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Chemical composition of suspended sediments in World Rivers: New insights from a new database

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ABSTRACT

The aim of this paper is to present a new database on the chemical composition of suspended matter in World Rivers, together with the associated elemental fluxes. There is a lack of any recent attempt in the literature to update the pioneering work of Martin and Meybeck [Martin, J.-M., Meybeck, M., 1979. Elemental mass balance of material carried by major world rivers. *Mar. Chem.* 7, 173–206.] and Martin and Whitfield [Martin, J.-M., Whitfield, M., 1983. The significance of the river input of chemical elements to the ocean. Trace metals in sea water Wong, Boyle, Bruland, Burton, Goldberg (Eds) Plenum Publishing Corporation.] regarding the worldwide average major and trace element chemistry of riverine particulate matter.

Apart from compiling a new database on particulate matter, this paper also aims to give a “snap-shot” of elemental fluxes for each continent. This approach should allow us to obtain new insights on weathering conditions in different environments and assess the influence of human activities on natural geochemical cycles. Finally, this study demonstrates the large uncertainties currently associated with estimating the flux of sediments transported by rivers.

By comparing the riverine suspended sediment fluxes of some metals (Cd, Zn, Ni, Cu, Cr and Pb) given in this study with estimates of the anthropogenic fluxes of these metals to the atmosphere, soils and waters (natural ecosystems) [Nriagu, J.O., 1988. A silent epidemic of environmental poisoning. *Environ. Pollut.* 50, 139–161.], we can see that riverine fluxes are similar to anthropogenic fluxes. This casts light on the effect of human activities on the cycles of trace elements at the Earth's surface.

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1. Introduction

Eroded material transported from the continents to the oceans is mainly transported by rivers (Martin and Whitfield, 1983). Rivers transport this material both in dissolved and solid form (suspended and bed load sediment). The relative distribution of elements between the solute and particulate phases depends on the mobility of the chemical constituents (elements) during weathering and transport. The transport

mechanisms depend on the nature and concentration of mineral and organic ligands present in the dissolved phase and on the nature and amount of mineral and organic particles. The composition of suspended sediment (>0.20 or 0.45 μm) in World Rivers provides valuable information for the geochemical research community. The qualitative and quantitative analysis of the suspended load carried by major World Rivers allows us to i) assess the recycling of continental crust (Taylor and McLennan, 1985; Goldstein and Jacobsen, 1988), ii)

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estimate the denudation rates of continents (Milliman and Meade, 1983; Walling and Fang, 2003; Syvitski et al., 2005; Walling, 2006), iii) constrain the major parameters controlling these denudation rates (Allègre et al., 1996), and iv) estimate anthropogenic influence, since these sediments offer large specific surfaces for the sorption of metals coming from human activities (Nriagu and Pacyna, 1988; Audry et al., 2006). Recently, more attention has been paid to the suspended sediment transported by rivers in relation to silicate weathering, which represents a critical step in long-term climate moderation (Gaillardet et al., 1999; Dessert et al., 2003; Gislason et al., 2006).

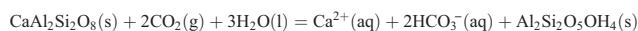
Since the industrial revolution, a multitude of anthropogenic emissions have taken place into the environment (soils, waters and atmosphere). The two major sources are mining and smelting, but other sources are also significant such as discharge of sewage sludge, use of commercial fertilizers and pesticides, animal manure spreading and waste water discharge (Nriagu, 1979, 1988). Trace metals are accumulated in soils because minerals offer large specific surfaces for the sorption of these constituents. Material derived from soil erosion is carried in suspension by rivers, and the trace elements contained in this particulate matter are transported over the continental areas and finally to the oceans. The fast economic expansion of countries like China and India, accounting for a population of about 2 billion, will lead to an increase in all these emissions to the environment.

The aim of this paper is to present a new database on the chemical composition of suspended matter in World Rivers, together with the associated elemental fluxes. Callender (2007) reports a lack of any recent attempt in the literature to update the pioneering work of Martin and Meybeck (1979) and Martin and Whitfield (1983) regarding the worldwide average major and trace element chemistry of riverine particulate matter. In a recent paper, Gaillardet et al. (2003) presented a similar database for the chemical composition of the dissolved phase. Apart from compiling a new database on particulate matter, this paper also aims to give a “snap-shot” of elemental fluxes for each continent. This approach should allow us to obtain new insights on weathering conditions in different environments and assess the influence of human activities on natural geochemical cycles. Finally, this study demonstrates the large uncertainties currently associated with estimating the flux of sediments transported by rivers.

2. Origin of suspended particulate matter in rivers

The weathering of most silicate minerals in fresh igneous rocks and soils takes place according to incongruent reactions (White and Brantley, 1995 and references therein). Most mobile elements (e.g., sodium (Na), calcium (Ca)) are present in a dissolved form in soil pore-waters, and are released into the drainage network. Other less soluble elements, such as aluminium (Al) and iron (Fe), are incorporated into secondary minerals such as clays (e.g., kaolinite, smectite, etc.) and metallic oxy-hydroxides (e.g., goethite, gibbsite) which accumulate in soils. This process is illustrated by the reaction reported below, which describes the dissolution of a calcic-

silicate primary mineral and the formation of a secondary mineral (kaolinite):



Hence, the stability of soils depends on the balance between production of secondary minerals by chemical weathering and erosion by physical processes transporting particles from the soils to rivers. Particles transported by rivers are composed of resistant primary minerals (e.g., quartz and zircon), secondary minerals (clays, metallic oxides and oxyhydroxides) and biogenic remains. The sedimentary material carried by rivers can be transported either as bed load or fine-grained suspended particles.

Both the nature and the amount of particles transported by rivers will depend on the weathering regime in the catchment area. The relative importance of physical weathering (releasing particles) compared with chemical weathering depends on the weathering regime as proposed by Carson and Kirby (1972) and more recently by Stallard and Edmond (1983). In a *weathering limited* regime, mechanical weathering is faster than chemical weathering, and fresh material is continuously being exposed to chemical weathering. This weathering regime will generate a high proportion of immature particles that are transported in the river. In a *transport limited* regime, chemical weathering is faster than physical weathering. Deep soils are developed that are characterized by depletion in highly mobile elements (e.g., Na, Ca) and enrichment in less soluble elements (e.g. Si, Al and Fe). In this case, the transported particles will be mature, implying that they are made up of a high proportion of secondary phases. For example, tropical rivers draining the stable cratonic area of southern Cameroon (Congo shield) transport highly mature materials (Olivie-Lauquet et al., 2000). The suspended sediment load (a few milligrams per litre) of these rivers consists mainly of quartz, poorly ordered kaolinite, goethite and particulate organic matter. In their study of Congo basin rivers, Dupré et al. (1996) report the distribution of major and trace elements between different fractions, i.e. the dissolved phase (i.e., <0.20 µm), particulates (i.e., >0.20 µm) and bed load/bottom sands. There is a strong depletion of uranium (U), rubidium (Rb), potassium (K), barium (Ba), strontium (Sr), Na, and Ca in the suspended sediment relative to the mean upper crust (Taylor and McLennan, 1985) and an enrichment of the same elements in the dissolved phase. Mass balance calculations show that the removal of the more mobile elements from the bedrock will concentrate all the remaining elements (e.g., Rare Earth Element (REE), thorium (Th), zirconium (Zr), hafnium (Hf) and Cobalt (Co)) in the weathered phases of the soils and/or in bedload rich in heavy minerals (e.g., zircon and rutile). By contrast, if we consider the suspended load of rivers draining temperate regions, such as the River Loire in France, the mineralogy of the suspended matter appears to be quite different from that observed in the tropical rivers of central Africa. In the case of the River Loire, the suspended particulate matter is composed of quartz, K-feldspar, illite, calcite and kaolinite (Négrel and Grosbois, 1999).

From the above, it appears that the nature of transported particles depends on the climate controlling the rock weathering and soil formation over a long period. There is much

discussion in the literature on the role of the different parameters likely to control the rate of chemical weathering of rocks (Bernier and Bernier, 1987; White and Blum, 1995; Gaillardet et al., 1997, 1999; Viers et al., 2007). Natural parameters influencing erosion rate include the relief and surface-area of the catchment, as well as the climate (temperature, precipitation, runoff, hydrological regime, intensity and number of flood events), the geology (lithology), and vegetation type. The amount of suspended particulate matter depends on natural factors as well as “anthropogenic” parameters directly dependent on human activities. Anthropogenic influence on the production and transport of suspended material is discussed in the following section.

In particular cases, suspended minerals are produced *in situ* within the fluvial environment (Ponter et al., 1992; McKnight and Benca, 1989; Tosiani et al., 2004). Suspended particulates may be formed either from the precipitation of minerals at the expense of soluble components or from the aggregation of colloids in the dissolved phase. The formation of particles in the river environment is illustrated by the precipitation of manganese (Mn) oxyhydroxide in Kalix River water (Ponter et al., 1992). In the Kalix River, high Mn/Al ratios are observed in the suspended load during the summer and early autumn months, when water temperatures and pH values are high and large quantities of biogenic particles (high Si/Al ratios) are present in the suspended particulate matter. There is an increase of suspended Mn together with a decrease of dissolved Mn. This precipitation of Mn in the river water can be explained by a biological mediation of oxidation, that is, an increased activity of Mn-oxidising bacteria when the water temperature reaches 15 °C.

Another process that may influence the chemical composition of suspended sediment is the direct release of dissolved elements from groundwater discharge to stream. These elements may precipitate or sorb to sediment particles in the stream. Increasingly, this process appears to be an important contributor to the redox-sensitive trace metal/metalloid load in a stream (Fuller and Harvey, 2000; Winde and Van der Walt, 2004; Charlet and Polya, 2006; Gandy et al., 2007).

3. Amount of suspended matter transported by rivers

Walling (2006) has recently compiled the various estimations of land–ocean sediment transfer by world’s rivers. The most recent estimations range from 12.6 to 24 Gt year^{−1} (Walling 2006 and references therein) but the common accepted value is around 15 Gt year^{−1}. However, most of the estimations available in the literature are based on old data regarding water discharge and sediment load and have to be updated due to recent anthropogenic influences or climatic change, or more simply because of the acquisition of new data. This is illustrated by Walling and Fang (2003) using simple trend analysis applied to time series of annual water discharge and sediment load of selected rivers. Based on monitoring from 1942 to 1989 of Kolyma River (Eastern Siberia, Russia), it appears that there is an increase in the yield of suspended sediment, while the flow shows no particular variation. This

increase is attributed to widespread gold mining in the catchment, which greatly increases soil dismantling and erosion. Human activities strongly affect the discharge load, reflecting land use changes (deforestation, agriculture and mining) in response to increasing population pressure. As pointed out by Walling and Fang (2003), there is a crucial need to i) compile a new database based on a rigorous survey of the world’s largest rivers, ii) incorporate newly acquired data to allow a more rigorous estimate of the annual sediment discharge. The monitoring of rivers requires a considerable investment that may be difficult for developing countries. A new satellite-based approach for the monitoring of water and sediment discharges could compensate in the future for the lack of terrestrial surveys (Calmant and Seyler, 2006; Martinez and Le Toan, 2007), particularly in the case of developing countries.

The sediment transport rate is different to the total rate of soil erosion. Indeed, particles released during erosion may be retained in the river catchment, in natural lowland areas or in artificial reservoirs (dams), without reaching estuarine zones. Let us consider the Amazon basin, which ranks number one in terms of global mass transfer from the continents to the oceans. Indeed, the River Amazon supplies ~20% of the water (Callede et al., 2004) and ~10% of the suspended load input to the sea (Filizola and Guyot, 2004). Recently, Filizola and Guyot (2004) estimated a mean annual suspended sediment discharge of nearly 800×10⁶ tonnes at Obidos (Para state, Brazil), where 97% of the flux is due to inputs from Andean tributaries (62 and 35% from the Solimões and Madeira rivers, respectively). These results were obtained owing to the Amazon basin survey undertaken by the French research programme Hybam (<http://www.ore-hybam.org>). Note that a large fraction of the sediments delivered by the Andean chain are stored in the subandean zone where active subsidence is occurring (Roddaz et al., 2005). Particles may also be deposited in areas of “varzea” (flooded forest) bordering the main channel system of the lower Amazon (Moreira-Turcq et al., 2004; Maurice Bourgoin et al., 2007). The River Amazon exhibits a monomodal flood pulse, during which the water discharge increases and overflows onto the surrounding plains. The whole area of varzea can reach 300,000 km², and it is estimated that 30% of the water transported by the Amazon transits each year through this zone (Richey et al., 1989).

Artificial storage can be illustrated by the case of the River Nile. Indeed, the impounding of the Nile (Schamp and El-Ali, 1983) is one of the most spectacular examples because it nearly eliminated the sediment discharge from north-eastern Africa to the ocean. Before construction of the Aswan Dam, the Nile carried 10⁸ tonnes/year, which corresponds to approximately 1% of the total suspended sediment load delivered by World Rivers to the oceans. At present, the sediment discharge to the sea is 10 times less than before the building of the dam (Schamp and El-Ali, 1983). Reductions of sediment discharge due to the building of dams can be also described for the Mississippi (and one of its largest tributaries, the Missouri) and the Danube, as well as a series of rivers in China such as the Zhujiang (Pearl River). According to Vörösmarty et al. (1997), about 25% of the contemporary sediment flux from the land to the oceans is trapped behind dams. More recently, Walling (2006) using the current annual loss of storage has calculated that the annual trapping of sediment by major dams was

about 25 Gt year⁻¹. This value is much higher the estimation proposed by Vöröstmarty et al. (1997) corresponding to about 4–5 Gt year⁻¹.

Classified in order of decreasing importance, the main rivers responsible for the transport of suspended sediments to the oceans are the Amazon, the Huanghe (Yellow River), the Ganges and Brahmaputra and the Yangtze. According to Berner and Berner (1987), 70% of the total world suspended sediment load comes from southern Asia and the large Pacific and Indian Ocean Islands (e.g., Taiwan, New Guinea, New Zealand). Unfortunately, there is no significant monitoring of the rivers draining these areas, and this might explain the large uncertainty on estimating the global discharge of riverine sediment. According to Martin and Whitfield (1983) more than 90% of the riverine suspended sediment settles out with the colloidal material in estuaries, where river water mixes with sea water. However, the mechanisms controlling these processes are still poorly understood and attempts to quantify the fluxes remain very hazardous.

4. Location of basins used in compiling the present database (see Fig. 1)

4.1. South America

Due to its importance in terms of water discharge and drainage area ($\sim 6 \times 10^6$ km²), the Amazon river system has been well documented for a number of parameters. The data presented here concern mainly the Amazon River basin with the main tributaries draining the Andes Mountains, the Brazil-central and Guyana shields. Most of the rivers sampled in Brazil and Bolivia are located in the Beni and Mamore sub-basins, respectively. These rivers are: Amazon, Beni, Challana, Coroico, Ichilo, Negro, Solimões, Madeira, Mapiri, Iça, Itaquai, Japura Javari, Jurua, Jutai, Madeira, Mamore, Purus, Rio Grande, San Mateo, Tapajos, Taquesi, Tipuani, Tokantins, Trombetas, Xingu.

We also report data from the Cujuni basin (south Venezuela) draining the Guyana shield (Chicanan, Chivao, Cuyuni, Botanamo, Hacha, Muince, Supamo, Urico, Uroy, Venamo, Yuruari, Yuruan) and from specific regions of Argentina (Patagonia, Parana and Uruguay river basins, La Rioja province) (Achavil, Agua Negra, Angulo, Amarillo, Capayan, Chico, Chubut, Chuschin, Colorado, Copacabana, Coyle, Deseado, Fenix, Gallegos, Higuieritas, Infiernillo, Miranda, Negro, Parana, Pircas, Potrerillo, Puerto, Sanogasta, Santa Cruz, Sarmiento, Uruguay, Vallehermoso, Villa Castelli, Villa Union, Vinchina).

4.2. North America

Data are reported from different rivers (21) draining different areas of the U.S.A. These rivers are: Allegheny, Colorado, Connecticut, Cumberland, Greenbriar, Illinois, James, Milwaukee, Mississippi, Missouri, Neuse, Ohio, Pecos, Platte, Rio Grande, Sabine, Sciota, Tombigbee, Wabash, Wolf. We also include data from the St Lawrence River and from northern Canada (Mackenzie River, Peel River, Red Arctic River).

4.3. Africa

Recently published studies have considerably improved our knowledge of trace-element concentrations in the dissolved phase of rivers of Central Africa. Data on sediments are still scarce. In the present study, we compile data for the Congo-Zaire River (the second largest river in the world in terms of discharge) along with its main tributaries (Alima, Kasai, Likouala, Lobaye Oubangui, Sangha), from the upper Niger and Douna (the main tributary of the Niger River), as well as the Nile, Tigris and the Zarka (Jordan).

4.4. Oceania

We report data from the Murray-Darling River system in Australia (Darling, Namoi, and Murray rivers), from New Zealand (Whan Gaehu River) and from Réunion Island.

4.5. Asia

A couple of studies have focused on the riverine input of metals to the Arctic and Pacific oceans. The main rivers flowing into the Arctic Ocean which have been studied for trace element composition are the Ob, Yenisey, Lena, N. Dvina, the main tributaries of the Ob River (Demjanka, Irtysch, Ishym, Konda, Tara, Tobol, Tuy) and the main rivers draining the Kola Peninsula (Kola and Kitsa Rivers). The Russian Arctic has attracted the attention of scientists not only because of climate change but also owing to the development and exploitation of new oil and gas deposits. We present data from the Huanghe (Yellow River) and Changjiang, as well as various rivers entering the Bohai Sea (Daliaohe, Haihe, Luanhe, Shuangtaizihe), the Yellow Sea (Yalujiang), the East China Sea (Jiaojiang, Jiulongjiang, Minjiang, Qiantangjiang) and the South China Sea (Zhujiang). Water discharge and sediment load vary from north to south, and the drainage basins of these rivers cover a wide range of climate zones from semi-arid temperate (Daliaohe, Luanhe, Haihe, Huanghe and Shuangtaizihe) to subtropical (Zhujiang and Hanjiang). The Changjiang, Jiulongjiang, Minjiang and Qiantangjiang rivers are located in intermediate zones. Rivers in north China have relatively low water discharge and high sediment load concentrations, whereas rivers in South China exhibit abundant water discharge with low suspended sediment loads. The other Asian rivers considered are: Amudaria, Da, Don, Ganges–Brahmaputra, HongHa, Kuji, Mekong, Ural, Volga, Yamuna.

4.6. Europe

Data are reported for several rivers of southern and northern Europe. The rivers of southern Europe are impacted by human activities. In the north, the rivers are representative of pristine environments (e.g., Kalix river basin, Sweden). These rivers are: Danube, Daugava, Dordogne, Elbe, Garonne, Kalix, Loire, Po, Rautas, Rhine, Rhone, Scheldt, Seine, Vene, Vosges).

5. Trace element composition of riverine suspended particulate matter

In Section 2, we show that the mineralogical composition of the suspended matter is different depending on the

geographical location of the catchment and its intrinsic properties (lithology, geomorphology, etc.). These minerals are mainly composed of major elements such as Si, O, Al, Fe, Mg, Ca, Na, K and Ti. Trace elements may be incorporated in the crystal lattice of minerals or adsorbed onto their surface. The uptake of trace elements by mineral surfaces is due to the presence of sites similar to ligands complexing ions in solution. Most experimental studies of adsorption/desorption are based on metal oxides (Stumm and Morgan, 1996) and clay minerals (Coppin et al., 2002). According to Schindler and Stumm (1987), the adsorption of metals onto oxide surfaces involves one or two surface hydroxyl groups and can be represented by the following reaction:



where S-OH represents the hydroxyl group, Me^{z+} a metal of charge $z+$ and H^+ a proton. This type of reaction can be treated in the same way as equilibrium in solution. In this way, we can define equilibrium/adsorption constants that quantify the affinity of the cation for the surface. As reported by Gaillardet et al. (2003), taking TSS as the total suspended sediment concentration in the river, K_D the concentration in the suspended sediment divided by the dissolved concentration,

then the proportion D of a given element in the dissolved phase relative to the bulk solution can be expressed as:

$$D = 1/(1 + K_D \cdot \text{TSS})$$

Assuming an average value of 350 mg/L for the TSS of World Rivers (Berner and Berner, 1987), Gaillardet et al. (2003) show that, even for the most mobile elements, the dominant form of transport is in the solid form. This implies that, to estimate elemental fluxes from the continent to the oceans, we have to take account of the suspended load, which requires a much better estimation of both their chemical composition and material fluxes. The most important carriers for trace element in suspended particulate matter are clay minerals, along with Fe, Al and Mn oxides/hydroxides as well as particulate organic matter (see Hochella and White, 1990). Trace-element concentrations in the particulate load have been compiled for a number of World Rivers classified by continents (see references in Fig. 1). The summary table is available on the web site. Table 1 presents the average concentrations together with the data of Martin and Meybeck (1979) and Savenko (2006), as well as the estimation of the chemical composition of the upper continental crust proposed by Taylor and McLennan (1985). The chemical composition of the suspended particulates was generally determined by filtering to separate the solid matter

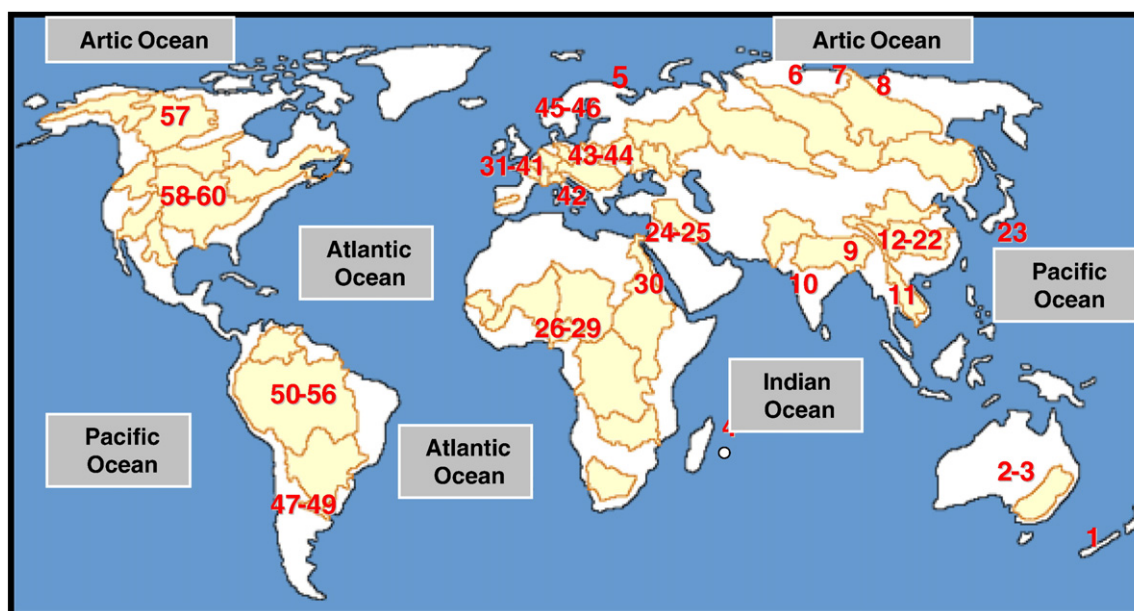


Fig. 1 – Location of river basins used to compile the present database. The world map is taken from Revenga et al. (1998). (1: Deely and Sheppard, 1996; 2: Douglas et al., 1999; 3: Martin and McCulloch, 1999; 4: Louvat and Allègre, 1997a,b; 5: Pekka et al., 2004; 6: Gordeev et al., 2004; 7: Martin et al., 1993; 8: Savenko, 2006; 9: Stummeyer et al., 2002; 10: Singh, 2001; 11: Cenci and Martin, 2004; 12: Zhang and Liu, 2002; 13: Zhang and Wang, 2001; 14: Zhang et al., 1994a; 15: Zhang et al., 1994b; 16: Zhang et al., 1998; 17: Zhang, 1995; 18: Zhang, 1999; 19: Gaillardet et al., 1999; 20: Yang et al., 2004; 21: Li et al., 1988; 22: Lin et al., 1989; 23: Nagano et al., 2003; 24: Al-Jundi, 2000; 25: Sabri et al., 1993; 26: Picouet et al., 2002; 27: Dupré et al., 1996; 28: Gaillardet et al., 1999; 29: Martin et al., 1978; 30: Dekov et al., 1997; 31: Cauwet et al., 1980; 32: Kraepiel et al., 1997; 33: Semhi, 1998; 34: Thomas and Martin, 1982; 35: Négrel and Grosbois, 1999; 36: Tricca et al., 1999; 37: Gaillardet et al., 1999; 38: Roy et al., 1999; 39: Ben Othman et al., 1997; 40: Zwolsman and van Eck, 1999; 41: Brüggmann, 1995; 42: Davide et al., 2003; 43: Guieu et al., 1998; 44: Yurkovskis, 2004; 45: Ingri, 1996; 46: Andersson et al., 1998; 47: Gaiero et al., 2004; 48: Fernandez-Turiel et al., 1995; 49: Depetris et al., 2003; 50: Elbaz-Poulichet et al., 1999; 51: Seyler and Boaventura, 2003; 52: Bonotto and da Silveira, 2003; 53: Gerard et al., 2003; 54: Guyot et al., 1993; 55: Gordeev et al., 1985; 56: Tosiani et al., 2004; 57: Gaillardet et al., 1999; 58: Canfield, 1997; 59: Tefry and Presley, 1976; 60: Shafer et al., 1997).

Table 1 – Average concentration of major and trace elements in the suspended sediment of World Rivers

	Unit	Suspended sediment average concentration	Standard deviation (σ)	n	Upper crust ¹	Martin and Meybeck ²	Savenko ³
Al	%	8.72	6.01	140	8.04	9.4	8.63
As	μg/g	36.3	27.0	40	–	5	14
Ba	μg/g	522	472	139	550	600	500
Bi	μg/g	0.85	1.29	20	0.127	–	0.3
Br	μg/g	21.5	17.3	5	–	5	9
Ca	%	2.59	2.80	118	3	2.15	2.60
Cd	μg/g	1.55	4.15	70	0.098	–	0.5
Ce	μg/g	73.6	38.4	110	64	95	68
Co	μg/g	22.5	19.6	82	10	20	19
Cr	μg/g	130	155	149	35	100	85
Cs	μg/g	6.25	4.68	71	3.7	6	5.2
Cu	μg/g	75.9	135	143	25	100	45
Dy	μg/g	4.25	2.07	90	3.5	–	4.5
Er	μg/g	2.23	1.00	90	2.3	–	2.6
Eu	μg/g	1.29	0.58	109	0.88	1.5	1.4
Fe	%	5.81	4.81	144	3.5	4.8	5.03
Ga	μg/g	18.1	4.97	33	17	25	20
Gd	μg/g	5.25	2.73	90	3.8	–	5.6
Ge	μg/g	1.23	0.36	18	–	–	1.4
Hf	μg/g	4.04	1.70	83	5.8	6	4.4
Ho	μg/g	0.88	0.34	78	0.8	–	0.9
K	%	1.69	1.04	119	2.8	2	2.15
La	μg/g	37.4	24.1	110	30	45	32
Li	μg/g	8.50	13.7	34	–	25	35
Lu	μg/g	0.35	0.23	75	0.32	0.5	0.4
Mg	%	1.26	1.40	93	1.33	1.18	1.44
Mn	μg/g	1679.00	5011	148	600	1050	1150
Mo	μg/g	2.98	4.53	49	–	3	1.8
Na	%	0.71	0.93	108	2.89	0.71	0.82
Nb	μg/g	13.5	7.44	35	25	–	13
Nd	μg/g	32.2	15.5	105	26	35	29
Ni	μg/g	74.5	100	164	20	90	50
P	μg/g	2010	3257	24	–	1150	1000
Pb	μg/g	61.1	91.2	132	20	100	25
Pr	μg/g	7.95	3.73	72	7.1	–	7.7
Rb	μg/g	78.5	53.9	126	112	100	77
Sb	μg/g	2.19	2.41	41	0.2	2.5	1.4
Sc	μg/g	18.2	9.30	47	–	18	14
Si	%	25.4	11.7	68	30.8	28.5	25.6
Sm	μg/g	6.12	2.76	108	4.5	7	5.8
Sn	μg/g	4.57	4.23	55	5.5	–	2.9
Sr	μg/g	187	272	135	350	150	150
Ta	μg/g	1.27	0.51	55	2.2	1.25	0.88
Tb	μg/g	0.82	0.41	98	0.64	1	0.79
Te	μg/g	0.54	0.23	22	–	–	7?
Th	μg/g	12.1	5.86	93	10.7	14	10
Ti	%	0.44	0.32	51	0.3	0.56	0.39
Tl	μg/g	0.53	0.24	14	0.75	–	0.56
Tm	μg/g	0.38	0.22	55	0.33	–	0.38
U	μg/g	3.30	3.09	122	2.8	3	2.4
V	μg/g	129	100	65	60	170	120
W	μg/g	1.99	2.13	15	–	–	1.4
Y	μg/g	21.9	9.40	70	22	30	25
Yb	μg/g	2.11	1.28	111	2.2	3.5	2.5
Zn	μg/g	208	237	134	71	250	130
Zr	μg/g	160	66.7	94	190	–	150

For comparison, we report the composition of the continental crust proposed by [Taylor and McLennan \(1985\)](#) (2), as well as the chemical composition of riverine suspended sediments given by [Martin and Meybeck \(1979\)](#) (3) and [Savenko \(2006\)](#) (4).

^{1,2,3} are estimations of the chemical composition of the Upper Crust (Taylor and McLennan, 1985), of riverine suspended sediments by [Martin and Meybeck \(1979\)](#) and [Savenko \(1986\)](#), respectively.

(using either 0.22 μm or 0.45 μm pore size membranes) or by centrifugation. For simplicity, elements are ranked in alphabetical order. However, the concentration data presented in this paper is focused on the Rare Earth elements, the transition metals and the major elements. To discuss the behaviour of these elements, the data are reported in the form of an enrichment factor (EF) defined as follows:

$$EF = [X]/[Al]_{\text{sample}}/[X]/[Al]_{\text{upper crust}}$$

where [X] represents the concentration of the element X, and [Al] the Al concentration, assuming that Al is solely of terrigenous origin. A ratio close to 1 means that the concentration of X can be explained by a terrigenous origin alone, while a ratio >1 implies an anthropogenic input. However, ratios >1 may also indicate that the reference used is not representative of the geological substratum of the catchment area. A ratio below 1 indicates a depletion of the element.

5.1. The Rare Earth Elements (REE)

Fig. 2 shows the REE patterns, normalized to the Upper Crust (Taylor and McLennan, 1985), for selected World Rivers. This group of elements is often used as a tracer to constrain weathering processes and element mobility in catchments (Braun et al., 1998). This approach is mainly based on comparing the REE abundance pattern of the geological material (e.g., soil) with that of the supposed source material (e.g., rock). In terms of absolute abundance, the suspended particulate matter in World Rivers generally displays REE concentrations that are close to those reported for the upper continental crust (for illustration around 30 ppm for Lanthanum (La)). However, a more detailed examination of the data reveals some differences. Among the Amazon basin rivers that carry the erosion products of the Andean cordillera, the Madeira River (Porto Velho, Rondonia state, Brazil) and the River Amazon (Obidos station, Para state, Brazil) have much higher concentrations of light rare earth elements (LREE) and middle rare earth elements MREE (e.g., >150 ppm for La) (Gérard et al., 2003). By contrast, rivers draining the Cujuni basin in the south of Venezuela exhibit much lower concentrations, with an average value of 18 ppm for La (Tosiani et al., 2004). Considering the other rivers of the database, the suspended particulates of rivers draining volcanic islands, such

as in the Azores archipelago, appear to have high REE concentrations (between 75 and 106 ppm for La). The other rivers exhibit REE concentrations close to the Upper Crust composition. Globally, REE concentrations are close to the UC values, which suggest a relative low mobility of these elements.

If we consider the REE geochemistry of suspended particulate matter, it appears that World Rivers have contrasted patterns of abundance in these elements. The Amazon Basin Rivers show enrichment in LREE (this is more pronounced for the Amazon at Obidos (Para state, Brazil) and the Madeira River (Porto Velho, Rondonia state, Brazil)). The REE patterns of rivers draining the Cujuni basin are flat with a positive Eu anomaly (this anomaly is also encountered in the riverine suspended particulates of the Amazon basin). Among other rivers, the Niger and Danou (Niger River basin, Africa) appear to have a significantly fractionated REE pattern with LREE enrichment. Particulates in rivers draining the volcanic island of Azores exhibit a LREE enriched pattern with a strong negative Eu anomaly. This Eu anomaly may be explained by a preferential weathering of Eu-bearing minerals such as plagioclase or segregation (physical sorting) of mineral phases between the suspended load and the bottom sands (Louvrat and Allègre, 1997a). With the exception of the Amazon and the Madeira River, the Cujuni basin rivers, the Niger River and volcanic island rivers, other rivers generally exhibit a relatively flat REE pattern with a slight enrichment compared to the Upper Crust. Based on this database, it appears that REE fractionation occurs in environments where physical weathering is strongly dominant over chemical weathering. This is the case for the Andean cordillera and volcanic islands such as La Reunion or the Azores.

5.2. The trace elements (Cd, Sb, Ni, V, Cu, Cr, Zn, Co, Pb and Cs)

Fig. 3 presents EFs for the whole dataset, with elements ranked by decreasing order of average enrichment factor. We can see that the majority of the rivers are strongly enriched in all these metals compared with the continental crust. In the case of elements such as cadmium (Cd), we note that the enrichment factor can be higher than 100. These high EFs reflect the influence of anthropogenic activities. In decreasing order of magnitude, the average EF values are: Cd (~15)>Sb (~10)>Ni (~5.2)>V (~4.1)>Cu (~4)>Cr (~2.5)>Zn (~2.8)>Co (2.3)>Pb (~2)>Cs (~1.7).

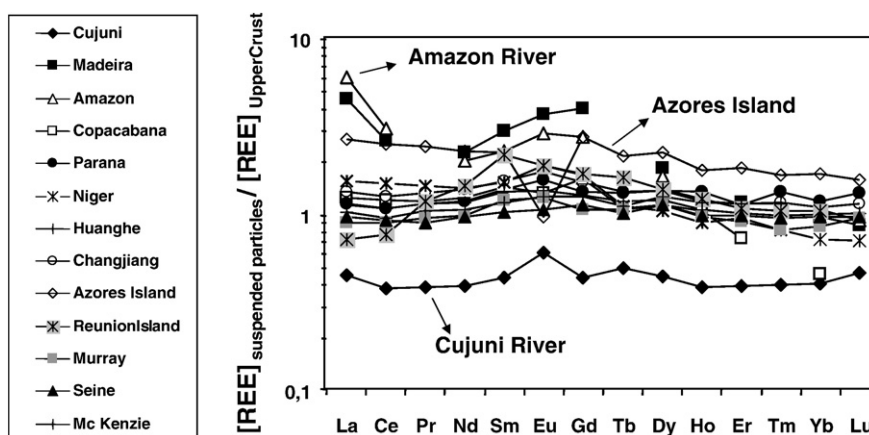


Fig. 2 – Rare Earth Element (REE) abundance patterns for the suspended particulate matter of some rivers. The REE concentrations are normalized to the Upper Crust (Taylor and McLennan, 1985).

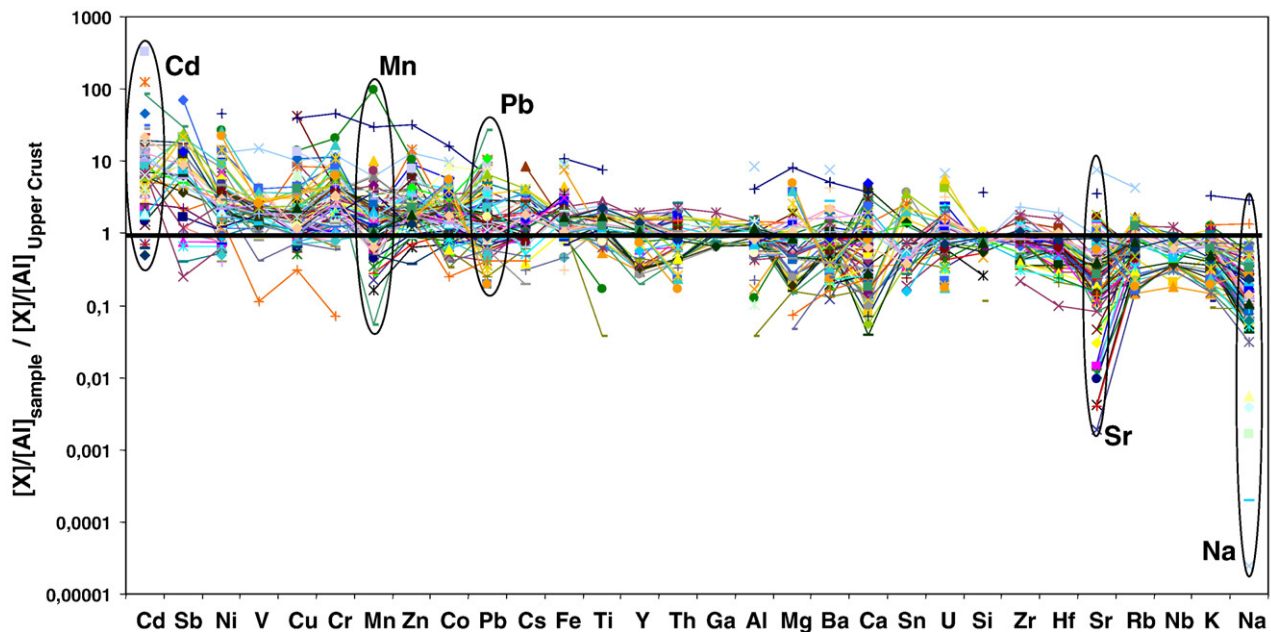


Fig. 3 – Enrichment factors calculated for the whole database. Element concentrations are normalized to aluminium (Al) and the Upper Crust reference (Taylor and McLennan, 1985).

However, the EF should be considered with prudence. Indeed, a high enrichment factor does not necessarily represent an additional source due to human activities. It could mean that the Upper Crust reference used for normalization is not representative of the local geological substratum. We consider two examples here to illustrate this point. Rivers of the Cujuni basin exhibit concentrations of Ni, Zn, V, Cd, Pb and Cr that are much higher than the Upper Crust, while this catchment area is located in a part of south-eastern Venezuela free of anthropogenic activities. Indeed, the geological basement of this basin is formed of large granite bodies with intercalated greenstone belts (Tosiani et al., 2004). The Khatanga River as well as rivers on Reunion Island are other examples of pristine rivers systems exhibiting high metal concentrations in the suspended particulate matter (Louvât and Allègre, 1997a). Suspended particulates of the Reunion Island Rivers have high concentrations in Cu, Ni and Cr. For most elements, the concentrations in riverine suspended particulates and bed loads are in the same range as the basaltic rocks making up this island. This implies that the weathering of rocks on Reunion Island does not significantly fractionate elements during the time between soil formation and the removal of erosion products to the ocean as suspended particles, contrary to the situation observed for the Congo basin, for example (Dupré et al., 1996).

By contrast, the Kola River (Russia) and Po River (Italy, Europe) exhibit high enrichment factors that can be attributed to anthropogenic activities. EF is particularly high for Cu, Ni, and V. As reported by Davide et al. (2003), industrial, agricultural and stockbreeding activities in the river Po basin account for about 40%, 35%, and 50% of the total Italian national product in these respective economic sectors. For example, very high Cu concentrations may be related to vineyards due to extensive application of copper-bearing mixtures for pest control. Another example of an extremely

polluted area is the Kola river basin (Russia). Rivers of the Kola Peninsula present high concentrations of Co, Cu, Cr, Ni and Zn. For Ni and Cr, the concentration in suspended matter is 50 times the value given for the Upper Crust. Indeed, the Kola Peninsula has been a major industrial centre for mining (open-cast mine) and smelting (Cu–Ni) for about 60 years. Pollution is transported via the atmosphere (airborne pollutants) and through the leaching of improperly treated wastes/tailings. Despite the lack of specific studies on the nature of the trace-element-bearing particulates, Pekka et al. (2004) have suggested a key role of the Mn-rich particles formed in the Kola River, and especially in lakes where high Mn/Al ratios are recorded compared with the mean upper crust value. If we consider the metal concentrations in particulates of the Kola River at its mouth (unaffected by human activities), the ranges are similar to those obtained for other boreal rivers of circumpolar regions devoid of anthropogenic influence.

The enrichment factors presented here are average values. We should bear in mind that the values are weighted heavily by rivers flowing through Europe, as well as some regions of Northern Russia and Asia (China and India). This is illustrated by Fig. 4, which reports the enrichment factors calculated for South America, North America, Africa, Asia (China and Russia) and Europe.

5.3. The major elements Na, Mg, K, Ca, Al, Fe and Mn

The increasing number of studies in recent decades on the chemical composition of sedimentary material transported by rivers is clearly related to the increasing concern about chemical weathering and climate change (Gislason et al., 2006). Indeed, the consumption of CO₂ by chemical weathering of silicate rocks over geological time has played a key role in climate regulation (Bernier et al., 1983; Dessert et al., 2003). Fig. 3 shows that the major elements are depleted in the suspended

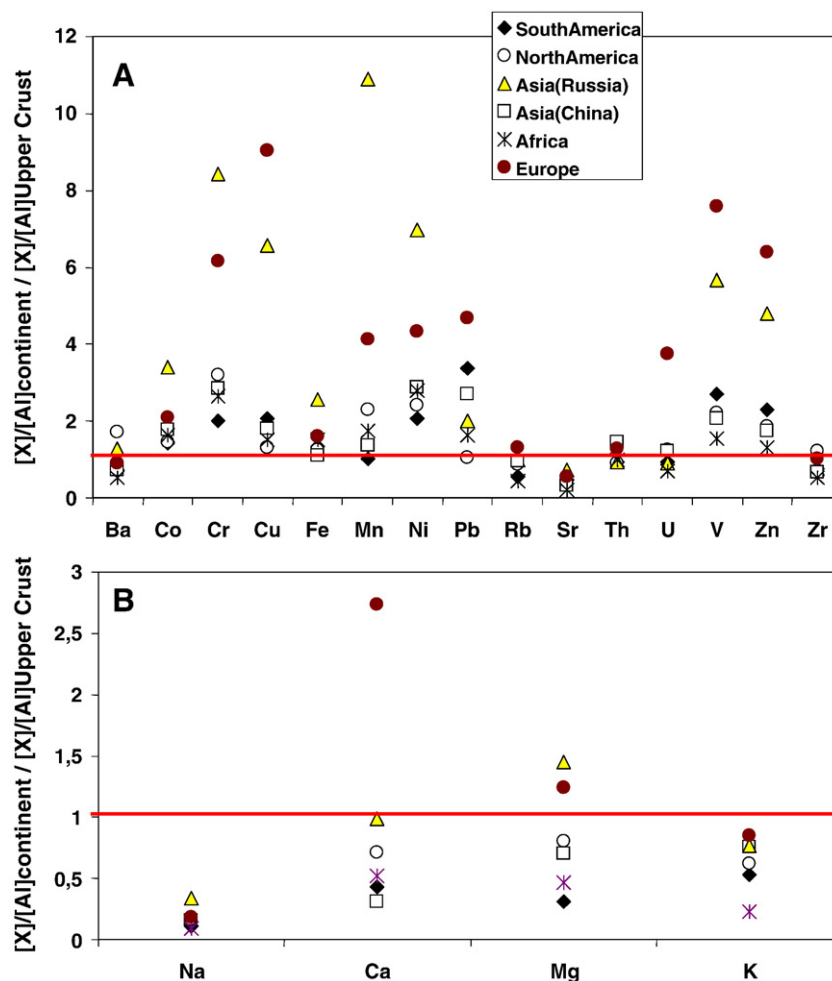


Fig. 4 – Enrichment factors for major elements in suspended particulate matter with respect to Upper Crust composition. Calculated from concentrations of Na, Mg, K, Ca, Al, Fe and Mn in riverine sediment samples from Africa, Europe, South America, North America, Asia (China) and Asia (Russia).

particulate phase compared with average crust. This is particularly pronounced for Na and Sr, which are known to be very mobile during weathering and hence become enriched in the dissolved phase. This behaviour has been shown by Dupré et al. (1996) for the rivers of the Congo basin. These elements are released by the breakdown of primary rock-forming minerals (e.g., feldspar) and are not controlled by the precipitation of secondary minerals, as opposed to elements such as Al or Fe. Using the approach of Savenko (2006), we compare the chemical compositions of suspended sediments from rivers draining contrasted climatic environments (temperate, tropical and arctic). Fig. 4 compares the major element concentrations (Na, Mg, K, Ca, Al, Fe and Mn) in the riverine suspended particulates of Africa, Europe, South America, North America, Asia (China), Asia (Russia) based on enrichment factors. These data are also given in Table 2. It appears that Mg, Na and K are more strongly depleted in tropical environments than in temperate or boreal zones. Contrary to the results reported by Savenko (2006) for K, we find that this element is most depleted in humid tropical zones. The present data reflect the high degree of weathering in tropical environments.

Fe is enriched in the riverine suspended sediments of tropical, arctic and temperate zones (Europe), but this enrichment is much more pronounced in the case of Arctic rivers. In a study of 21 rivers draining the USA, Canfield (1997) showed that the low-runoff rivers of the continental USA display Al, Fe and Mn contents closest to the continental crust average. Furthermore, this author reported a significant positive correlation of Al, Fe and Mn concentrations versus runoff. The explanation is that chemical weathering becomes more intense at higher runoff rates with a higher proportion of soluble rock components being leached from the rock, thus concentrating Al, Fe, and Mn in the residual particulate phase. On Fig. 5, we plot the database points on a Al vs. Fe diagram, with lines representing the mean ratio for Upper Crust given in Taylor and McLennan (1985) as well as suspended sediment given in Martin and Meybeck (1979) and Savenko (2006).

Some riverine particulates have drastically lower Al/Fe ratios compared with the Upper Crust and values reported from other World Rivers, due to abnormally high Fe concentrations. This group is chiefly made up of the Kalix (northern Sweden), the Negro (Amazonian basin), the Kola and Siberian rivers (northern Russia). The suspended particulates of rivers

Table 2 – Average concentration of some major and trace elements in the suspended sediment of World Rivers continent by continent

	Unit	South America	North America	Asia (Russia)	Asia (China)	Africa	Europe
Na	%	0.4	0.5	1.0	0.4	0.3	0.7
Ca	%	1.5	2.2	2.6	1.1	2.2	6.3
Mg	%	0.5	1.1	1.7	1.1	0.9	1.3
K	%	1.7	1.8	1.9	2.5	0.9	1.8
Al	%	9.1	8.3	7.1	9.5	11.3	6.1
Ba	μg/g	460	971	621	476	402	375
Co	μg/g	16	15	30	21	23	16
Cr	μg/g	79	115	260	117	130	164
Cu	μg/g	59	34	145	53	53	172
Fe	%	5.29	4.5	7.88	4.6	7.5	4.3
Mn	μg/g	700	1430	5767	970	1478	1884
Ni	μg/g	46	50	123	68	78	66
Pb	μg/g	76	22	35	64	46	71
Rb	μg/g	70	101	98	128	68	111
Sr	μg/g	184	204	228	126	94	148
Th	μg/g	11.32	10.1	8.8	18	15	11
U	μg/g	2.98	3.6	2.2	4	2.8	8
V	μg/g	131	188	128	135	116	85
Zn	μg/g	184	137	300	145	130	346
Zr	μg/g	166	238	129	149	143	147

draining the Siberian traps are known to have high Fe concentrations due to the presence of primary ferromagnesian silicates or Fe-rich secondary phases (Pokrovsky et al., 2005).

As mentioned previously, Mn is one of the elements displaying the highest enrichment factor relative to the Upper Crust (up to 100). High Mn concentrations are encountered in both polluted and pristine rivers. The extremely highly polluted Yamuna River in India exhibits Mn concentrations close to the value given by Martin and Meybeck (1979).

Pristine catchment areas of northern Europe (e.g., Kalix River basin) have high Mn concentrations due to the formation of authigenic particles in the fluvial environment (Ponter et al., 1992; Andersson et al., 1998). Some pristine rivers exhibit very high enrichment factors that are comparable to values for the much more polluted River Scheldt (northern Europe). While polluted rivers in Europe have high Mn concentrations (close to the value of Martin and Meybeck), the highest Mn concentrations encountered in certain rivers are not explained by pollution since the enrichment is due to natural processes

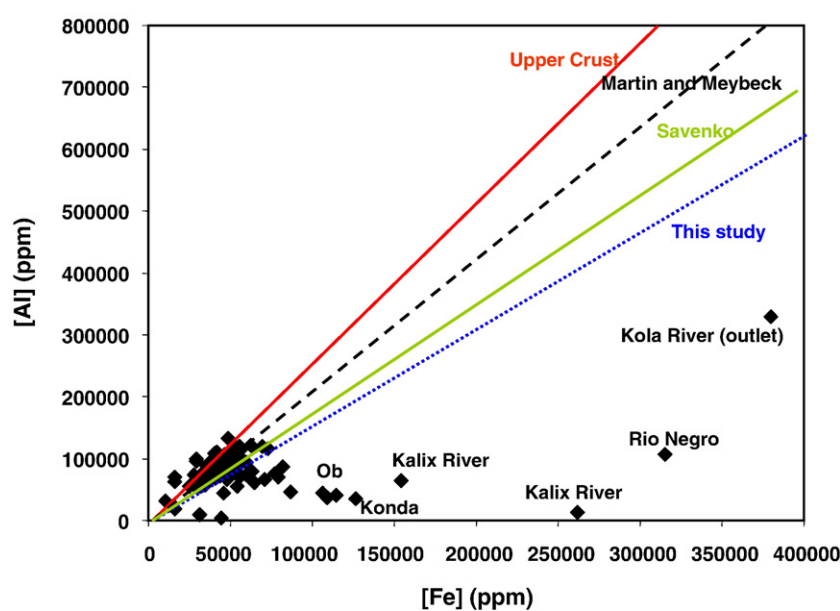


Fig. 5 – Al/Fe ratio for suspended particulate matter of the whole database. For comparison, we report the corresponding ratio for the Upper Crust given in Taylor and McLennan (1985) as well as ratios for suspended sediment given in Martin and Meybeck (1979) and Savenko (1986).

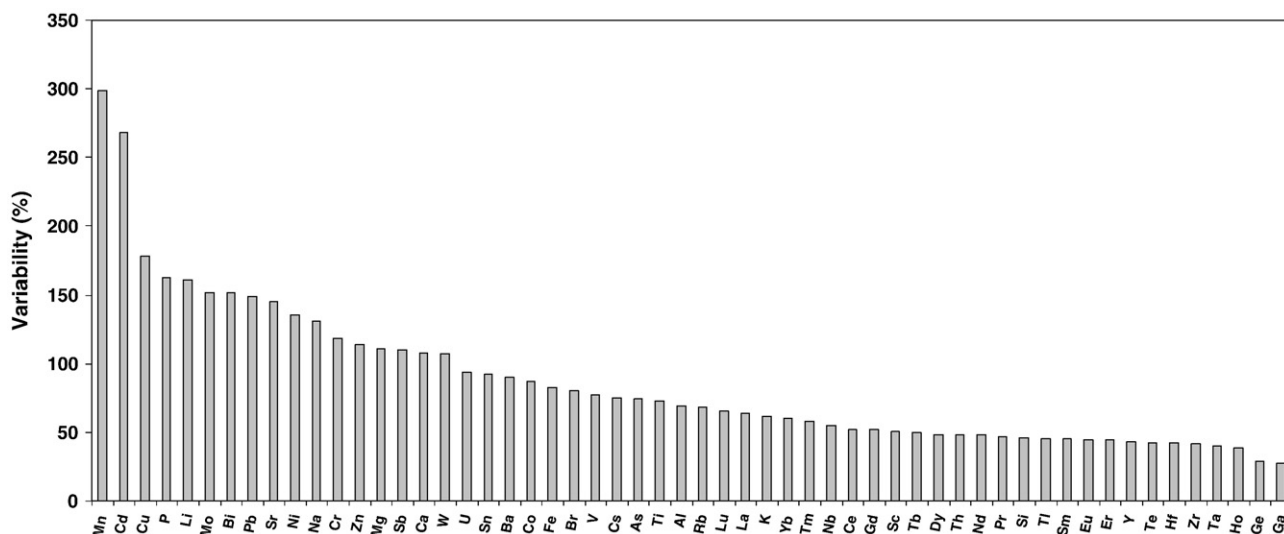


Fig. 6– Variability of elemental concentrations of suspended particulate matter calculated for the present database. The variability (in %) is expressed as the standard deviation divided by the mean and multiplied by 100.

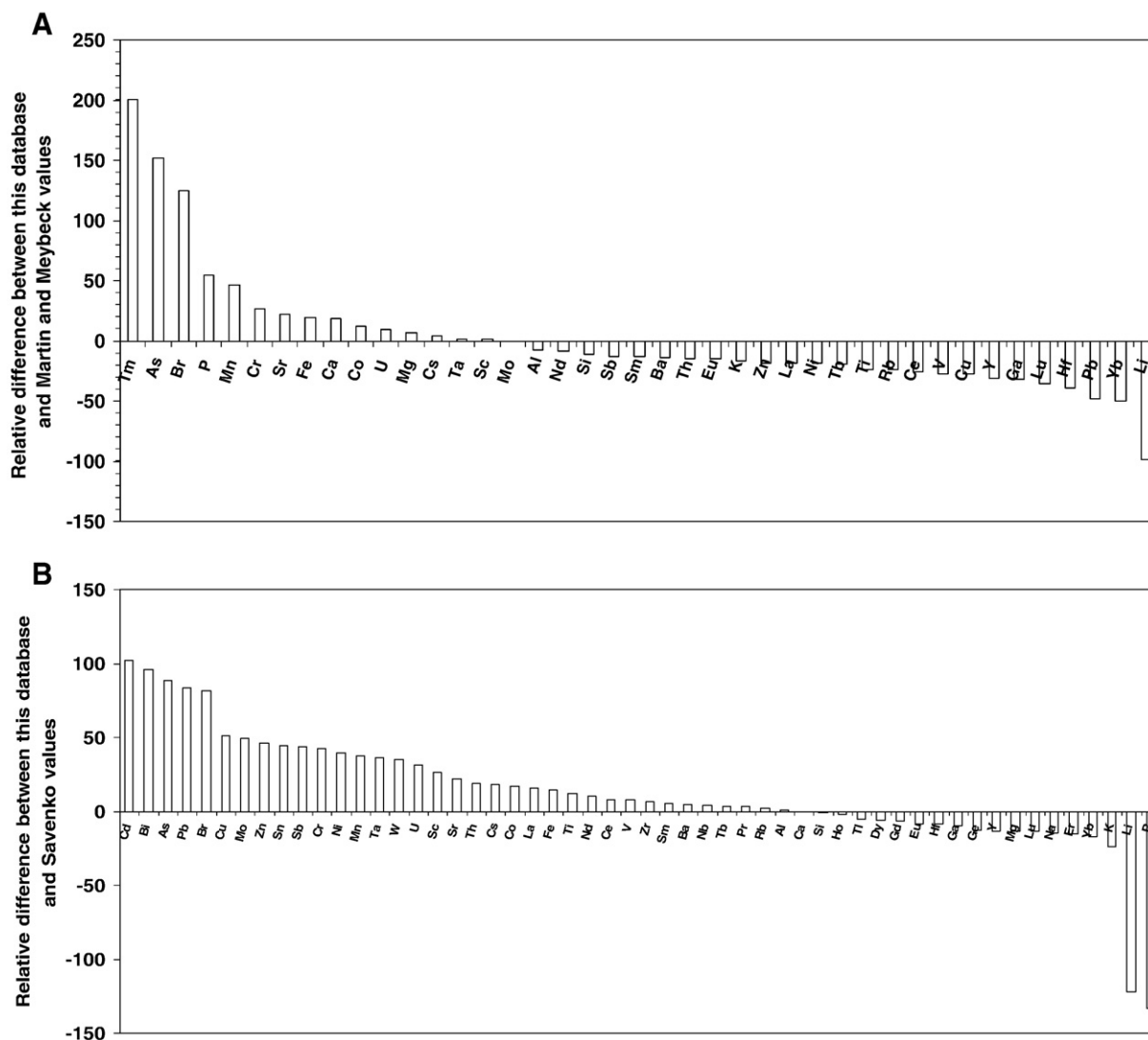


Fig. 7– Relative difference between the average concentrations given in this study and the previous data of [Martin and Meybeck \(1979\)](#) (A) and [Savenko \(2006\)](#) (B).

Table 3 – The global elemental flux carried by riverine suspended sediments to the oceans is calculated using the elements concentrations compiled during this study and the value of 15 Gt year⁻¹ for the world suspended flux

	Suspended world flux (10 ³ tonnes/year)	Standard deviation (σ)	Dissolved phase concentration ($\mu\text{g/L}$) ¹	Dissolved world flux (10 ³ tonnes/year) ²
Al	1,308,000	901,500	32.00	1200
As	544	405	0.62	23
Ba	7835	7087	23.00	860
Bi	13	19	–	–
Br	322	259	–	–
Ca	388,500	420,000	0.0346*	317,054*
Cd	23	62	0.08	3.0
Ce	1105	576	0.26	10
Co	338	294	0.15	5.5
Cr	1960	2327	0.70	26
Cs	94	70	0.01	0.40
Cu	1140	2027	1.48	55
Dy	64	31	0.03	1.1
Er	33	15	0.02	0.8
Eu	19	9	0.01	0.37
Fe	871,500	721,500	66.00	2470
Ga	272	75	0.03	1.10
Gd	79	41	0.04	1.50
Ge	18	5	0.01	0.25
Hf	61	26	0.01	0.22
Ho	13	5	0.01	0.27
K	253,500	156,000	0.0035*	29,897*
La	562	361	0.12	4.5
Li	128	205	1.84	69
Lu	5	3	0.00	0.1
Mg	189,000	210,000	0.0114*	80,777*
Mn	25,184	75,165	34.00	1270
Mo	45	68	0.42	16
Na	106,500	139,500	0.0302*	135,082*
Nb	203	112	0.00	0.1
Nd	483	233	0.15	5.7
Ni	1118	1511	0.80	30
P	30,158	48,855	–	–
Pb	916	1368	0.08	3.0
Pr	119	56	0.04	1.5
Rb	1178	808	1.63	61
Sb	33	36	0.07	2.6
Sc	274	140	1.20	45
Si	3,816,000	1,753,500	0.00351*	67,857*
Sm	92	41	0.04	1.3
Sn	69	63	–	–
Sr	2810	4086	60.00	2240
Ta	19	8	0.00	40
Tb	12	6	0.01	0.2
Te	8	3	–	–
Th	182	88	0.04	1.5
Ti	66,000	48,000	0.49	0.018
Tl	8	4	–	–
Tm	6	3	0.00	0.1
U	50	46	0.37	14
V	1941	1503	0.71	27
W	30	32	0.10	3.7
Y	329	141	0.04	1.5
Yb	32	19	0.02	0.6
Zn	3123	3564	0.60	23
Zr	2408	1000	0.04	1.5

such as occurring in the Kalix River (Sweden) (more than 6000 ppm Mn).

6. Average chemical composition and fluxes

Table 1 presents the average chemical composition of suspended sediments in World Rivers, using values obtained with this new database. These data are compared with the values proposed by Taylor and McLennan (1985) for the upper continental crust, along with the average chemical composition given by Martin and Meybeck in 1979 and more recently by Savenko (2006). On Fig. 6, we present the variability of the average concentrations. This variability is expressed in % and corresponds to the standard deviation divided by the mean. From this diagram, we can identify some elements exhibiting similar concentrations all over the world or, on the contrary, other elements with highly variable concentrations. Fig. 6 shows that certain major elements display very high variability (Na, Ca, Mg and K), being very sensitive to the weathering regime (geographic location) in the drainage area of these rivers. Some trace elements (such as Sr) exhibit geochemical behaviour similar to the major elements (such as Ca), while others are known to be very sensitive to anthropogenic activities (Pb, Ni, Zn, Cr, Cu and Cd). The elements with the lowest variability are known to be much less mobile (REE, Th and Zr). Table 2 reports the average concentrations for selected elements continent by continent.

Fig. 7A and B shows the relative difference between the average compositions proposed in this study and the average elemental contents given by Martin and Meybeck (1979) and Savenko (2006). Using the values of Martin and Meybeck (1979), we obtain a discrepancy of more than 40% for V, Cu, Ga, Lu, Tm, Yb, Hf, Pb, Li, P, As, Br and Mn. Compared with the data of Savenko (2006), we observe a large difference (more than 40%) for the following elements: Cd, Bi, As, Pb, Br, Cu, Mo, Zn, Sn, Sb, Cr, Ni, Mn, Ta, W, Li and P.

In Table 3, we give the elemental flux transported by the suspended matter from the continents to the oceans. The elemental flux has been calculated using the global sediment flux of 15 Gt year⁻¹ and our synthesis of elements concentrations. The uncertainties reported on the elemental fluxes are the uncertainties obtained on the elemental concentrations. For information, we report on Table 3 the elemental flux delivered in a dissolved form by rivers to the oceans. These data are taken from Gaillardet et al. (2003) for trace elements and from Gaillardet et al. (1999) for major elements. With the exception of Ba, Ca, Mg, K, Na, Li, Sr, Sc, Ta, U and W, elements are largely transported by the suspended particulate matter. In

Notes to Table 3

For comparison, we also report the average concentrations of dissolved elements in river water (3) and their associated fluxes (4) (Gaillardet et al., 2003).

^{1,2} correspond to the average chemical composition of the riverine dissolved phase and the associated fluxes to the oceans (Gaillardet et al., 2003).

* signifies that the data were taken from Gaillardet et al. (1999) and not from Gaillardet et al. (2003).

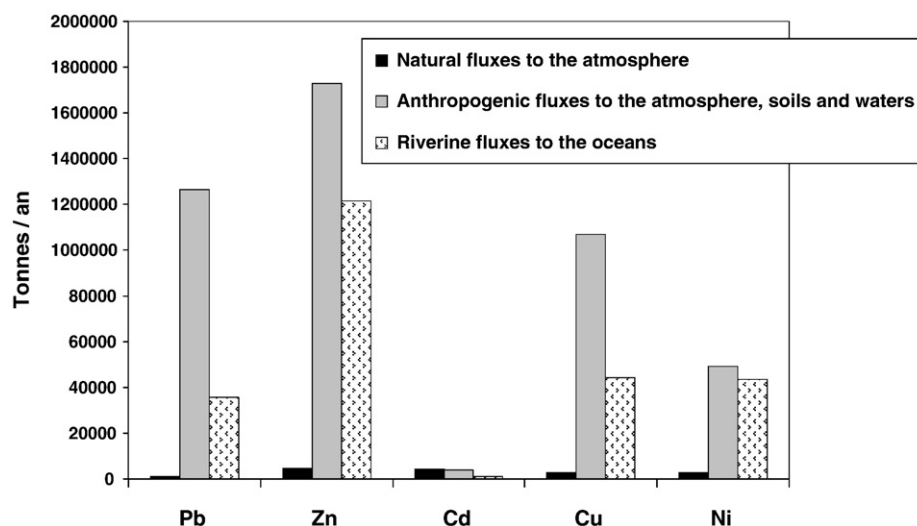


Fig. 8 – Comparison between the natural fluxes of some metals to the atmosphere, soils and waters (Nriagu, 1988) and the suspended riverine fluxes (this study).

view of this result, there is a need to obtain a much better estimation of the flux of suspended matter transported by rivers worldwide.

7. Conclusion

This paper presents a new database on the elemental composition of riverine suspended sediment together with an estimation of the associated fluxes. With the exception of Ca, Mg, K and Na, most of the elements are mainly transported by the solid phase. These data are required to provide better constraints on geochemical cycles at the Earth surface.

It appears that transition metals are enriched in suspended matter compared with the continental crust composition. Since the beginning of the industrial era, metals have been released and deposited in the environment. Metals are emitted into the atmosphere both as particles and gases, and are also released directly into the natural systems. While soils are the major recipient for pollutants in terrestrial ecosystems, sediments represent the major sink in aquatic ecosystems. By comparing the riverine suspended sediment fluxes of some metals (Cd, Zn, Ni, Cu, and Pb) given in this study with estimates of the anthropogenic fluxes of these metals to the atmosphere, soils and waters (natural ecosystems) (Nriagu, 1988), we can see that these fluxes are similar (see Fig. 8). This casts light on the effect of human activities on the cycles of trace elements at the Earth's surface.

However, high metal concentrations in the suspended sediment do not necessarily reflect inputs from human activities. These high concentrations may result from a specific lithology that is different from the reference used for continental crust. Alternatively, they may arise from natural processes such as described for manganese in the case of the Kalix river basin (Sweden). There is a crucial need to acquire more data not only on the elemental fluxes but also on the chemical composition of suspended particulate matter.

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