption of cobalt and caesium onto river Fe–Mn coatings. Reversible adsorption of strontium was also observed.

A study of iron, cadmium and lead mobility in remote mountain streams of California by Erel et al. (1990) showed that the excess of atmospheric pollution-derived lead and cadmium is rapidly removed downstream. The comparison of

truly dissolved, colloidal, and surface particle concentrations measured in the stream with the results of a model of equilibrium adsorption indicates that the mechanism of removal in this organic-poor environment is essentially by uptake onto hydrous iron oxides. The experimentally determined partition coefficients (Dzomback and Morel, 1990) explain the behavior of lead; however, they fail to explain the cadmium removal. It is proposed by the authors that cadmium is taken up by surfaces other than hydrous iron oxides.

Another attempt at modeling trace metals (copper, nickel, lead, and zinc) in river water is presented by Mouvet and Bourg (1983) for the Meuse River. In this study, K_d partition coefficients (between adsorbed and dissolved species) are calculated, based on field measurements and compared to model calculations in which the stability constants were estimated from the adsorption of trace metals by sediments of the Meuse River in laboratory experiments. The adsorption curves of copper, zinc, and cadmium by the Meuse River bottom sediments are shown in Figure 22. Under the natural conditions, most of the copper and lead are adsorbed onto the river suspended sediments. Nickel is the least solid-bound element and zinc has an intermediate behavior. The results of the model show a general agreement between predicted and observed partition coefficients (Figure 22). Especially for the periods of high suspended sediment concentrations ($\text{TSS} > 30 \text{ mg L}^{-1}$), adsorption onto suspended solids explains relatively well the measured river concentrations. When the suspended sediment concentrations are low, the calculated percentages of adsorbed elements are underestimated, suggesting the importance of the association of organic material and suspended material in the river. The poor affinity of nickel in the Meuse River for suspended sediments is due to its dominant aqueous speciation as the NiCO_3 complex.

The adsorption of thorium has been documented experimentally by several studies (Langmuir and Herman, 1980, and references therein). As with other cationic trace elements, sorption onto surfaces is maximum at high pH and corresponds, in the absence of dissolved organic ligands, to the scavenging of hydroxy complexes. Interestingly, it has been shown for thorium that the presence of organic ligands in solution, such as fulvic acids and EDTA, inhibits adsorption and favors desorption, indicating that the affinity of thorium for organic sites is greater than for surface sites. However, our current knowledge of adsorption coefficients for the natural materials is not sufficient to allow a quantitative

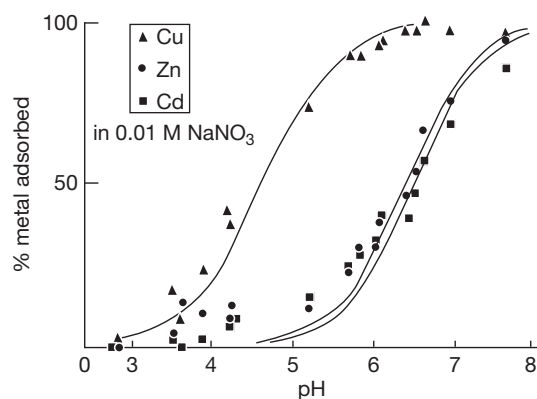


Figure 22 Adsorption of trace metals by the Meuse River bottom sediments: measured data in NaNO_3 0.01 M and interpretation (curves) in terms of adsorption.

modeling of the role of thorium adsorption on surfaces. Because the stability of manganese and iron oxides is redox sensitive, the behavior of trace elements controlled by adsorption on these surfaces is expected to vary with redox state. Two examples of this are given below.

In the Clark Fork river, Montana, Brick and Moore (1996) showed that the diel cyclicity of dissolved manganese and zinc and acid-soluble particulate aluminum, iron, manganese, copper, and zinc are related to diel changes in biogeochemical processes, such sorption or redox changes, related to pH and dissolved oxygen cycles caused by photosynthesis and respiration in the river. The highest pH values, associated with the lowest dissolved concentrations, are consistent with this scenario. It is also possible that the evapotranspiration by stream-bank vegetation could change the contribution of the hyporheic zone (reduced waters sampled from piezometers beneath the river) as a function of time and induce the observed variations in trace-element concentrations. The uptake of alkali and alkaline-earth elements on suspended iron and manganese oxides in the Kalix River has been documented by Ingri and Widerlund (1994). In this river, a significant part of sodium, potassium, calcium, magnesium, and also trace elements such as strontium and barium are scavenged by manganese and iron oxides that constitute most of the suspended sediments of the river. The calculated K_d for strontium is, however, two orders of magnitude larger than the K_d values determined experimentally by Dzomback and Morel (1990), which suggested to the authors that DOC might play an additional role in the scavenging of alkali and alkaline-earth cations. The Kalix River is, however, not representative of a "world average" river, as the composition of its suspended load is dominated by minerals that are usually minor phases in the suspended sediments of large rivers. At a global scale, the adsorption of alkali and alkaline-earths does not affect the conservative behavior of alkali and alkaline-earths in river systems. The same conclusion was reached by Chen et al. (2008) for Zn measured in the Seine River, France.

The strong seasonal variability of trace concentrations in the Mississippi River water has been ascribed to the local dynamic balance of redox conditions (Shiller and Boyle, 1997). The variations in redox conditions not only affects the dissolved concentrations of iron and manganese but also the concentrations of elements sorbed onto iron and manganese oxides such as zinc and lead. Reducing conditions will destabilize manganese and iron oxides and release zinc and lead in waters. Conversely, the reduced forms of molybdenum, vanadium, and uranium are more readily adsorbed on sediment surfaces (Emerson and Husted, 1991); these elements will tend to be scavenged under reducing conditions. If the variations in the redox state of rivers are bacterially mediated, then the seasonal variations of elements such as zinc, lead, molybdenum, vanadium, or uranium in rivers are of biological origin and should be affected by nutrient supply and pollution.

7.7.6.5 The Sorption of REEs: Competition between Aqueous and Surface Complexation

The particle/solution interactions of REEs have attracted the attention of a number of workers trying to model the REE pattern of seawater or groundwaters (e.g., Byrne and Kim, 1990; Erel and Stolper, 1992; Turner et al., 1981). Freshwater systems are more complex and, as of early 2000s, no model

taking into account complexation by colloids, surface adsorption and complexation by inorganic ligands has been attempted. The question of the adsorption of REEs onto suspended solids in freshwaters has been addressed by Elderfield et al. (1990) and Sholkovitz (1995).

Suspended sediments from the Connecticut and Mississippi rivers were leached with acetic acid or seawater in order to remove the more labile (adsorbed) fraction of REEs on sediments. The so-mobilized REEs have very low concentrations. Although significant differences exist in the leached REE patterns, the desorption of REEs from suspended sediments preferentially releases LREEs. The enrichment of dissolved HREEs in estuarine waters also confirms the preferential scavenging of LREEs on surfaces. This allowed Sholkovitz (1995) to conclude that the composition of REEs in the dissolved form of rivers is mainly controlled by surface reactions. The trend of an overall LREE enrichment in the adsorbed component relative to the dissolved component is in agreement with quantitative thermodynamic models of REE adsorption (e.g., Byrne and Kim, 1990; Erel and Morgan, 1991; Erel and Stolper, 1992) in which the competitive complexation of REEs between the solution and the oxygen-donor groups (e.g., carbonate, hydroxide, phosphate) on particle surfaces is postulated. Erel and Stolper (1992) reported a linear relationship between adsorption constants and the first hydroxide binding constants, which is supported by the data of Dzomback and Morel (1990). A strong cerium anomaly in the Mississippi River dissolved load is attributed by Sholkovitz (1995) to the oxidation of dissolved Ce(III) to particulate Ce(IV) oxides in the suspended sediments of the river. These reactions would produce a cerium anomaly only in rivers of high pH and with abundant surface areas on suspended particles. Bau (1999) has experimentally observed oxidative scavenging of cerium during the sorption of REEs onto iron oxyhydroxides.

7.7.6.6 Importance of Adsorption Processes in Large River Systems

The particles transported by large rivers are a complex mixing of primary minerals, carbonates, clays, oxides and biogenic remains. The assessment of adsorption processes in controlling the levels of trace elements in large rivers has been documented by a couple of studies that will be described below.

Various chemical extraction techniques have been introduced in order to selectively remove metals from the different adsorption or complexation sites of natural sediments (e.g., Erel et al., 1990; Leleyter et al., 1999; Tessier et al., 1979). It is, for example, shown by Leleyter et al. (1999) that between 20% and 60% of REE in various suspended river sediments are removed by successive extractions by water, by $\text{Mg}(\text{NO}_3)_2$ (exchangeable fraction), sodium acetate (acid-soluble fraction), $\text{NH}_2\text{OH} + \text{HCl}$ (manganese oxide dissolution); ammonium oxalate (iron oxide dissolution) and a mixture of $\text{H}_2\text{O}_2 + \text{HNO}_3$ (oxidizable fraction). The complexity of the extraction procedure and the absence of consensus on the specificity of the reagents for particular mineral phases make the results of sequential extraction procedures difficult to interpret.

The dissolved concentrations of zinc in the Yangtze, Amazon, and Orinoco rivers have been shown to strongly decrease with pH, between 5 and 8.5 (Shiller and Boyle, 1985). This decrease is similar to that obtained in an experiment

in which the pH of unfiltered Mississippi River water was adjusted to various pH values, and to isotherms of zinc adsorption on various natural and synthetic metal oxides surfaces (Figure 23). According to Shiller and Boyle (1985), alkaline rivers have less dissolved zinc because they are more suspended sediment-rich than acidic rivers. K_d values between adsorbed (acid-leachable) zinc and dissolved zinc approach 10^5 for the Mississippi, which indicates that the Mississippi transports 10 times more adsorbed zinc than dissolved zinc.

Zhang et al. (1993) have examined trace-element data from *in situ* measurements and laboratory experiments. The analysis of both dissolved concentrations and bulk particulate concentrations allowed them to calculate "partition coefficients." They showed, in the Huanghe River, significant variations in K_d for the different elements. The lowest K_d values are reported for copper and the highest for iron. Parameters such as pH, temperature and total suspended matter concentrations affected trace metal partitioning coefficients in the Huanghe, although the dominant effect was due to pH. As expected, adsorption of metals was favored at high pH. These experiments showed a great affinity of the Huanghe suspended solids for trace metals such as cadmium, copper and lead and showed that the kinetics of adsorption are rapid. Thus, river particulates may have the potential of regulating trace metal inputs to aquatic systems from pollution.

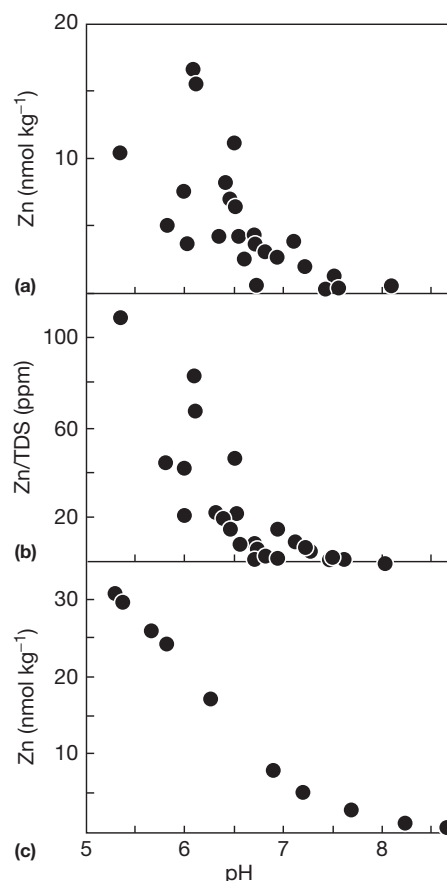


Figure 23 (a) Dissolved Zn concentrations and (b) dissolved Zn concentrations normalized to TDS as a function of pH in large rivers from the Changjiang, Amazon and Orinoco river basins. (c) Zn in pH-adjusted aliquots of Mississippi River (after Shiller and Boyle, 1985).

Beryllium is an alkaline-earth elements whose behavior drastically differs from that of the other alkaline-earth elements. Its low mobility in natural waters is attributed to its affinity for surfaces. Laboratory experiments have been performed to examine the partitioning of ^7Be between sediments from natural systems and water (You et al., 1989). The partition coefficient depends strongly on pH in the range 2–7. The curve of K_d as a function of pH (Figure 24) can be explained by a thermodynamic model by taking into account beryllium speciation in freshwater and the partition coefficient of each species. Data on ^{10}Be and ^9Be measured in the Orinoco system (Brown et al., 1992b) also fit well the model curve and experimental data. Note that the K_d values given here are the partition coefficients between soluble beryllium and exchangeable beryllium (leached from sediments with hydroxylamine). The high K_d value of beryllium clearly shows that beryllium is transported mainly in adsorbed form. The K_d values measured for beryllium between surfaces and dissolved load show that for the sediment yields present in the Orinoco, 90% of beryllium is transported in a suspended form. The low mobility of beryllium in river waters is therefore due to its attraction for surfaces. Similar to beryllium is the case of caesium, an alkali metal whose behavior in freshwaters differs from that of sodium because of its adsorption properties.

7.7.6.7 Anion Adsorption in Aquatic Systems

Boron is present in freshwater as nonionized boric acid and negatively charged borate ion ($\text{B}(\text{OH})_4^-$). The ability of boron to adsorb on surfaces is a well-known characteristic of its geochemical cycle at the surface of the Earth. Spivack et al. (1987) determined partition coefficients of boron in the marine

sediments off the Mississippi and showed that K_d ($B_{\text{adsorbed}}/B_{\text{aqueous}}$) is close to 1.5. The two isotopes of boron do not behave similarly during adsorption on surfaces: the light isotope is preferentially attached to surfaces. This adsorption of boron onto particles has a significant effect on the boron isotopic composition of seawater, but is probably not significant in freshwaters due to the relatively low amount of dissolved boron in freshwaters.

Among the other trace anions, the concentration of arsenic in natural waters is probably controlled by solid–solution interaction (Smedley and Kinniburgh, 2002). In sediments, the element that most frequently correlates with arsenic is iron and numerous studies have been reported on the sorption of arsenic (as arsenate ion, HAsO_4^{2-}) onto iron oxides, manganese oxides or aluminum oxides (see references in Smedley and Kinniburgh (2002)). K_d values up to 10^6 (L kg^{-1}) are found for the experimental adsorption of arsenic onto hydrous ferric oxides. The desorption of arsenic, like the desorption of other anion-forming elements (vanadium, boron, molybdenum, selenium, and uranium), especially from iron oxides, is one of the key processes invoked to explain high levels of arsenic in natural waters and associated toxicity problems. This desorption is favored at pH values above 8 and when iron oxides undergo reductive dissolution.

7.7.6.8 Adsorption and Organic Matter

The extrapolation of experimental studies on trace-metal adsorption to natural waters is difficult: a particular problem is the formation of both ternary surface complexes involving dissolved organic matter and the aqueous complexation of trace elements by dissolved organic matter. The number of

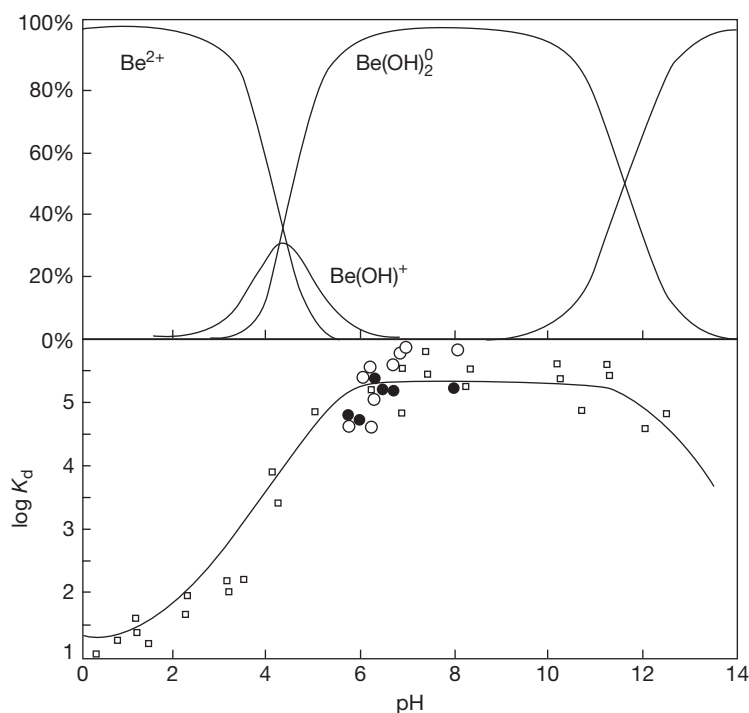


Figure 24 Bulk partitioning coefficients between dissolved and adsorbed Be on particles measured in the Orinoco for ^9Be (filled circles) and ^{10}Be (open circles). Open squares are experimental distribution coefficients determined by You et al. (1989) by adsorption of Be onto riverine particles. The line is deduced from a speciation-dependent model of adsorption (after Brown et al., 1992b).

studies trying to shed light on the complexity of these interactions by combined studies of organic matter in the suspended phase and the dissolved phase is incredibly low.

Sholkovitz and Copland (1980) used the organic-rich water of the Luce River and a tributary of the Luce River, Scotland, to investigate the relations between pH-related adsorption and organic complexation in solution. They concluded that, under their experimental conditions, the control of organic matter is much more important for determining the levels of dissolved trace elements in the river than adsorption onto the suspended sediments (composed either of clays plus organics or iron oxides plus organics). These results are not in agreement with, and are even opposite to, those inferred from artificial solutions and chemical models (see Sholkovitz and Copland (1980) for references).

Shafer et al. (1997) addressed the influence of dissolved organic carbon, suspended particulates and hydrology on the concentration and partitioning of trace metals in two contrasting (one agricultural, one forested) Wisconsin (USA) watersheds. As expected, the forested watershed had higher DOC levels (mean value of 7 mg L^{-1} versus 4 mg L^{-1}), but lower suspended particulate matter (SPM) (mean value of 2 mg L^{-1} versus 18 mg L^{-1}). The high concentrations of DOC and the low concentrations of potential inorganic ligands in the two rivers suggested that the dominant speciation of aluminum, cadmium, copper, lead, and zinc in solution was organic. This study shows the partitioning preferences of selected metals in these two DOC-rich and SPM-poor watersheds. Lead appears as the most strongly adsorbed element with an intermediate affinity for dissolved organic matter. Kd values for lead are uniform in low-DOC and high-SPM waters, but somewhat variable in high-DOC and low clay environments. Copper exhibits the opposite behavior. It shows a stronger affinity for DOC than for surfaces. As a consequence, copper partitioning is rather insensitive to variations in DOC concentration. The intermediate affinity of zinc for SPM and DOC makes zinc partitioning highly sensitive to changes in either SPM or DOC. Accordingly, Kd values are ranked in the order $\text{Pb} > \text{Zn} > \text{Cd} > \text{Cu}$. Note that the trends observed in these two Wisconsin watersheds are probably not representative of larger systems, which generally have higher suspended sediment concentrations.

As shown by Laxen (1985), the adsorption of cadmium, copper, and nickel onto hydrous ferric oxides in the presence of dissolved humic substances is significantly modified. The adsorption of cadmium and nickel is enhanced by the presence of humics. The model favored by the authors is the complexation of metals with adsorbed humics, which is stronger than binding with the dissolved humics. The adsorption of copper is enhanced but more sensitive to the competitive formation of soluble copper-humic complexes. An important implication of these experiments is that metals will be more strongly adsorbed at low pH values in the presence of humics than in their absence. Radiotracer experiments have shown that, in the ocean, interactions of organic-rich colloids and particles (through sorption and coagulation) occur in estuaries. This mechanism is termed "colloidal pumping" and plays a crucial role in the fate of many trace elements in estuarine waters (Wen et al., 1997). The extent of this mechanism in rivers has not been explored. Finally Davranche et al. (2004) investigated experimentally the adsorption of REE onto hydrous ferric

oxides using solution containing free REE (III) or REE (III)-organic complexes. They showed that the REE patterns are modified by organic speciation and that the REE-humate complex remain stable during adsorption. The mechanism seems to be the adsorption of the anionic REE-humate complex onto HFO surface. While the adsorption of the free REE favor the intermediate REE, the adsorption of humate complex lead to flat Kd REE patterns.

Finally, one should not end this section without mentioning the uptake of trace elements by living biomass. This process can be of quantitative importance in river systems of low velocity or draining lakes or stagnant water bodies. For example, a study in the St. Lawrence river (Qu  merais and Lum, 1997) has shown that an uptake of cadmium by phytoplankton occurs in the summer. In lakes, the uptake of trace elements by living organisms has been demonstrated for a number of trace elements with known biological activity (copper, zinc, iron, molybdenum, manganese), or unknown biological function (cadmium, arsenic) (cf. Sigg et al., 2000).

7.7.6.9 Particle Dynamics

Regulation of concentration of trace elements by surfaces plays a key role in river water systems. This applies to both colloids and larger particles. Over the past decades, the physicochemical understanding of sorption processes has considerably improved. Mass transfer codes (see Chapter 7.2) such as PHREEQE (Parkhurst et al., 1990), PHREEQC (Parkhurst, 1995), SOLMIN EQ.88 (Kharaka et al., 1988), MINTEQA2 (Allison et al., 1991), MINTEQ(4.00) (Eary and Jenne, 1992), MINEQL+ (Schecher and McAvoy, 1991), and EQ3/6 (Wollery, 1992) perform specialized calculations and predict changes in solution chemistry caused by different processes such as dissolution/precipitation, ion exchange/adsorption, or mixing of water masses. However, so far, these models, which explain the results from the laboratory experiments well, are not able, in general, to predict the pathways of trace elements in the natural system. This is due to the complexity of the natural systems characterized by the diversity of substrates, of surface sites, of ligands in solution, and the abundance of organic material, the presence of colloids that pass through filters and preclude the strict separation between aqueous and solid phase concentrations, and finally the dynamics of colloids and particles within the river system. The transfer of experimental data to natural systems is not straightforward because natural surfaces are far more complex than the experimentally synthesized ones. Studies of the kinetics of adsorption/desorption of trace elements on natural sediments should be encouraged, even if severe experimental artifacts exist. More data on concentrations of dissolved, adsorbed and colloidal material in natural systems are necessary, particularly on a worldwide scale, in order to improve our knowledge of trace-element behavior in natural waters and to improve the quality of modeling and the accuracy of prediction. Because trace metals are carried on the finer fraction of sediments in river systems (Horovitz, 1991), due to a surface area effect, the sedimentary dynamics and the post-depositional stability of sediments (residence times) in watersheds are important factors to take into account for the transport of trace elements. For example, the preferential deposition of fine-grained material in floodplains, lakes or reservoirs will strongly influence the pathways of

metals through catchments. An integrated approach of chemistry, geochemistry, and geomorphology is therefore in order.

7.7.7 Conclusion

This review focuses on the concentration of trace elements occurring in river waters, based on the data obtained from natural sources. The determination of concentrations of many trace elements in river waters is facilitated in particular by the technical advances of ICP-MS allowing rapid measurement of a large number of elements. Trace-element measurements are not only motivated by the requirements of pollution and toxicology studies, but also by the need for better understanding and modeling of the behavior of elements during continental weathering and transport, which constitute the two major aspects of the geological cycle.

So far, the global systematics of trace elements in river waters are still poorly understood and limited either to industrial countries, where the natural levels are overwhelmed by anthropogenic inputs, or to regions of the world where rivers are organic-rich, namely, the tropics and the high-latitude areas. Continents such as Asia, Australia and the numerous Pacific peninsulas have been very poorly investigated, except for a few elements of geochemical importance (osmium, uranium, thorium, strontium).

Trace-element concentrations in river waters span over 10 orders of magnitude, similar to the range of crustal abundances. However, the normalization of trace-element levels in river waters to mean continental abundances shows that the abundance of trace elements in river waters depends not only on their continental abundances, but also on their mobility in weathering and transport processes. Normalized abundances of elements in river water vary over five orders of magnitude from highly immobile elements such as titanium, niobium, zirconium, aluminum, and tantalum to highly mobile elements such as selenium, rhenium, boron, arsenic, molybdenum, and sodium. An important feature of trace-element concentrations in river water is a large variability in space and time, even over very short periods of time (days). In addition, the abundance of elements such as REEs is a function of river chemistry as exemplified by the worldwide correlation observed between dissolved neodymium and pH. It is a major characteristic of trace-element concentrations in river waters that they not only depend on their abundance in the source rocks but that they are also strongly dependent on the chemical conditions prevailing in the river. There are a few exceptions to this rule, notably the most mobile elements that correlate fairly well with the major elements.

The mobility of trace elements in river waters results from a complex combination of several factors: their solubility in water, the input to the system of nonweathering sources such as atmospheric and/or anthropogenic sources, the ability of the elements to be complexed by fine ($< 0.2 \mu\text{m}$) colloidal material, and the affinity of the elements for solids (adsorption, co-precipitation, solubility equilibrium). The "chemical" solubility of elements depends on the solubility of the minerals that contain the elements and is approximately related to the atomic and molecular properties of the elements. Elements of small atomic radii tend to form polycharged oxyanions that make

them soluble (e.g., boron, arsenic, tungsten, vanadium). Elements of higher atomic radii, and of +1 or +2 valency tend to be soluble as free cations (sodium, potassium, barium, lithium, strontium). Elements such as aluminum, REEs, thorium, and iron fall in between and form poorly soluble oxyanions or hydroxyanions. Nonweathering inputs comprise atmospheric inputs, anthropogenic inputs or plant inputs. Owing to the global present-day contamination of the atmosphere by anthropogenic emissions (e.g., combustion dusts, detrital particles, industrial aerosols, gases etc.), it is difficult to estimate the natural input of trace elements to hydrosystems, but even in the most remote areas, rain can be a significant source of elements transported by the rivers. In the industrialized countries and to a lesser extent, at a global scale, clear evidence of direct contamination of rivers by anthropogenic sources exists, especially for heavy metals and other metals.

Although it controls the mobility of trace elements in water, the aqueous speciation of many elements in river waters is not well known, principally when organic complexes are involved. However, one of the most striking characteristics of the behavior of trace elements for which chemical aqueous species are known, is that their concentrations are usually not predictable by classical speciation calculations involving the major inorganic or organic ligands in solution. This is due to two competitive mechanisms. The first is the existence in rivers, especially in rivers of low pH, of a colloidal phase made of intimately coupled organic and inorganic material, which can pass through the pores of filtration membranes (conventionally $0.2 \mu\text{m}$; and therefore analyzed and considered as dissolved material). The more the colloidal material "contaminates" the dissolved phase, the higher the concentrations of chemically insoluble elements will be. Although colloidal material is poorly known, and its affinity for trace elements still debated, the affinity of organic colloid for trace metals increases with the first hydrolysis constant of the metal. The competing mechanism that tends to lower the levels of "dissolved" trace elements is the affinity of the elements for particles larger than $0.2 \mu\text{m}$, which leads to the removal of these elements from the dissolved phase during filtration. In rivers, a great variety of surfaces can exist and uptake mechanisms can be very diverse. Adsorption or co-precipitation on hydrous oxides, organic particles or clays, and uptake by living organisms are possible mechanisms, and they are not easy to distinguish. Although colloids are small particles and should obey the same formalism as surface complexation on larger particles, our understanding and modeling of colloidal and surface uptake in natural hydrosystems is far from being clear and complete. Surface sorption, like aqueous complexation, increases with the first hydrolysis constant. Although, an impressive literature exists on the interaction between solutes and hydrous oxides, the use of the experimentally derived affinity constants adapting to the natural systems is a difficult task. The principal obstacle in this attempt is the complexity of naturally occurring material, the poor physical description we have of colloids, the potential experimental artifacts associated with the isolation of colloids (fractionation, coagulation), and the extremely variable chemistry of rivers from one continent to another. The pH-sensitivity of stability of colloids in the aquatic system, as well as the varying extent of adsorption of ions as a function of pH, can explain the dependence of concentration of the trace elements in river water on pH and other chemical variables.

Much work is clearly needed to gain an understanding of the control on concentrations of trace elements in river waters and aquatic systems. It seems clear that further studies should focus on the physical characterization of the colloid pool and comprehension of its dynamics. Estuarine studies have shown that the behavior of elements in the mixing zones between rivers and ocean water is controlled by the flocculation, coagulation, or degradation of colloidal material. The technological advances in filtration membranes should allow a better size fractionation and isolation of colloids. Nanofiltration and dialysis are other promising techniques that need to be developed and should lead to a better characterization of the "true" dissolved pool and of the colloidal-size material. So far, trace-element concentrations have been measured in a restricted number of environments, which may not be typical. Extended investigations on rivers of high pH, high suspended material yields, and mountainous rivers, or rivers of variable climatic or lithologic settings are necessary to get a better world-scale overview of trace-element levels and controlling parameters. From a more theoretical point of view, the relationships between the periodic table properties and the geochemical behavior of trace element in natural hydrosystems, through organic and inorganic complexation, solid uptake and affinity for life in river systems need to be explored.

Finally, the recent technical progress in the new generation of multicollector ICP-MS instruments that enable the measurement of the isotopic ratios of a number of trace metals, whose isotopes are fractionated by complexation processes, is a new challenge for aquatic sciences, which, no doubt, will improve our knowledge and prediction of trace-element dynamics in hydrosystems.

Acknowledgments

J. I. Drever and M. Meybeck provided the first impulse for this chapter. We thank O. Pokrovski, J. Schott, J. L. Dandurand, S. Deberdt, R. Millot, P. Seyler, E. Lemarchand, B. Bourdon, J.B. Chen, G. Gruau, A. Dia, and M. Benedetti for their help and discussions. This chapter benefited from a detailed review by J. I. Drever. This is IGP contribution no. 1947.

References

- Alasonati E, Slaveykova VI, Gallard H, Croué JP, and Benedetti M (2010) Characterization of the colloidal organic matter from the amazonian basin by asymmetrical flow field-fractionation and size exclusion chromatography. *Water Research* 44: 223–231.
- Allègre CJ (2008) *Isotope Geology*, 512 pp. New York: Cambridge University Press.
- Allison JD Brown DS and Novo-Gradac KJ (1991) *MINTEQA2: A Geochemical Assessment Data Base and Test Cases for Environmental Systems*, vers. 3.0 user's manual. Report EPA/600/3-91-21. Athens, GA, US EPA.
- Ammann AA (2002) Speciation of heavy metals in environmental water by ion chromatography coupled to ICP-MS. *Analytical and Bioanalytical Chemistry* 372: 448–452.
- Akinfiev NN (1976) "Balance": IBM computer code for calculating mineral aqueous solution-gas equilibria. *Geochemistry* 6: 882–890 (in Russian).
- Artaxo P, Maenhaut W, Storms H, and Van Grieken R (1990) Aerosol characteristics and sources for the Amazon basin during the wet season. *Journal of Geophysical Research* 95: 16971–16985.
- Baes CF and Mesmer RE (1976) *The Hydrolysis of Cations*. New York: Wiley 489 pp.
- Bagard ML, Chabaux F, Pokrovsky OS, et al. (2011) Seasonal variability of element fluxes in two central Siberian Rivers draining high latitude permafrost dominated areas. *Geochimica et Cosmochimica Acta* 75: 3335–3357.
- Bau M (1999) Scavenging of dissolved yttrium and rare earths by precipitating iron hydroxide: experimental evidence for Ce oxidation, Y–Ho fractionation and lanthanide tetrad effect. *Geochimica et Cosmochimica Acta* 63: 67–77.
- Bau M and Dulski P (1996) Anthropogenic origin of positive gadolinium anomalies in river waters. *Earth and Planetary Science Letters* 143: 345–355.
- Benoit G (1995) Evidence of the particle concentration effect for lead and other metals in fresh waters based on ultrafiltration technique analyses. *Geochimica et Cosmochimica Acta* 59(13): 2677–2687.
- Benoit G and Rozan TF (1998) The influence of size distribution on the particle concentration effect and trace metal partitioning in rivers. *Geochimica et Cosmochimica Acta* 63(1): 113–127.
- Berg T, Royset O, and Steinnes E (1994) Trace element in atmospheric precipitation at Norwegian background stations (1989–1990) measured by ICP-MS. *Atmospheric Environment* 28: 3519–3536.
- Berner EK and Berner RA (2012) *Global environment: water, air, and geochemical cycles (second edition)*. Englewood Cliffs, NJ: Prentice-Hall 460.
- Brick CM and Moore JN (1996) Diel variation of trace metals in the upper Clark Fork river, Montana. *Environmental Science and Technology* 30: 1953–1960.
- Brown ET, Measures CI, Edmond JM, Bourlès DL, Raibeck GM, and Yiou F (1992a) Continental inputs of beryllium to the oceans. *Earth and Planetary Science Letters* 114: 101–111.
- Brown E, Edmond JM, Raibeck GM, Bourlès DL, Yiou F, and Measures CI (1992b) Beryllium isotope geochemistry in tropical river basins. *Geochimica et Cosmochimica Acta* 56: 1607–1624.
- Bruno J, Duro L, and Grivé M (2002) The applicability and limitations of thermodynamic geochemical models to simulate trace element behavior in natural waters: lessons from natural analogue studies. *Chemical Geology* 190: 371–393.
- Buffle J and Van Leeuwen HP (1992) *Environmental particles: 1. In Environmental Analytical and Physical Chemistry Series*. London: Lewis Publishers 554p.
- Burba P, Shkinev V, and Spivakov BY (1995) On-line fractionation and characterisation of aquatic humic substances by means of sequential-stage ultrafiltration. *Journal of Analytical Chemistry* 351: 74–82.
- Byrne RH and Kim KH (1990) Rare earth element scavenging in seawater. *Geochimica et Cosmochimica Acta* 54: 2645–2656.
- Cameron EM, Hall GEM, Veizer J, and Roy Krouse H (1995) Isotopic and elemental hydrogeochemistry of a major river system: Fraser river, British Columbia, Canada. *Chemical Geology* 122: 149–169.
- Cantrell KJ and Byrne RH (1987) Rare earth element complexation by carbonate and oxalate ions. *Geochimica et Cosmochimica Acta* 51: 597–605.
- Cerling TE and Turner RR (1982) Formation of freshwater Fe–Mn coatings on gravel and the behavior of ⁶⁰Co, ⁹⁰Sr, and ¹³⁷Cs in a small watershed. *Geochimica et Cosmochimica Acta* 46: 1333–1343.
- Chabaux F, Riotte J, Clauer N, and France-Lanord Ch (2001) Isotopic tracing of the dissolved U fluxes in Himalayan rivers: implications for the U oceanic budget. *Geochimica et Cosmochimica Acta* 65: 3201–3217.
- Chabaux F, Riotte J, and Dequincey O (2003) U–Th–Ra fractionation during weathering and river transport. In: Bourdon B, Turner S, Henderson G, and Lundstrom CC (eds.) *U-series Geochemistry and Applications, Reviews in Mineralogy and Geochemistry*. Mineralogical Society of America and Geochemical Society.
- Chen JB, Gaillardet J, and Louvat P (2008) Zinc isotopes in the Seine River Waters, France: A probe of anthropogenic contamination. *Environmental Science and Technology* 42: 6494–6501.
- Colodner D, Sachs J, Ravizza G, Turekian K, Edmond J, and Boyle E (1993) The geochemical cycle of rhenium: a reconnaissance. *Earth and Planetary Science Letters* 117: 205–221.
- Cossa D, Tremblay GH, and Gobeil C (1990) Seasonality in iron and manganese concentrations in the St. Lawrence river. *Science of the Total Environment* 97/98: 185–190.
- Dahlqvist R, Benedetti M, Andersson K, et al. (2004) Association of calcium with colloidal particles and speciation of calcium in the Kalix and Amazon rivers. *Geochimica et Cosmochimica Acta* 68: 4059–4075.
- Dai M and Martin J-M (1995) First data on trace metal level and behaviour in two major Arctic river-estuarine systems (Ob and Yenisey) and in the adjacent Kara Sea, Russia. *Earth and Planetary Science Letters* 131: 127–141.
- Dalai TK, Singh SK, Trivedi JR, and Krishnaswami S (2001) Dissolved rhenium in the Yamuna river system and the Ganga in the Himalaya: Role of black shale weathering on the budgets of Re, Os, and U in rivers and CO₂ in the atmosphere. *Geochimica et Cosmochimica Acta* 66(1): 29–43.

- Davranche M, Pourret O, Gruau G, and Dia A (2004) Impact of humate complexation on the adsorption of REE onto Fe oxyhydroxide. *Journal of Colloid and Interface Science* 277: 271–279.
- Deberdt S, Viers J, and Dupre B (2002) New insights about the rare earth elements (REE) mobility in river waters. *Bulletin de la Société Géologique de France* 173(2): 147–160.
- De Caritat P, Reimann C, Ayras M, Niskavaara H, Chekushin VA, and Pavlov VA (1996) Stream water geochemistry from selected catchments on the Kola peninsula (NW Russia) and the neighbouring areas of Finland and Norway: 1. Element levels and sources. *Aquatic Geochemistry* 2: 149–168.
- Dia A, Gruau G, Olivié-Lauquet G, Riou C, Molénat J, and Curmi P (2000) The distribution of rare earth elements in shallow groundwaters: Assessing the role of source-rock composition, redox conditions and colloidal particles. *Geochimica et Cosmochimica Acta* 64(24): 4131–4151.
- Douglas GB, Gray CM, Hart BT, and Beckett R (1995) A strontium isotopic investigation of the origin of suspended particulate matter (SPM) in the Murray-Darling river system, Australia. *Geochimica et Cosmochimica Acta* 59: 3799–3815.
- Drever JI (1997) *Geochemistry of Natural Waters*, 3rd edn. Englewood Cliffs, NJ: Prentice-Hall.
- Dupré B, Gaillardet J, and Allègre CJ (1996) Major and trace elements of river-borne material: the Congo Basin. *Geochimica et Cosmochimica Acta* 60: 1301–1321.
- Dupré B, Viers J, Dandurand JL, et al. (1999) Major and trace elements associated with colloids in organic-rich river waters: Ultrafiltration of natural and spiked solutions. *Chemical Geology* 160: 63–80.
- Dzombak DA and Morel FMM (1990) *Surface Complexation Modelling*. New York: Wiley.
- Eary LE and Jenne EA (1992) *Version 4.00 of the MINTEQA Code*. Report PNL-8190/UC-204. Richland, WA, Pacific Northwest Laboratory.
- Edmond JM, Spivack A, Grant BC, et al. (1985) Chemical dynamics of the Changjiang estuary. *Continental Shelf Research* 4(1/2): 17–36.
- Edmond JM, Palmer MR, Measures CI, Grant B, and Stallard RF (1995) The fluvial geochemistry and denudation rate of the Guyana shield in Venezuela, Columbia and Brazil. *Geochimica et Cosmochimica Acta* 59: 3301–3325.
- Edmond JM, Palmer MR, Measures CI, Brown ET, and Huh Y (1996) Fluvial geochemistry of the eastern slope of the northeastern Andes and its foredeep in the drainage of the Orinoco in Colombia and Venezuela. *Geochimica et Cosmochimica Acta* 60: 2949–2975.
- Elbaz-Poulichet F, Seyler P, Maurice-Bourgoin L, Guyot JL, and Dupuy C (1999) Trace element geochemistry in the upper Amazon drainage basin (Bolivia). *Chemical Geology* 157: 319–334.
- Elderfield H, Upstill-Goddard R, and Sholkovitz ER (1990) The rare earth element in rivers, estuaries, and coastal seas and their significance to the composition of ocean waters. *Geochimica et Cosmochimica Acta* 54: 971–991.
- Emerson SR and Huested SS (1991) Ocean anoxia and the concentrations of molybdenum and vanadium in seawater. *Marine Chemistry* 34: 177–196.
- Erel Y and Morgan JJ (1991) The effect of surface reactions on the relative abundances of trace metals in deep sea waste. *Geochimica et Cosmochimica Acta* 55: 1807–1813.
- Erel Y and Stolper EM (1992) Modelling of rare-earth element partitioning between particles and solution in aquatic environments. *Geochimica et Cosmochimica Acta* 57: 513–518.
- Erel Y, Morgan JJ, and Patterson CC (1990) Natural levels of lead and cadmium in remote mountain stream. *Geochimica et Cosmochimica Acta* 55: 707–719.
- Eyrolle F, Fevrier D, and Benaim JU-Y (1993) Etude par D. P. A. S. V. de l'aptitude de la matière organique colloïdale à fixer et à transporter les métaux: exemples de bassins versants en zone tropicale. *Environmental Technologies* 14: 701–717.
- Eyrolle F, Benedetti MF, Benaim J-Y, and Fevrier D (1996) The distributions of colloidal and dissolved organic carbon, major elements and trace elements in small tropical catchments. *Geochimica et Cosmochimica Acta* 60: 3643–3656.
- Forner SK, Mark BG, McKenzie JM, et al. (2011) Elevated stream trace and minor element concentrations in the foreland of receding tropical glaciers. *Applied Geochemistry* 26: 1792–1801.
- Foster IDL and Charlesworth SM (1996) Heavy metals in the hydrological cycle: trends and explanation. *Hydrological Processes* 10: 227–261.
- Fox LE (1988) The solubility of colloidal ferric hydroxide and its relevance to iron concentrations in river water. *Geochimica et Cosmochimica Acta* 52: 771–777.
- Frei M, Bielert U, and Heinrichs H (1998) Effects of pH, alkalinity and bedrock chemistry on metal concentrations of springs in an acidified catchment (Ecker dam, Harz Mountains, FRG). *Chemical Geology* 170: 221–242.
- Freydier R, Dupré B, and Lacaux JP (1998) Precipitation chemistry in intertropical Africa. *Atmospheric Environment* 32: 749–765.
- Froelich PN, Hambrick GA, Andreae MO, Mortlock RA, and Edmond JM (1985) The geochemistry of inorganic germanium in natural waters. *Journal of Geophysical Research* 90(C1): 1133–1141.
- Gaillardet J, Dupré B, Allègre CJ, and Négrel P (1997) Chemical and physical denudation in the Amazon river basin. *Chemical Geology* 142: 141–173.
- Gaillardet J, Dupré B, Louvat P, and Allègre CJ (1999a) Global silicate weathering of silicates estimated from large river geochemistry. *Chemical Geology (Special Issue Carbon Cycle 7)* 159: 3–30.
- Gaillardet J, Dupré B, and Allegre CJ (1999b) Geochemistry of large river suspended sediments: Silicate weathering or crustal recycling? *Geochimica et Cosmochimica Acta* 63(23/24): 4037–4051.
- Gaillardet J, Millot R, and Dupré B (2003) Trace elements in the Mackenzie river basin (in preparation).
- Goldstein SJ and Jacobsen SB (1988) Rare earth elements in river waters. *Earth and Planetary Science Letters* 89: 35–47.
- Gu B, Schmitt J, Chen Z, Liang L, and McCarthy JF (1995) Adsorption and desorption of different organic matter fractions on iron oxide. *Geochimica et Cosmochimica Acta* 59: 219–229.
- Henderson P, et al. (1984) General geochemical properties and abundances of the rare earth elements. In: *Developments in Geochemistry: 2. Rare Earth Element Geochemistry*, pp. 1–32. Amsterdam: Elsevier.
- Herrera Ramos AC and McBride MB (1996) Goethite dispersibility in solutions of variable ionic strength and soluble organic matter content. *Clay Clays Minerals* 44: 286–296.
- Hoffmann SR, Shafer MM, Babiarz CL, and Armstrong DE (2000) A critical evaluation of tangential-flow ultrafiltration for trace metals studies in freshwater systems: 1. Organic carbon. *Environmental Science and Technology* 34: 3420–3427.
- Horowitz AJ, Lum KR, Garbarino JR, Gwendy EMH, Lemieux C, and Demas CR (1996) The effect of membrane filtration on dissolved trace element concentrations. *Water Air Soil Pollution* 90: 281–294.
- Huang WW, Martin JM, Seyler Zhang J, and Zhong XM (1988) Distribution and behavior of arsenic in the Huanghe (Yellow river) estuary and Bohai Sea. *Marine Chemistry* 25: 75–91.
- Huh Y, Chan LH, Zhang L, and Edmond JM (1998) Lithium and its isotopes in major world rivers: Implications for weathering and the oceanic budget. *Geochimica et Cosmochimica Acta* 62: 2039–2051.
- Hummel W, Glaus M, Van Loon LR (1995) Binding of radionuclides by humic substances: the "Conservative Roof" approach. In: *Proceedings of an NEA Workshop, September 14–16, 1994, Bad Zurzach, Switzerland*. OECD documents, ISBN no. 92-94, 251–262.
- Ingri J and Widerlund A (1994) Uptake of alkali and alkaline earth elements on suspended iron and manganese in the Kalix River, northern Sweden. *Geochimica et Cosmochimica Acta* 58: 5433–5442.
- Ingri J, Widerlund A, Land M, Gustafsson Ö, Andersson P, and Öhlander B (2000) Temporal variations in the fractionation of the rare earth elements in a boreal river: The role of colloidal particles. *Chemical Geology* 166: 23–45.
- Johannesson K, Stetzenbach K, Hodge VF, and Lyons WB (1996) Rare earth element complexation behavior in circumneutral pH groundwaters: assessing the role of carbonate and phosphate ions. *Earth and Planetary Science Letters* 139: 305–319.
- Johannesson KH, Lyons WB, Graham EY, and Welch CA (2000) Oxyanion concentrations in eastern Sierra Nevada rivers: 3. Boron, Molybdenum, Vanadium, and Tungsten. *Aquatic Geochemistry* 6: 19–46.
- Kaasalainen H and Stefansson A (2012) The chemistry of trace elements in surface geothermal waters and stream, Iceland. *Chemical Geology* 330–331: 60–85.
- Kharaka YK, Gunter WD, Aggarwal PK, Perkins EH, and Debraal JD (1988) SOLMINEQ: 88. A computer program for geochemical modelling of water rock interactions. In: *US Geological Survey Water Resources Investigation 88-4227*. Meno Park, CA: US Geological Survey.
- Keasler KM and Loveland WD (1982) Rare earth elemental concentrations in some Pacific Northwest rivers. *Earth and Planetary Science Letters* 61: 68–72.
- Koshinen WC and Harper SS (1990) The retention process: mechanisms. In: Cheng HH (ed.) *Pesticides in the Soil Environment: Processes, Impacts, and Modelling*, pp. 51–77. Madison, WI: Soil Science Society of America Book Series 2.
- Lakshman S, Mills R, Patterson H, and Cronan C (1993) Apparent differences in binding site distributions and aluminum(III) complexation for three molecular weight fractions of a coniferous soil fulvic acid. *Analytica Chimica Acta* 282: 101–108.
- Langmuir D (1997) *Aqueous Environmental Geochemistry*. New Jersey: Prentice-Hall 600p.
- Langmuir D and Herman JS (1980) The mobility of thorium in natural waters at low temperatures. *Geochimica et Cosmochimica Acta* 44: 1753–1766.
- Laxen DPH (1985) Trace metals adsorption/co-precipitation on hydrous ferric oxide under realistic conditions. *Water Research* 19: 1229–1236.
- Laxen DPH, Davison X, and Wook C (1984) Manganese chemistry in rivers and streams. *Geochimica et Cosmochimica Acta* 48: 2107–2111.

- Lead JR, Davison W, Hamilton-Taylor J, and Buffle J (1997) Characterizing colloidal material in natural waters. *Aquatic Geochemistry* 3: 213–232.
- Lee JH and Byrne RH (1993) Complexation of trivalent rare earth elements by carbonate ions. *Geochimica et Cosmochimica Acta* 57: 295–302.
- Leleyter L, Probst JL, Depetris P, et al. (1999) Distribution des terres rares dans les sédiments fluviaux: fractionnement entre les phases labiles et résiduelles. *Comptes rendus de l'Académie des Sciences Paris* 329: 45–52.
- Lemarchand D, Gaillardet J, Lewin E, and Allègre CJ (2000) Boron isotopes river fluxes: Limitation for seawater pH reconstruction over the last 100 Myr. *Nature* 408: 951.
- Levasseur S (1999) *Contribution à l'étude du cycle externe de l'osmium*. PhD Thesis, University of Paris 7.
- Levasseur S, Birck JL, and Allègre CJ (1999) The osmium riverine flux and the oceanic mass balance of osmium. *Earth and Planetary Science Letters* 174: 7–23.
- Li Y (2000) A compendium of geochemistry. In: *From Solar Nebula to the Human Brain*. Princeton, Oxford: Princeton University Press.
- Liu X and Byrne RH (1997) Rare earth and yttrium phosphate solubilities in aqueous solution. *Geochimica et Cosmochimica Acta* 61: 1625–1633.
- Luck JM and Ben Othman D (1998) Geochemistry and water dynamics: II. Trace metals and Pb–Sr isotopes as tracers of water movements and erosion processes. *Chemical Geology* 150: 263–282.
- Marsac R, Davranche M, Gruau G, and Dia A (2010) Metal loading effect on rare earth element binding to humic acid: Experimental and modelling evidence. *Geochimica et Cosmochimica Acta* 74: 1749–1761.
- Martin JM and Meybeck M (1979) Elemental mass balance of material carried by world major rivers. *Marine Chemistry* 7(2): 173–206.
- Martin JM, Hoggdahl O, and Philippot JC (1976) Rare earth element supply to the ocean. *Journal of Geophysical Research* 81(18): 3119–3124.
- Martin JM, Guan DN, Elbaz-Poulichet F, Thomas AJ, and Gordeev VV (1993) Preliminary assessment of the distributions of some trace elements (As, Cd, Cu, Fe, Ni, Pb, Zn) in a pristine aquatic environment: The Lean River estuary (Russia). *Marine Chemistry* 43: 185–199.
- Martel AE and Hancock RD (1996) *Metal complexes in Aqueous solutions*. New York: Plenum, 253 pp.
- Martell AE and Smith RM (1977) Critical stability constants. *Other Organic Ligands* Volume 3. New York: Plenum.
- McCleskey RB, Nordstrom DK, Susong DD, Ball JW, and Taylor HE (2010) Source and fate of inorganic solutes in the Gibbon River, Yellowstone National Park Wyoming, USA. II: Trace element chemistry. *Journal of Volcanology and Geothermal Research* 196: 139–155.
- McKnight DM and Bencala KE (1989) Reactive iron transport in an acidic mountain stream in Summit County, Colorado: A hydrologic perspective. *Geochimica et Cosmochimica Acta* 53: 2225–2234.
- McKnight DM and Bencala KE (1990) The chemistry of iron, aluminium, and dissolved organic material in three acidic, metal-enriched, mountain streams, as controlled by watershed and in-stream processes. *Water Resources Research* 26(12): 3087–3100.
- McKnight DM, Kimball BA, and Bencala KE (1989) Iron photoreduction and oxydation in an acidic mountain stream. *Science* 240: 637–640.
- Michard G (1989) *Equilibres chimiques dans les eaux naturelles*. Paris: Edition Publisud.
- Millero FJ (1992) Stability constants for the formation of rare earth inorganic complexes as a function of ionic strength. *Geochimica et Cosmochimica Acta* 56: 3123–3132.
- Morel FMM and Gschwend PM (1987) The role of colloids in the partitioning of solutes in natural waters. In: Stumm W (ed.) *Aquatic Surface Chemistry*, pp. 405–422. New York: Wiley.
- Morel FMM and Hering JG (1993) *Principles and Applications of Aquatic Chemistry*. New York: Wiley.
- Mouvet C and Bourg ACM (1983) Speciation (including adsorbed species) of copper, lead, nickel, and zinc in the Meuse River: Observed results compared to values calculated with a chemical equilibrium computer program. *Water Research* 6: 641–649.
- Murnane RJ and Stallard RJ (1990) Germanium and silicon in rivers of the Orinoco drainage basin. *Nature* 344: 749–752.
- Néglé P, Allègre CJ, Dupré B, and Lewin E (1993) Erosion sources determined by inversion of major and trace element ratios in river water: The Congo Basin case. *Earth and Planetary Science Letters* 120: 59–76.
- Nriagu JO (1979) Global inventory of natural and anthropogenic emissions of trace metals to the atmosphere. *Nature* 279: 409–411.
- Nriagu JO and Pacyna JM (1988) Quantitative assessment of worldwide contamination of air, water, and soils by trace metals. *Nature* 333: 134–139.
- Olivé-Lauquet G, Allard T, Benedetti M, and Muller JP (1999) Chemical distribution of trivalent iron in riverine material from a tropical ecosystem: A quantitative EPR study. *Water Research* 33: 2276–2734.
- Olivé-Lauquet G, Allard T, Bertaux J, and Muller JP (2000) Crystal chemistry of suspended matter in a tropical hydrosystem, Nyong basin (Cameroon, Africa). *Chemical Geology* 170: 113–131.
- Palmer MR and Edmond JM (1993) Uranium in river water. *Geochimica et Cosmochimica Acta* 57: 4947–4955.
- Parkhurst DL (1995) Users Guide to PHREEQC: A Computer Program for Speciation, Reaction-path, Advective-transport, and Inverse Geochemical Calculations. *US Geological Survey Water Resources Investigation Report*, 95-4227.
- Parkhurst DL, Thorstenson DC, and Plummer NL (1990) *PHREEQC: A Computer Program for Geochemical Calculations*. Rev. US Geological Survey Water Resources Inv. Report, 80-96.
- Pédrot M, Dia A, and Davranche M (2009) Double pH control on humic substance-borne trace element distribution in soil waters as inferred from ultrafiltration. *Journal of Colloid and Interface Science* 339: 390–403.
- Perdue EM, Beck KC, and Reuter JH (1976) Organic complexes of iron and aluminum in natural waters. *Nature* 260: 418–420.
- Perdue EM, Reuter JH, and Parrish RS (1984) A statistical model of proton binding by humus. *Geochimica et Cosmochimica Acta* 48: 1257–1263.
- Pereiro R and Carro Díaz A (2002) Speciation of mercury, tin, and lead compounds by gas chromatography with microwave-induced plasma and atomic-emission detection (GC–MIP–AED). *Analytical and Bioanalytical Chemistry* 372: 74–90.
- Perret D, Newman ME, Negre JC, Chen Y, and Buffle J (1994) Submicron particles in the Rhine river: I. Physicochemical characterization. *Water Research* 28: 91–106.
- Peucker-Ehrenbrink and Hannigan (2000) Effects of black shale weathering on the mobility of rhenium and platinum group elements. *Geology* 28: 475–478.
- Picouet C, Dupré B, Orange D, and Valladon M (2001) Major and trace element geochemistry of the upper Niger (Mali): Physical and chemical weathering rates and CO₂ consumption. *Chemical Geology* 93–124.
- Pierson-Wickman AC, Reisberg L, and France-Lanord C (2000) The Os isotopic composition of Himalayan river bedloads and bedrocks: Importance of black shales. *Earth and Planetary Science Letters* 176: 201–216.
- Plummer LE, Jones BF, and Truesdell AH (1984) WATEQF—A FORTRAN IV Version of WATEQ: A Computer Program for Calculating Chemical Equilibria of Natural Waters. *Rev. US Geological Survey Water Resources Inv. Report* 76-13. US Geological Survey, Reston, VA.
- Pokrovski OS and Schott J (2002) Iron colloids/organic matter associated transport of major and trace elements in small boreal rivers and their estuaries (NW Russia). *Chemical Geology* 190: 141–181.
- Pokrovsky OS, Viers J, Shirokova LS, Shevchenko VP, Filipov AS, and Dupré B (2010) Dissolved, suspended and colloidal fluxes of organic carbon, major and trace elements in the Severnaya Dvina River and its tributary. *Chemical Geology* 273: 136–149.
- Ponter C, Ingri J, and Boström K (1992) Geochemistry of manganese in the Kalix river, northern Sweden. *Geochimica et Cosmochimica Acta* 56: 1485–1494.
- Pourret O, Davranche M, Gruau G, and Dia A (2007) Organic complexation of rare earth elements in natural waters: Evaluating model calculations from ultrafiltration data. *Geochimica et Cosmochimica Acta* 71: 2718–2735.
- Pourret O, Dia A, Gruau G, Davranche M, and Bouhnik-Le Coz M (2012) Assessment of vanadium distribution in shallow groundwaters. *Chemical Geology* 294–295: 89–102.
- Pourret O, Gruau G, Dia A, Davranche M, and Molénat J (2010) Colloidal control on the distribution of rare earth elements in shallow groundwaters. *Aquatic Geochemistry* 16: 31–59.
- Porcelli D, Andersson PS, Wasserburg GJ, Ingri J, and Baskaran M (1997) The importance of colloids and mires for the transport of uranium isotopes through the Kalix River watershed and Baltic Sea. *Geochimica et Cosmochimica Acta* 61: 4095–4113.
- Quémenerais B and Lum KR (1997) Distribution and temporal variation of Cd in the St. Lawrence river basin. *Aquatic Sciences* 59: 243–259.
- Roy S (1996) *Utilisation des isotopes du plomb et du strontium comme traceurs des apports anthropiques et naturels dans les précipitations et rivières du bassin de Paris*. PhD Thesis, Université Paris 7.
- Sarin MM, Krishnaswami S, Somayajulu BLK, and Moore WS (1990) Chemistry of U, Th, and Ra isotopes in the Ganga–Brahmaputra river system: weathering processes and fluxes to the Bay of Bengal. *Geochimica et Cosmochimica Acta* 54: 1387–1396.
- Schäfer J and Blanc G (2002) Relationship between ore deposits in river catchments and geochemistry of suspended particulate matter from six rivers in southwest France. *Science of the Total Environment* 298(1–3): 103–118.
- Schecher WD and McAvoy DC (1991) *MINEQL +: A Chemical Equilibrium Program for Personal Computers*, user's manual ver. 2.1. Edgewater, MD, Environmental Research Software.

- Schindler PW and Stumm W (1987) The surface chemistry of oxides, hydroxides and oxide minerals. In: Stumm W (ed.) *Aquatic Surface Chemistry*, pp. 83–110. New York: Wiley.
- Sen IS and Peuker-Ehrenbrink B (2012) Anthropogenic disturbance of element cycles at the Earth's surface. *Environmental Science and Technology* 46: 8601–8609.
- Seyler P and Boaventura G (2001) Trace metals in the mainstem river. In: McClain M, Victoria RL, and Richey JE (eds.) *The Biogeochemistry of the Amazon Basin and its Role in a Changing World*, pp. 307–327. Oxford: Oxford University Press.
- Seyler P and Boaventura G (2002) Distribution and partition of trace elements in the Amazon basin. In: *Hydrological Processes, Special Issue of International Symposium on Hydrological and Geochemical Processes in Large Scale River Basins*, Nov. 15–19, 1999, Manaus, Br sil.
- Shafer MM, Overdier JT, Hurley JP, Armstrong J, and Webb D (1997) The influence of dissolved organic carbon, suspended particulates, and hydrology on the concentration, partitioning and variability of trace metals in two contrasting Wisconsin watersheds (USA). *Chemical Geology* 136: 71–97.
- Sharma M, Wasserburg GJ, Hofmann AW, and Chakrapani GJ (1999) Himalayan uplift and osmium isotopes in oceans and rivers. *Geochimica et Cosmochimica Acta* 63: 4005–4012.
- Shiller AM (1997) Dissolved trace elements in the Mississippi River: Seasonal, interannual, and decadal variability. *Geochimica et Cosmochimica Acta* 51(20): 4321–4330.
- Shiller AM (2002) Seasonality of dissolved rare earth elements in the lower Mississippi River. *Geochimica, Geophysics, Geosystems* 3(11): 1068.
- Shiller AM and Boyle E (1985) Dissolved zinc in rivers. *Nature* 317: 49–52.
- Shiller AM and Boyle E (1987) Variability of dissolved trace metals in the Mississippi River. *Geochimica et Cosmochimica Acta* 51: 3273–3277.
- Shiller AM and Boyle E (1997) Trace elements in the Mississippi River delta outflow region: behavior at high discharge. *Geochimica et Cosmochimica Acta* 55: 3241–3251.
- Shiller AM and Mao L (2000) Dissolved vanadium in rivers: effects of silicate weathering. *Chemical Geology* 165: 13–22.
- Shiller AM and Frilot DM (1995) The geochemistry of gallium relative to aluminium in Californian streams. *Geochimica et Cosmochimica Acta* 60: 1323–1328.
- Sholkovitz ER (1978) The flocculation of dissolved Fe, Mn, Al, Cu, Ni, Co, and Cd during estuarine mixing. *Earth and Planetary Science Letters* 41: 77–86.
- Sholkovitz ER (1992) Chemical evolution of REE: fractionation between colloidal and solution phases of filtered river water. *Earth and Planetary Science Letters* 114: 77–84.
- Sholkovitz ER (1995) The aquatic chemistry of rare earth elements in rivers and estuaries. *Aquatic Chemistry* 1: 1–34.
- Sholkovitz ER and Copland D (1980) The coagulation, solubility and adsorption properties of Fe, Mn, Cu, Ni, Cd, Co, and humic acids in a river water. *Geochimica et Cosmochimica Acta* 45: 181–189.
- Sholkovitz ER, Boyle ER, and Price NB (1978) Removal of dissolved humic acid and iron during estuarine mixing. *Earth and Planetary Science Letters* 40: 130–136.
- Sigg L, Behra P, and Stumm W (2000) *Chimie des Milieux Aquatiques*, 3rd edn., Parris: Dunod.
- Smedley PL and Kinniburgh DG (2002) A review of the source, behavior and distribution of arsenic in natural waters. *Applied Geochemistry* 17: 517–568.
- Spivack AJ, Palmer MR, and Edmond JM (1987) The sedimentary cycle of the boron isotopes. *Geochimica et Cosmochimica Acta* 51: 1939–1949.
- Steinmann M and Stille P (2008) Controls on transport and fractionation of the rare earth elements in stream water of a mixed basaltic-granitic catchment (Massif Central, France). *Chemical Geology* 254: 1–18.
- Stevenson FJ (1994) *Humus Chemistry: Genesis, Composition, Reactions*, 2nd edn. New York: Wiley.
- Stumm W (1993) Aquatic colloids as chemical reactants: surface structure and reactivity. *Colloids and Surfaces A73*: 1–18.
- Taran Y, Rouwet D, Inguaggiato S, and Aiuppa A (2008) Major and trace element geochemistry of neutral and acidic thermal springs at El Chichon volcano, Mexico. Implication for monitoring volcanic acidity. *Journal of Volcanology and Geothermal Research* 178: 224–236.
- Taylor SR and McLennan SM (1985) *The Continental Crust: Its Composition and Evolution*. Oxford: Blackwell 312p.
- Tessier A, Campbell PGC, and Bisson M (1979) Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry* 51: 844–851.
- Thurman EM (1985) *Organic Geochemistry of Natural Waters*. Dordrecht: Nijhoff and Junk publishers.
- Tipping E (1981) The adsorption of humic substances by iron oxides. *Geochimica et Cosmochimica Acta* 45: 191–199.
- Tricca A, Stille P, Steinmann M, Kiefel B, Samuel J, and Eikenberg J (1999) Rare earth elements and Sr and Nd isotopic compositions of dissolved and suspended loads from small river systems in the Vosges mountains (France), the river Rhien and groundwater. *Chemical Geology* 160: 139–158.
- Turner DR, Whitfield M, and Dickson AG (1981) The equilibrium speciation of dissolved components in fresh- water and seawater at 25 °C and 1 atm pressure. *Geochimica et Cosmochimica Acta* 45: 855–881.
- Vasyukova E, Pokrovsky OS, Viers J, and Dupr  B (2012) New operational method for testing colloid complexation with metals in natural waters. *Applied Geochemistry* 27: 1226–1237.
- Vasyukova EV, Pokrovsky OS, Viers J, et al. (2010) Trace elements in organic- and iron-rich surficial fluids of the boreal zone: Assessing colloidal forms via dialysis and ultrafiltration. *Geochimica et Cosmochimica Acta* 74: 449–468.
- Viers J and Wasserburg GJ (2002) Behavior of Sm and Nd in a lateritic soil profile. *Geochimica et Cosmochimica Acta* (inpress).
- Viers J, Dupr  B, Polv  M, Schott J, Dandurand JL, and Braun JJ (1997) Chemical weathering in the drainage basin of a tropical watershed (Nsimi-Zoetele site, Cameroon) comparison between organic-poor and organic-rich waters. *Chemical Geology* 140: 181–206.
- Viers J, Dupr  B, Deberdt S, et al. (2000) Major and traces elements abundances, and strontium isotopes in the Nyong basin rivers (Cameroon) constraints on chemical weathering processes and elements transport mechanisms in humid tropical environments. *Chemical Geology* 169: 211–241.
- Vigier N, Bourdon B, Turner S, and All gre CJ (2001) Erosion timescales derived from U-decay series measurements in rivers. *Earth and Planetary Science Letters* 193: 549–563.
- Willenbring JK and von Blanckenburg F (2010) Meteoric cosmogenic Beryllium-10 adsorbed to river sediment and soil: Applications for Earth-surface dynamics. *Earth-Science Reviews* 98: 105–122.
- Wollery TJ (1992) EQ3/6, A software package for geochemical modelling of aqueous systems: package overview and installation guide (ver. 7.0). UCRL-MA-110662: Part I. Lawrence Livermore Natl. Lab.
- Wood SA (1990) The aqueous geochemistry of the rare earth elements and yttrium. *Chemical Geology* 82: 159–186.
- Wen LS, Santschi PH, and Tang D (1997) Interactions between radioactively labelled colloids and natural particles: evidence for colloidal pumping. *Geochimica et Cosmochimica Acta* 61: 2867–2878.
- Yee HS, Measures CI, and Edmond JM (1987) Selenium in the tributaries of the Orinoco in Venezuela. *Nature* 326: 686–689.
- Yeghicheyan D, Carignan J, Valladon M, et al. (2001) A compilation of silicon and thirty one trace elements measured in the natural river water reference SLRS-4 (NRC-CNRS). *Geostandards Newsletter* 35(2–3): 465–474.
- You CF, Lee T, and Li YH (1989) The partition of Be between soil and water. *Chemical Geology* 77: 105–118.
- Zhang J (1994) Geochemistry of trace metals from Chinese river/estuary systems: An overview. *Estuarine, Coastal and Shelf Science* 41: 631–658.
- Zhang J and Huang WW (1992) Dissolved trace metals in the Huanghe, the most turbid river large river in the world. *Water Research* 27(1): 1–8.
- Zhang J, Huang WW, and Wang JH (1993) Trace element chemistry of the Huanghe (Yellow river), China: Examination of the data from *in situ* measurements and laboratory approach. *Chemical Geology* 114: 83–94.
- Zhang C, Wang L, Zhang S, and Li X (1998) Geochemistry of rare earth elements in the mainstream of the Yangtze river, China. *Applied Geochemistry* 13: 451–462.