

5.06

Global Occurrence of Major Elements in Rivers

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S0005 5.06.1 INTRODUCTION

P0005 Major dissolved ions (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , HCO_3^- , and CO_3^{2-}) and dissolved silica (SiO_2) in rivers have been studied for more than a hundred years for multiple reasons: (i) geochemists focus on the origins of elements and control processes, and on the partitioning between dissolved and particulate forms; (ii) physical geographers use river chemistry to determine chemical denudation rates and their spatial distribution; (iii) biogeochemists are concerned with the use of carbon, nitrogen, phosphorus, silica species, and other nutrients by terrestrial and aquatic biota; (iv) oceanographers need to know the dissolved inputs to the coastal zones, for which rivers play the dominant role; (v) hydrobiologists and ecologists are interested in the temporal and spatial distribution of ions, nutrients, organic carbon, and pH in various water bodies; (vi) water users need to know if waters comply with their standards for potable water, irrigation, and industrial uses.

The concentrations of the major ions are commonly expressed in mg L^{-1} ; they are also reported in meq L^{-1} or $\mu\text{eq L}^{-1}$, which permits a check of the ionic balance of an analysis: the sum of cations (Σ^+ in eq L^{-1}) should equal the sum of anions (Σ^- in eq L^{-1}). Dissolved silica is generally not ionized at pH values commonly found in rivers; its concentration is usually expressed in mg L^{-1} or in $\mu\text{mol L}^{-1}$. Ionic contents can also be expressed as percent of Σ^+ or Σ^- ($\%C_i$), which simplifies the determination of ionic types. Ionic ratios (C_i/C_j) in eq eq^{-1} are also often tabulated (Na^+/Cl^- , $\text{Ca}^{2+}/\text{Mg}^{2+}$, $\text{Cl}^-/\text{SO}_4^{2-}$, etc). As a significant fraction of sodium can be derived from atmospheric sea salt and from sedimentary halite, a chloride-corrected sodium concentration is commonly reported ($\text{Na}^\# = \text{Na}^+ - \text{Cl}^-$ (in meq L^{-1})). The export rate of ions and silica, or the yield ($Y_{\text{Ca}^{2+}}$, Y_{SiO_2}) at a given station is the average mass transported per year divided by the drainage area: it is expressed in units of $\text{t km}^{-2} \text{yr}^{-1}$ (equal to $\text{g m}^{-2} \text{y}^{-1}$) or in $\text{eq m}^{-2} \text{yr}^{-1}$.

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P0015 This chapter covers the distribution of riverine major ions, carbon species, both organic and inorganic, and silica over the continents, including internal regions such as Central Asia, and also the major factors such as lithology and climate that control their distribution and yields.

P0020 Based on an unpublished compilation of water analyses in 1,200 pristine and subpristine basins, I am presenting here an idealized model of global river chemistry. It is somewhat different from the model proposed by Gibbs (1970), in that it includes a dozen major ionic types. I also illustrate the enormous range of the chemical composition of rivers—over three orders of magnitude for concentrations and yields—and provide two global average river compositions: the median composition and the discharge-weighted composition for both internally and externally draining regions of the world.

P0025 A final section draws attention to the human alteration of river chemistry during the past hundred years, particularly for Na^+ , K^+ , Cl^- , and SO_4^{2-} ; it is important to differentiate anthropogenic from natural inputs.

S0010 5.06.2 SOURCES OF DATA

P0030 Natural controls of riverine chemistry at the global scale have been studied by geochemists since Clarke (1924) and the Russian geochemists Alekin and Brazhnikova (1964). Regional studies performed prior to industrialization and/or in remote areas with very limited human impacts are rare (Kobayashi, 1959, 1960) and were collected by Livingstone (1963). Even some of his river water data are affected by mining, industries, and the effluents from large cities. These impacts are obvious when the evolution of rivers at different periods is compared; Meybeck and Ragu (1995, 1997) attempted this comparison for all the rivers flowing to the oceans from basins with areas exceeding 10^4 km^2 . More recently interest in the carbon cycle and its riverine component has been the impetus for a new set of field studies (Stallard and Edmond, 1981, 1983; Degens *et al.*, 1991; Gaillardet *et al.*, 1997, 1999; Millot *et al.*, 2002; Guyot, 1993) that build on observations made since the 1970s (Reeder *et al.*, 1972; Stallard and Edmond, 1981, 1983). These data were used to construct the first global budgets of river dissolved loads (Meybeck, 1979) and their controls (Meybeck, 1987, 1994; Bluth and Kump, 1994; Berner, 1995; Stallard, 1995a,b).

P0035 Most of the annual means derived from these data have been collected into a global set of pristine or subpristine rivers and tributaries (PRISRI, $n = 1,200$) encompassing all the continents, including exorheic and endorheic (internal drainage) runoff. The largest basins, such as the

Amazon, Mackenzie, Lena, Yenisei, and Mekong, have been subdivided into several smaller subbasins. In some regions (e.g., Indonesia, Japan) the size of the river basins included in these summaries may be less than $1,000 \text{ km}^2$. In the northern temperate regions only the most reliable historic analyses prior to 1920 have been included. Examples are analyses performed by the US Geological Survey (1909–1965) in the western and southwestern United States and in Alaska.

In order to study the influence of climate, total cationic contents (Σ^+) of PRISRI rivers have been split into classes based on annual runoff (q in mm yr^{-1}) and Σ^+ (meq L^{-1}). A medium-sized subset has also been used (basin area from $3,200 \text{ km}^2$ to $200,000 \text{ km}^2$, $n = 700$). The PRISRI data base covers the whole globe but has poor to very poor coverage of western Europe, Australia, South Africa, China, and India due to the lack of data for pre-impact river chemistry in these regions. PRISRI includes rivers that flow permanently ($q > 30 \text{ mm yr}^{-1}$) and seasonally to occasionally ($3 < q < 30 \text{ mm yr}^{-1}$). Lake outlets may be included in PRISRI.

S0015 5.06.3 GLOBAL RANGE OF PRISTINE RIVER CHEMISTRY

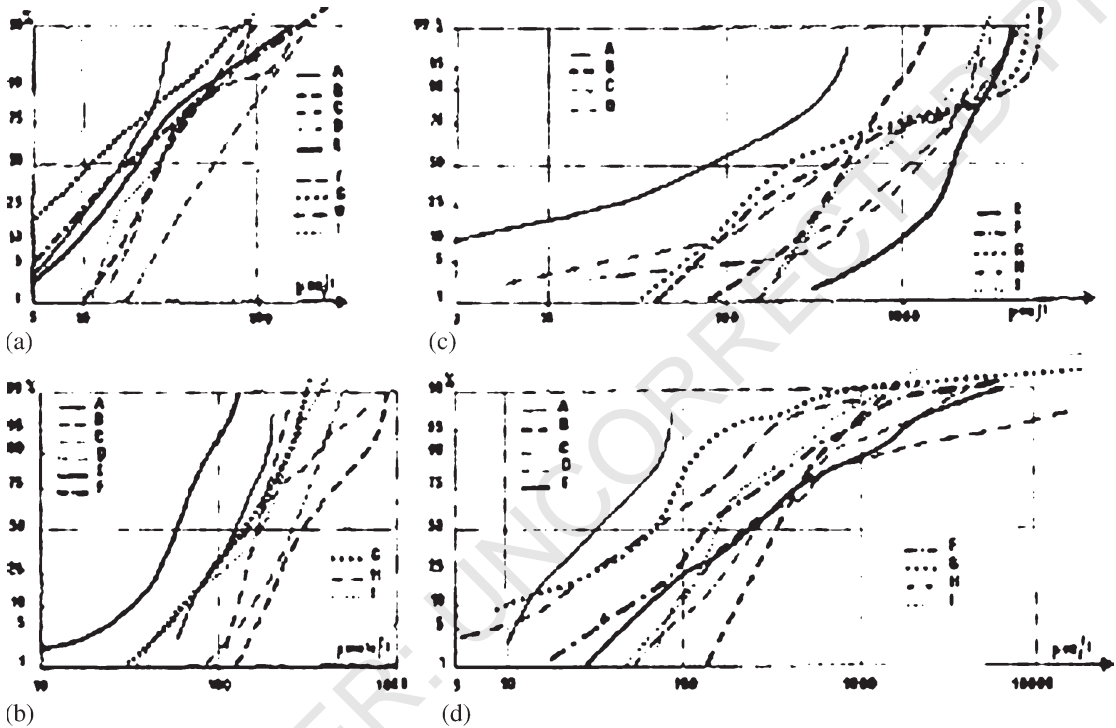
P0045 The most striking observation in global river chemistry is the enormous range in concentrations (C_i), ionic ratios (C_i/C_j), and the proportions of ions in cation and anion sums ($\%C_i$) as illustrated by the 1% and 99% quantiles (Q_1 and Q_{99}) of their distribution (Table 1). The Q_{99}/Q_1 ratio of solute concentrations is the lowest for potassium and silica, about two orders of magnitude, and it is very high for chloride and sulfate, exceeding three orders of magnitude. The concept of “global average river chemistry,” calculated from the total input of rivers to oceans divided by the total volume of water, can only be applied for global ocean chemistry and elemental cycling; it is not a useful reference in either weathering studies, river ecology, or water quality.

P0050 Ionic ratios and ionic proportion distributions also show clearly that all major ions, except potassium, can dominate in multiple combinations: ionic ratios also range over two to three orders of magnitude, and they can be greater or less than unity for all except the Na^+/K^+ ratio, in which sodium generally dominates. River compositions found in less than 1% of analyses can be termed *rare*; for analyses from Q_1 to Q_{10} and Q_{90} to Q_{99} , I propose the term *uncommon*, from Q_{10} to Q_{25} and Q_{75} to Q_{90} , *common*, and between Q_{25} and Q_{75} , *very common*. An example of this terminology is shown in the next section (Figure 2) for dissolved inorganic carbon (DIC).

T0005 **Table 1** Global range of pristine river chemistry (medium-sized basins).

	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	SO_4^{2-}	HCO_3^-	SiO_2	Σ^+
<i>Ionic contents (C_i)</i>									
Q_{99}	9,300	5,900	14,500	505	17,000	14,500	5,950	680	32,000
Q_1	32	10	18	3.9	3.7	5	47	3.3	128
Q_{99}/Q_1	290	590	805	129	4,600	2,900	126	206	250
<i>Ionic proportions (%C_i)</i>									
Q_{99}	84	48	72	19.5	69	67	96		
Q_1	11	0.1	1	0.1	0.1	0.1	9		
	$\frac{Ca^{2+}}{Mg^{2+}}$	$\frac{Ca^{2+}}{Na^+}$	$\frac{Mg^{2+}}{Na^+}$	$\frac{Na^+}{K^+}$	$\frac{Na^+}{Cl^-}$	$\frac{Ca^{2+}}{SO_4^{2-}}$	$\frac{SO_4^{2-}}{HCO_3^-}$	$\frac{Cl^-}{SO_4^{2-}}$	$\frac{SiO_2}{\Sigma^+}$
<i>Ionic ratios (C_i/C_j)</i>									
Q_{99}	20.3	56	20	164	29	51	3.5	8.5	1.3
Q_1	0.01	0.14	0.01	0.95	0.33	0.19	0.01	0.01	0.0

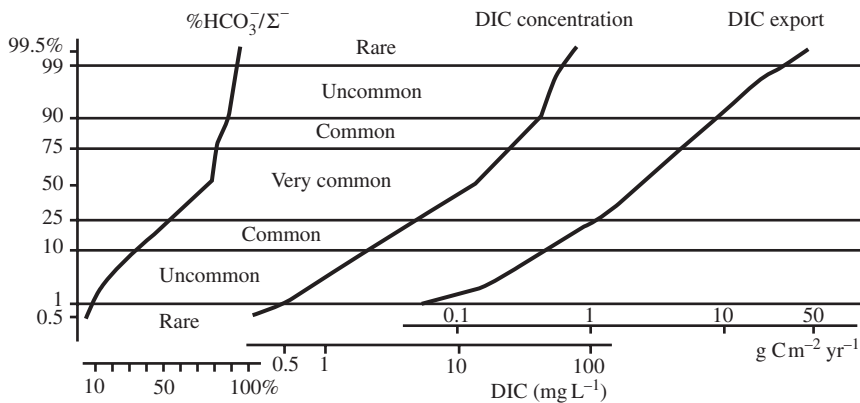
C_i : ionic contents ($\mu eq L^{-1}$ and $\mu mol L^{-1}$ for silica); % C_i : proportion of ions in the sum of total cations or anions; C_i/C_j : ionic ratios; and Q_1 and Q_{99} : lowest and highest percentiles of distribution.



F0005 **Figure 1** Cumulative distributions of major dissolved elements in pristine regions: (a) K^+ , (b) SiO_2 , (c) HCO_3^- , and (d) Na^+ . A: Central and lower Amazon, B: Japan, C: Andean Amazon Basin, D: Thailand, E: Mackenzie Basin, F: French streams, G: temperate stream model, H: monolithologic miscellaneous streams, I: major world rivers (source Meybeck, 1994).

P0055 When plotted on a log-probability scale (Henry's law diagram) the distributions of elemental concentrations show four patterns (Figure 1): (i) lognormal distribution as for potassium in Thailand (a, D), that can be interpreted as a single source of the element and limited control on its concentration; (ii) retention

at lower concentrations (there is a significant break in the distribution as for silica in the Mackenzie Basin (b, E)); (iii) retention at higher concentrations (there is a significant break in the distribution as for bicarbonate (DIC) (c, C, E, F, G, I)); and (iv) additional source at higher concentrations (the break in the distribution is in



P0010 **Figure 2** Global distribution of DIC concentration, ratio and export rate (yield) in medium-sized basins (3,500–200,000 km²).

the opposite direction, as for chloride, suggesting another source of material than the one observed between Q_{10} and Q_{90} (d, all except central Amazon)).

S0020 5.06.4 SOURCES, SINKS, AND CONTROLS OF RIVER-DISSOLVED MATERIAL

P0060 The observed distribution patterns have been interpreted by many authors (Likens *et al.*, 1977; Drever, 1988; Hem, 1989; E. K. Berner and R. Berner, 1996) in terms of multiple sources, sinks, and controls on riverine chemistry (Table 2). The sources of ions may be multiple: rainfall inputs, generally of oceanic origin, (rich in NaCl and also in MgSO₄), differential weathering of silicate minerals and carbonate minerals, dissolution of evaporitic minerals contained in some sedimentary rocks (gypsum and anhydrite, halite) or leached during rainstorms from surficial soils of semi-arid regions (Garrels and Mackenzie, 1971; Drever, 1988; Stallard, 1995a,b). Sinks are also multiple: silica may be retained in lakes and wetlands due to uptake by aquatic biota. Carbonate minerals precipitate in some eutrophic lakes and also precipitate when the total dissolved solids increases, generally above $\Sigma^+ = 6 \text{ meq L}^{-1}$, due to evaporation.

P0065 In semi arid regions ($30 < q < 140 \text{ mm yr}^{-1}$) and arid regions (chosen here as $3 < q < 30 \text{ mm yr}^{-1}$) surface waters gradually evaporate and become concentrated, reaching saturation levels of calcium and magnesium carbonates first, and then of calcium sulfate: these minerals are deposited in soils and in river beds during their drying stage, a process termed evaporation/crystallization by Gibbs (1970).

P0070 There is also growing evidence of active recycling of most major elements, including silica, in terrestrial vegetation, particularly in

forested areas (Likens *et al.*, 1977). Each element may, therefore, have multiple natural sources and sinks. The main controlling factors for each element are also multiple (Table 2). They can be climatic: higher temperature generally increases mineral dissolution; water runoff increases all weathering rates. Conversely, soil retention increases at lower runoff. The weathering of silicate and carbonate minerals is also facilitated by organic acids generated by terrestrial vegetation (see Chapter 5.06). Higher lake residence times ($\tau > 6$ months) favor biogenic silica retention and the precipitation of calcite (e.g., $30 \text{ g SiO}_2 \text{ m}^{-2} \text{ yr}^{-1}$ and $300 \text{ g CaCO}_3 \text{ m}^{-2} \text{ yr}^{-1}$ in Lake Geneva). The distance to the oceans is the key factor controlling the inputs of sea salts.

Tectonics also exercises important regional controls: active tectonics in the form of volcanism and uplift is associated with the occurrence at the Earth's surface of fresh rock that is more easily weathered than surficial rocks that have been exposed to weathering for many millions of years on a stable craton: there, the most soluble minerals have been dissolved and replaced by the least soluble ones such as quartz, aluminum and iron oxides, and clays. Active tectonics also limits the retention of elements by terrestrial vegetation, and retention in arid soils due to high mechanical erosion rates. Rifting is generally associated with inputs of saline deep waters that can have a major influence on surface water chemistry at the local scale. In formerly glaciated shields as in Canada and Scandinavia, glacial abrasion slows the development of a weathered soil layer. This limits silicate mineral weathering even under high runoff. These low relief glaciated areas are also characterized by a very high lake density, an order of magnitude higher than in most other regions of the world; lakes are sinks for silica and nutrients. The effects of Quaternary history in semi-arid and arid regions can be

T0010 **Table 2** Dominant sources, sinks, and controls of major ions in present day rivers.

	Major ions							Controls								
	SiO ₂	K ⁺	Na ⁺	Cl ⁻	SO ₄ ²⁻	Mg ²⁺	Ca ²⁺	DIC	T°	τ	q	d	QH	V	T	
<i>Natural sources</i>																
Atmosphere	←-----→															
Silicate weathering	←-----→					←-----→	←-----→	+		+			×	+	+	
Pyrite	←-----→				←-----→					+						
Carbonate						←-----→	←-----→			+				+		
Gypsum					←-----→					+						
Halite			←-----→							+						
Deep waters	←-----→														+	
<i>Natural sinks</i>																
Terrestrial vegetation	←-----→							+		+				+	-	
Soils	←-----→									-			×		-	
Lakes	←-----→								+				×			
<i>Anthropogenic sources</i>																
Mines	←-----→							prod								
Industries	←-----→							+					+			
Cities		←-----→							+							
Agriculture		←-----→									+					
<i>Anthropogenic sinks</i>																
Reservoirs	←-----→														+	
Irrigated soils	←-----→													+		

+ , - : increase and decrease with related control; ×: complex relation; DIC: dissolved inorganic carbon.
 T°: temperature; q: runoff; d: distance to ocean; QH: Quaternary history; V: terrestrial biomass; τ: water residence time; T: volcanism, tectonic uplift and rifting.
 Prod: production; pop: urban population; fert: fertilization rate; treat: wastewater treatment and recycling; irrig: water loss through irrigation; nb: volume of reservoirs and eutrophication.

considerable, due to the inheritance of minerals precipitated under past climatic conditions. Due to the effect of local lithology, distance to the ocean, regional climate and tectonics, and the occurrence of lakes, river chemistry in a given area may be very variable.

5.06.4.1 Influence of Lithology on River Chemistry

Lithology is an essential factor in determining river chemistry (Garrels and Mackenzie, 1971; Drever, 1988, 1994), especially at the local scale (Strahler stream orders 1–3) (Miller, 1961; Meybeck, 1986). On more regional scales, there is generally a mixture of rock types, although some large river basins (area > 0.1 Mkm²) may contain one major rock type such as a granitic shield or a sedimentary platform. When selecting nonimpacted monolithologic river basins in a given region such as France (Table 3, A–E), the influence of climate, tectonics, and distance from the ocean can be minimized, revealing the dominant control of lithology, which in turn depends on (i) the relative abundance of specific minerals and (ii) the sensitivity of each mineral to weathering. The weathering scale most commonly adopted is that of Stallard (1995b) for mineral stability in tropical soils: quartz ≫ K-feldspar, micas ≫ Na-feldspar > Ca-

feldspar, amphiboles > pyroxenes > dolomite > calcite ≫ pyrite, gypsum, anhydrite ≫ halite (least stable).

Table 3F provides examples of stream and river chemistry under peculiar conditions: highly weathered quartz sand (Rio Negro), peridotite (Dumbea), hydrothermal inputs (Semliki and Tokaanu), evaporated (Saoura), black shales (Powder and Redwater), sedimentary salt deposits (Salt). They illustrate the enormous range of natural river chemistry (outlets of acidic lakes are omitted here).

Table 3 lists examples of more than a dozen different chemical types of river water. Although Ca²⁺ and HCO₃⁻ are generally present, Mg²⁺ dominance over Ca²⁺ can be found in rivers draining various lithologies such as basalt, peridotite, serpentinite, dolomite, coal, or where hydrothermal influence is important (Semliki). Sodium may dominate in sandstone basins, in black shales (Powder, Redwater in Montana), in evaporitic sedimentary basins (Salt), in evaporated basins (Saoura), and where hydrothermal and volcanic influence is important (Semliki, Tokaanu). K⁺ rarely exceeds 4% of cations except, in some clayey sands, mica schists, trachyandesite; it exceeds 15% in extremely dilute waters of Central Amazonia and in highly mineralized waters of rift lake outlets (Semliki, Ruzizi).

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Table 3 A–E: composition of pristine waters draining single rock types in France (medians of analyses corrected for atmospheric inputs) (from 3 to 26 analyses in each class, except for estimates that are based on one analysis only). **F:** other river chemistry from various origins uncorrected for atmospheric inputs (Meybeck, 1986). Cation and anion proportions in percent of their respective sums (Σ^+ and Σ^-).

	SiO_2 ($\mu\text{mol}^{-1}\text{L}$)	Σ^+ ($\mu\text{eq}^{-1}\text{L}$)	Ca^{2+} (%)	Mg^{2+} (%)	Na^+ (%)	K^+ (%)	Cl^- (%)	SO_4^{2-} (%)	HCO_3^- (%)
A. Noncarbonate detrital rocks									
Quartz sand and sandstones	170	170	30	20	45	5	0	(40)	(60)
Clayey sands	135	300	53	17	13	17	0	(30)	(70)
Arkosic sands	200	400	48	35	12	5	0	(20)	(80)
Graywacke	90	350	58	22	18	2	0	(20)	(80)
Coal-bearing formations	150	5,000	30	55	14	1	0	20–90	80–10
B. Carbonate-containing detrital rocks									
Shales	90	500	60	30	8	1.5	0	25	75
Permian shales	175	2,200	53	35	8	4	(0–20)	10	90–70
Molasse	280	2,500	80	17	3	0.3	0	2	98
Flysch	50	2,200	79	19	1.5	0.5	0	2	98
Marl	90	3,000	83	14	2.5	0.5	0	2	98
C. Limestones									
Limestones	60	4,500	95	3	0.6	0.4	0	2.5	97.5
Dolomitic limestones	60	4,500	72	26	0.6	0.4	0	3.5	96.5
Chalk ^a	200	4,500	95	2.5	2.2	0.5	0	2.5	97.5
Dolomite ^b	67	5,900	54	46	0.1	0.1	0	8.5	91.5
D. Evaporites									
Gypsum marl ^c	160	22,000	77	22	0.2	0.2	0	83	17
Salt and gypsum marl ^d	133	27,500	34	32	33	(0.8)	36	44	20
E. Plutonic, metamorphic, and volcanic rocks									
Alkaline granite, gneiss, mica schists	140	130	15	15	65	5	0	(30)	(70)
Calc-alkaline granite, gneiss, mica schists	100	300	54	25	17	4	0	(15)	(85)
Serpentine	225	1,500	38	60	7	1	0	(7)	93
Peridotite	180	600	5	93	1	1	0	(15)	(85)
Amphibolite	65	1,600	85	17	2	1	0	(7)	(93)
Marble ^a	150	3,400	86	11	1.8	0.6	0	(12)	88
Basalt	200	500	42	38	17	2.5	0	(2)	98
Trachyandesite	190	220	32	25	35	8	0	(2)	98
Rhyolite	190	550	53	15	25	2	0	(2)	98
Anorthosite	260	400	45	25	26	4	0	(2)	98
F. Miscellaneous river waters (not rain corrected)									
Rio Negro tributaries ^b	75	18.1	10.5	16.5	51.9	20.9			
Dumbea (New Caledonia)	232	1,175	3.9	84.7	10.9	0.3	14.2	7.1	78.5
Cusson (Landes, France) ^b	251	1,463	13.8	21.2	61.5	3.4	69	12.3	18.7
Semliki (Uganda) ^c	213	8,736	6.4	36.2	39.6	17.5	14.6	23.3	62.0
Powder (Montana)	148	20,200	27.2	20.3	51.5	0.9	15.0	62.8	22.2
Saoura (Marocco) ^d		26,150	23.3	16.8	59.2	0.7	62.8	27.7	9.6
Redwater (Montana)	116	40,700	10.7	24.5	64.1	0.6	1.0	72.2	26.7
Tokaanu (New Zeal.) ^c	4,760	41,600	14.4	3.0	79.5	3.1	90.6	5.8	3.5
Salt (NWT, Canada)	20	312,000	9.7	1.8	88.4	0.1	89.7	9.3	1.0

^a Estimates. ^b Rain dominated. ^c Hydrothermal inputs. ^d Evaporated.

The occurrence of highly reactive minerals, such as evaporitic minerals, pyrite and even calcite in low proportions—a percent or less—in a given rock, e.g., calcareous sandstone, pyritic shale, marl with traces of anhydrite, granite with traces of calcite, may determine the chemical character of stream water (Miller, 1961; Drever, 1988). In a study of 200 streams from mono-

lithologic catchments underlain by various rock types under similar climatic conditions in France, the relative weathering rate based on the cation sum (Meybeck, 1986) ranges from 1 for quartz sandstone to 160 for gypsiferous marl.

When the lithology in a given region is fairly uniform, the distribution of major-element concentrations is relatively homogeneous with

quantile ratios Q_{90}/Q_{10} well under 10 as, for example, in Japan (mostly volcanic), the Central Amazon Basin (detrital sand and shield) (Figure 1, distributions B); when a region is highly heterogeneous with regards to lithology, as in the Mackenzie Basin and in France, the river chemistry is much more heterogeneous (Figure 1, distributions E and F) and quantile ratios Q_{90}/Q_{10} , Q_{99}/Q_1 may reach those observed at the global scale (Figure 1, distributions G) (Meybeck, 1994). In the first set, regional geochemical background compositions can be easily defined, but not in the second set.

5.06.4.2 Carbon Species Carried by Rivers

The carbon cycle and its long-term influence on climate through the weathering of fresh silicate rocks (Berner *et al.*, 1983) has created a new interest in the river transfer of carbon. Bicarbonate (HCO_3^-) is the dominant form of DIC in the pH range of most world rivers ($6 < \text{pH} < 8.2$); carbonate (CO_3^{2-}) is significant only at higher pH, which occurs in a few eutrophic rivers such as the Loire River, where pH exceeds 9.2 during summer algal blooms, and in waters that have undergone evaporation. Undissociated dissolved CO_2 is significant only in very acidic waters rich in humic substances such as the Rio Negro (Amazonia), but this is unimportant at the global scale. In terms of fluxes, bicarbonate DIC dominates (Table 4). It has two different sources: (i) carbonic acid weathering of noncarbonate minerals, particularly of silicates such as feldspars, micas, and olivine, (ii) dissolution of carbonate minerals such as calcite and dolomite, in which half of the resulting DIC originates from soil and/or atmospheric CO_2 , and half from the weathered rock. Other forms of riverine carbon include particulate

inorganic carbon (PIC) due to mechanical erosion in carbonate terrains, and dissolved and particulate organic carbon (DOC and POC) that are largely due to soil leaching and erosion; fossil POC in loess and shale may also contribute to river POC; organic pollution and algal growth in eutrophic lakes and rivers contribute minor fluxes (Meybeck, 1993). The “ages” of these carbon species, i.e., the time since their original carbon fixation fall into two categories: (i) those from 0 to ~1,000 yr, representing the fast cycling external part of the cycle are termed total atmospheric carbon (TAC); (ii) those from 50 kyr (Chinese Loess Plateau) to 100 Myr representing “old” carbon from sedimentary rocks. The sensitivity of these transfers to global change is complex (Table 4).

River carbon transfers are also very variable at the global scale: DIC concentrations range from 0.06 mg DIC L^{-1} (Q_1) to 71 mg DIC L^{-1} (Q_{99}); DIC export, or yield, ranges from 0.16 g C $\text{m}^{-2} \text{yr}^{-1}$ (Q_1) to 33.8 g C $\text{m}^{-2} \text{yr}^{-1}$ (Q_{99}). In 50% of river basins bicarbonate makes up more than 80% of the anionic charge. The distribution quantiles for these variables are shown in Figure 2.

Organic acids, particularly those present in wetland-rich basins also play an important role in weathering (Drever, 1994; Viers *et al.*, 1997; see also Chapter 5.06 and Chapter 5.09).

5.06.4.3 Influence of Climate on River Chemistry

The influence of air temperature is nearly impossible to measure for large basins due to its spatial heterogeneity and its absence in most databases. Some studies of mountain streams have considered the effect of air temperature (Drever and Zobrist, 1992). It is generally agreed that silicate weathering is more rapid

Table 4 Riverine carbon transfer and global change.

Sources	Age (yr)	Flux ^a (10^{12} g C yr ⁻¹)	Sensitivity to global change						
			A	B	C	D	E	F	
PIC	Geologic	10^4 – 10^8	170	•					•
DIC	Geologic	10^4 – 10^8	140		•	•			•
	Atmospheric	0 – 10^{12}	245		•	•			•
DOC	Soils	10^0 – 10^3	200			•			•
	Pollution	10^{-2} – 10^{-1}	(15) ?					•	
CO ₂	Atmospheric	0	(20–80)		•	•	•		
POC	Soils	10^0 – 10^3	(100)	•					•
	Algal	10^{-2}	(<10)			•			•
	Pollution	10^{-2} – 10^0	(15) ?					•	
	Geologic	10^4 – 10^8	(80)	•					•

A = land erosion, B = chemical weathering, C = global warming and UV changes, D = eutrophication, E = organic pollution, F = basin management, TAC = total atmospheric carbon.

^a Present global flux to oceans mostly based on (8) and (9), 10^{12} g C yr⁻¹.

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Q20

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Q21

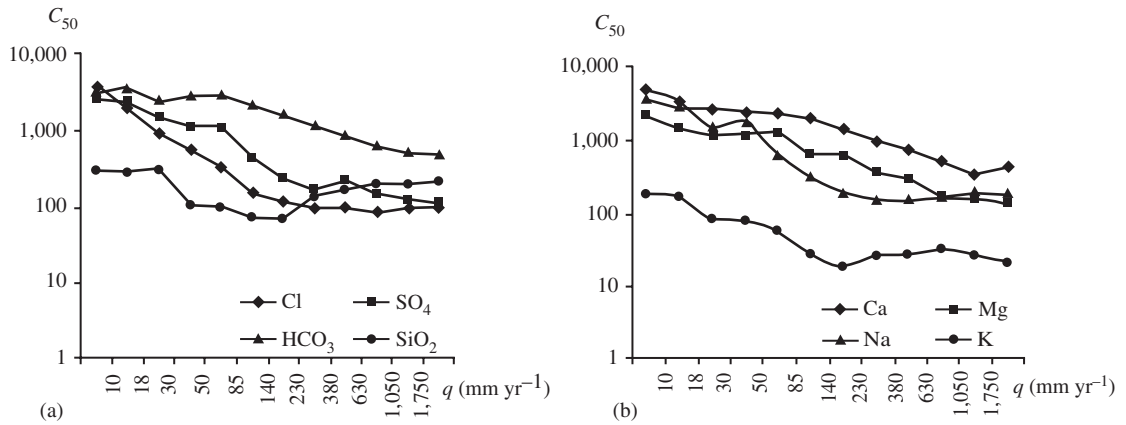


Figure 3 (a) and (b): Median concentrations C_{50} in 12 classes of river runoff (q_1 : <10 mm yr⁻¹, then 10–18, 18–30, 30–50, 50–85, 85–140, 140–230, 230–380, 380–630, 630–1,050, 1,050–1,750 and q_{12} : >1,750 mm yr⁻¹) (ions in $\mu\text{eq L}^{-1}$, silica in $\mu\text{mol L}^{-1}$) (total sample, $n = 1,091$).

in wet tropical regions (other than areas of very low relief) due to the combined effect of high temperature, vegetation impact and, most of all, high runoff. The influence of the water balance can be studied easily; annual river runoff, which is generally documented, integrates entire river basins (Meybeck, 1994; White and Blum, 1997).

The set of PRISRI rivers has been subdivided into 12 classes of runoff for which the median elemental concentrations have been determined (Figure 3). The Q_{25} and Q_{75} quantiles and, to some extent the Q_{10} to Q_{90} quantiles follow the same patterns for all elements. On the basis of Na^+ , K^+ , Cl^- , and SO_4^{2-} two different clusters can be distinguished: (i) above 140 mm yr⁻¹ the influence of runoff is not significant, (ii) below 140 mm yr⁻¹ there is a gradual increase in elemental concentrations as runoff decreases. This pattern is interpreted as due to evaporation. For other elements there is a gradual increase of Ca^{2+} , Mg^{2+} , and HCO_3^- from the highest runoff to 85 mm yr⁻¹ or 50 mm yr⁻¹, then a stabilization of these concentrations at lower runoff values ($q < 50$ mm yr⁻¹). The second part of this pattern is most probably due to the precipitation of carbonate minerals as a result of evaporative concentration. The decrease in Ca^{2+} , Mg^{2+} , and HCO_3^- concentrations at very high runoff, while the silicate-weathering related Na^+ and K^+ are stable, could be due to a lower occurrence of carbonate rocks in wetter regions. This does not imply a climate control of these rock types so much as the dominance of the Amazon and Congo basins, which are underlain by silicate rocks, and volcanic islands in the population of high-runoff rivers. The silica pattern is even more complex: the increase in silica concentration with runoff from 140 mm yr⁻¹ to >1,750 mm yr⁻¹ could be

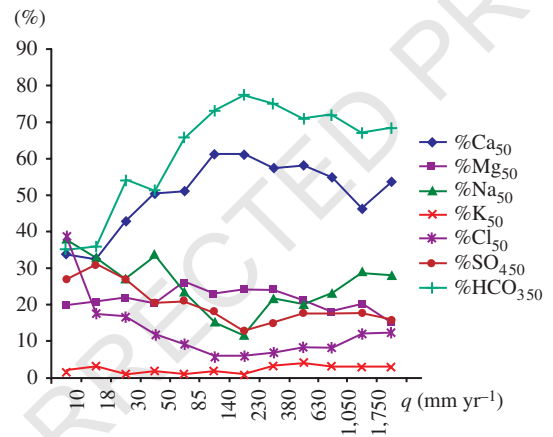


Figure 4 Median proportions (in percent of cations or anions sum) in 12 classes of river runoff (q_1 : <10 mm yr⁻¹, then 10–18, 18–30, 30–50, 50–85, 85–140, 140–230, 230–380, 380–630, 630–1,050, 1,050–1,750 and q_{12} : >1,750 mm yr⁻¹, sample $n = 1,091$).

linked with a greater occurrence of crystalline rocks, particularly of volcanic rocks, in wetter regions as in volcanic islands (Iceland, Japan, Indonesia) or coasts (Washington, Oregon), which are particularly abundant in the PRISRI database. These interactions between climate and lithology are possible but need to be verified. The lower silica value from 30 mm yr⁻¹ to 140 mm yr⁻¹ could also be attributed to the importance of the Canadian and Siberian rivers in these classes, where SiO_2 retention in lakes is important.

The relative median proportions of ions in the runoff classes of the PRISRI rivers confirm this pattern (Figure 4): below 140 mm yr⁻¹ the $\%\text{HCO}_3^-$ and $\%\text{Ca}^{2+}$ drop from 75% and 60%, respectively, to ~33%, while those of

Cl^- and SO_4^{2-} increase from 6% to 39% and from 13% to 27%, respectively: the proportion of K^+ does not vary significantly. There is a significant increase in the median proportions of Na^+ and Cl^- above $1,050 \text{ mm yr}^{-1}$ that could correspond with the increased marine influence in these categories. The median proportion of Mg^{2+} is the most stable of all ions: from 15% to 26%.

S0040 5.06.5 IDEALIZED MODEL OF RIVER CHEMISTRY

P0135 Gibbs (1970) defined three main categories of surface continental waters: rain dominated, with Na^+ and Cl^- as the major ions, weathering dominated with Ca^{2+} and HCO_3^- as the major ions, and evaporation/crystallization dominated, with Na^+ and Cl^- as the major ions. This typology can still be used, but it is too simplified. According to the PRISRI database there are many more types of water and controlling mechanisms, although the ones described by Gibbs may account for ~80% of the observed chemical types. The sum of cations (Σ^+), which is a good indicator of weathering, ranges from $50 \mu\text{eq L}^{-1}$ to $50,000 \mu\text{eq L}^{-1}$, and the corresponding types of water, characterized by the dominant ions may reach as many as a dozen (Table 3). The true rain dominance type is found near the edges of continents facing oceanic aerosol inputs, as in many small islands and in Western Europe: it is effectively of the $\text{Na}^+ - \text{Cl}^-$ type and Σ^+ may be as high as 1 meq L^{-1} , for example, the Cusson R. (Landes, France) draining arkosic sands (Table 3, F). In continental interiors, in some rain forests, this water type occurs with much lower ionic concentrations ($\Sigma^+ < 0.1 \text{ meq L}^{-1}$) in areas with highly weathered soils and very low mechanical erosion rates, such as the Central Amazon Basin (Rio Negro tributaries, Table 3F) or Cameroon: the very limited cationic inputs in rainfall are actively utilized and recycled by the forest and may even be stored (Likens *et al.*, 1977; Viers *et al.*, 1997). If the DOC level is high enough ($\sim 10 \text{ mg L}^{-1}$) the pH is often so low, that HCO_3^- is insignificant: the dominant anions are SO_4^{2-} and organic anions or Cl^- . This water chemistry is actually controlled by the terrestrial vegetation. The silica generated by chemical weathering is exported as dissolved SiO_2 and also as particulate biogenic SiO_2 from phytoliths or sponge spicules, as in the Rio Negro Basin and can have a variety of ionic assemblages.

P0140 Numerous water types reflect weathering control; these include $\text{Mg}^{2+} - \text{HCO}_3^-$, $\text{Ca}^{2+} - \text{HCO}_3^-$, $\text{Na}^+ - \text{HCO}_3^-$, $\text{Mg}^{2+} - \text{SO}_4^{2-}$, $\text{Ca}^{2+} - \text{SO}_4^{2-}$, $\text{Na}^+ - \text{SO}_4^{2-}$, $\text{Na}^+ - \text{Cl}^-$ types (Table 3). The evaporation–crystallization control found in semi-arid and

regions such as Central Asia (Alekin and Brazhnikova, 1964) also gives rise to multiple water types: $\text{Mg}^{2+} - \text{SO}_4^{2-}$, $\text{Ca}^{2+} - \text{SO}_4^{2-}$, $\text{Na}^+ - \text{SO}_4^{2-}$, $\text{Na}^+ - \text{Cl}^-$, $\text{Mg}^{2+} - \text{HCO}_3^-$, and even $\text{Mg}^{2+} - \text{Cl}^-$ (see Chapter 5.13). It is difficult to document the precipitation–redissolution processes (either during rare rain storms for occasional streams or in allochthonous rivers flowing from wetter headwaters such as the Saoura in Morocco, Table 3F), which are likely to have $\Sigma^+ > 6 \text{ meq L}^{-1}$ and/or run off below $140 - 85 \text{ mm yr}^{-1}$. In some Canadian and Siberian basins, very low runoff ($< 85 \text{ mm yr}^{-1}$) is not associated with very high evaporation but with very low precipitation: weathering processes still dominate.

In rift and/or volcanic regions and in recent mountain ranges such as the Caucasus, hydrothermal inputs may add significant quantities of dissolved material (Na^+ , K^+ , Cl^- , SO_4^{2-} , SiO_2) to surface waters. The Semliki River, outlet of Lake Edward, is particularly enriched in K^+ (Table 3, F); the Tokaanu River (New Zealand) drains a hydrothermal field with record values of silica, Na^+ and Cl^- (Table 3, F).

Overall, on the basis of ionic proportions and total concentrations, only 8.2% of the rivers (in number) in the PRISRI database can be described as evaporation controlled, 2.6% as rain dominated and vegetation controlled, and 89.2% as weathering dominated, including rivers affected by large water inputs.

A tentative reclassification of the major ionic types is presented on Figure 5 showing the occurrence of major ion sources for different

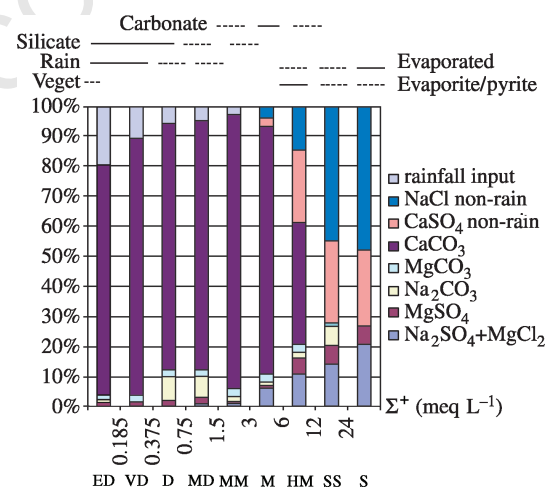


Figure 5 Idealized occurrence of water types (dominant ions and dominant control factors) per classes of increasing cationic content (Σ^+ in meq L^{-1}). ED: extremely dilute waters, VD: very dilute, D: dilute, MD: medium dilute, MM: medium mineralized, HM: highly mineralized, SS: subsaline, S: saline.

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classes of Σ^+ . The rainfall dominance types also include rivers with vegetation control and correspond to multiple ionic types ($\text{Ca}^{2+}-\text{SO}_4^{2-}$, Na^+-Cl^- , $\text{Ca}^{2+}-\text{Cl}^-$, $\text{Na}^+-\text{HCO}_3^-$). Other water types correspond to various rock weathering modes, including $\text{Mg}^{2+}-\text{HCO}_3^-$ waters observed in many volcanic regions. The most common type, $\text{Ca}^{2+}-\text{HCO}_3^-$, dominates from $\Sigma^+ < 0.185 \text{ meq L}^{-1}$ to 6 meq L^{-1} : in the most dilute waters it originates from silicate rock weathering, above 1.5 meq L^{-1} from weathering of carbonate minerals. This water type virtually disappears above 12 meq L^{-1} . “Non-rain” NaCl and CaSO_4 water types appear gradually above 6 meq L^{-1} . However, with these water types it is impossible to differentiate between evaporite rock dissolution, which can be observed even in the wet tropics (Stallard and Edmond, 1981) or in the Mackenzie (Salt R., Table 3F), from the leaching of salinized soils very common in Central Asia (Alekin and Brazhnikova, 1964). $\text{Mg}^{2+}-\text{SO}_4^{2-}$, $\text{Na}^+-\text{SO}_4^{2-}$, and $\text{Mg}^{2+}-\text{Cl}^-$ types are occasionally found in streams with Σ^+ values below 3 meq L^{-1} ; they are commonly the result of pyrite weathering that can lead to very high Σ^+ as in the Powder and Redwater Rivers (Table 3F).

5.06.6 DISTRIBUTION OF WEATHERING INTENSITIES AT THE GLOBAL SCALE

Present-day weathering intensities can theoretically be assessed by the export of dissolved material by rivers. Yet many assumptions and corrections have to be made: (i) human impacts (additional sources and sinks) should be negligible, (ii) atmospheric inputs should be subtracted, (iii) products of chemical weathering should not be carried as particulates (e.g., phytoliths), nor (iv) accumulated within river basins in lakes or soils. In addition, it must be remembered that 100% of the HCO_3^- may originate from the atmosphere in noncarbonate river basins (calcite is only found in trace amounts in granites) and ~50% in carbonate terrains (see Chapter 5.11). In basins of mixed lithologies the proportions range between 50% and 100%. The total cation export or yield Y^+ (which excludes silica) is used to express the weathering intensity. Y^+ , expressed in $\text{eq m}^{-2} \text{ yr}^{-1}$, the product of annual runoff (m yr^{-1}) and Σ^+ (meq L^{-1}), is extremely variable at the Earth’s surface since it combines both runoff variability and river chemistry variability (Table 5).

The concentration of elements that are derived from rock weathering (Ca^{2+} , Mg^{2+} , Na^+ , K^+), are less variable than runoff even in the driest conditions. The opposite is observed for Cl^- and SO_4^{2-} , which are characterized by very low Q_1 quantiles. The retention of silica, particularly under the driest conditions, makes its yield the most variable. The lowest yearly average runoff in this data set (3.1 mm yr^{-1} for Q_1) actually corresponds to the conventional limit for occasional river flow (3 mm yr^{-1}). Under such extremely arid conditions, flow may occur only few times per hundred years, as for some tributaries of Lake Eyre in Central Australia. The other runoff quantile Q_{99} corresponds to the wettest regions of the planet bordering the coastal zone.

Since the variability of runoff, represented by the percentile ratio Q_{99}/Q_1 , is generally much greater than the variability of concentration (Tables 1 and 5), ionic yields primarily depend on runoff. With a given rock type, there is a strong correlation between yield and runoff, that corresponds to clusters of similar concentrations as for Ca^{2+} and silica (Figure 6). This influence

P0160 The global proportions of the different water types depend on the global representativeness of the database. The exact occurrence of water types can only be estimated indirectly through modelling on the basis of lithologic maps, water balance, and oceanic fallout. Moreover, it will depend on spatial resolution: a very fine scale gives more importance to the smallest, rain-dominated coastal basins. In PRISRI, 70% of the basins have areas exceeding $3,200 \text{ km}^2$, thus limiting the appearance of oceanic influence.

P0165 A river salinity scale based on Σ^+ is also proposed (Figure 5). The least mineralized waters ($\Sigma^+ < 0.185 \text{ meq L}^{-1}$), termed here “extremely dilute” correspond to a concentration of total dissolved solids of $\sim 10 \text{ mg L}^{-1}$ in NaCl equivalent. The most mineralized waters ($\Sigma^+ > 24 \text{ meq L}^{-1}$) are here termed “saline” up to 1.4 g L^{-1} NaCl equivalent, a value slightly less than the conventional limit of 3 g L^{-1} NaCl adopted for “saline” lakes.

T0025 **Table 5** Global distribution of ionic ($\text{eq m}^{-2} \text{ yr}^{-1}$) and silica ($\text{mol m}^{-2} \text{ yr}^{-1}$) yields and annual runoff (q in mm yr^{-1}) in medium-sized basins ($3,200-200,000 \text{ km}^2$, $n = 685$).

Y_i	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	SO_4^{2-}	HCO_3^-	Σ^+	SiO_2	q
Q_{99}	2.77	0.95	1.3	0.115	1.05	1.25	2.82	3.0	0.82	3,040
Q_1	0.0045	0.002	0.002	0.0002	0.0003	0.0004	0.0046	0.0005	0.0001	3.1
Q_{99}/Q_1	615	475	650	575	3500	3100	613	600	8200	980

Q_1 and Q_{99} : lowest and highest percentiles.

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was used by Meybeck (1994), Bluth and Kump (1994), and Ludwig *et al.* (1998) to model ionic yields and inputs of carbon species to the ocean. If all PRISRI basins are considered, this runoff control on chemical yields is still observed, although the relationship is complex. The data set is subdivided into 12 classes of runoff from $q < 10 \text{ mm yr}^{-1}$ to $q > 1,750 \text{ mm yr}^{-1}$ (see Figure 3), for which the median yields of major ions and silica have been determined (Figure 7). In this log-log diagram, domains of equal concentration are parallel to the diagonal (1:1) line. Several types of evolution can be observed:

- (i) sulfate and chloride yields are fairly constant below 140 mm yr^{-1} , suggesting that lower runoff is compensated by a concentration increase through evaporation (except for SO_4^{2-} below 10 mm yr^{-1});
- (ii) above 140 mm yr^{-1} all ion and silica yields are primarily linked to runoff;

(iii) above 140 mm yr^{-1} the median concentrations of Ca^{2+} , Mg^{2+} , and HCO_3^- decrease gradually, whereas silica and potassium concentrations increase gradually, suggesting a greater influence of silicate weathering relative to carbonate weathering;

(iv) below 140 mm yr^{-1} median Ca^{2+} and Mg^{2+} concentrations are constant and median HCO_3^- concentration decreases slightly, which suggest a regulation mechanism through precipitation of carbonate minerals in semi-arid and arid regions;

(v) potassium yield is stable between 30 mm yr^{-1} and 140 mm yr^{-1} ; below 30 mm yr^{-1} it decreases, suggesting retention; and

(vi) median silica yield is the most complex: there is certainly a retention in the arid regions. These observed trends need to be confirmed particularly below 30 mm runoff, where there

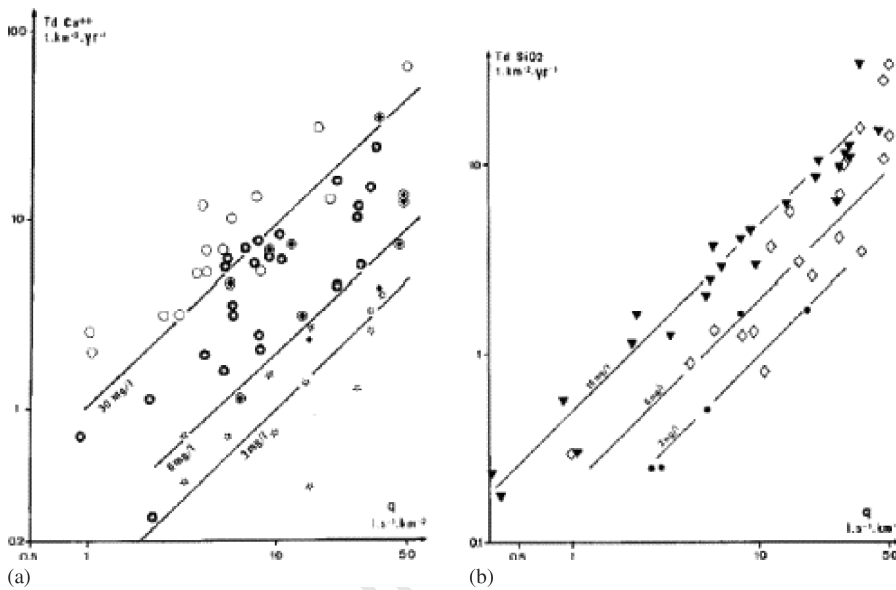


Figure 6 Relationship between calcium yield (a) and silica yield (b) for world rivers with three types of rock dominance: shield and plutonic, volcanic, and carbonate-sedimentary (source Meybeck, 1994). [Q17]

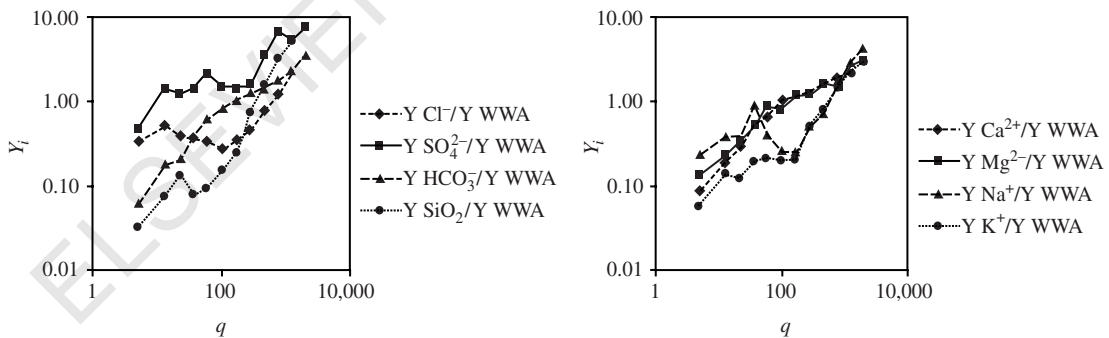


Figure 7 Median yields of ions and silica (Y_i in $\text{meq m}^{-2} \text{ yr}^{-1}$) for 12 classes of river runoff ($n = 1,091$, all basins). Yields = $C_{150} \times q_{50}$ in each class.

are fewer silica analyses in the PRISRI base than analyses of major ions.

representative at the global scale. The extremely dilute waters correspond in PRISRI to ~3% of the land area, but they are areas of very high runoff, therefore, their weight in terms of water volume is ~7.5%. However, their influence on the global ionic fluxes is very low, less than 1%. At the other end of the salinity scale the subsaline and saline waters, mostly found in semi-arid and arid areas, correspond to ~5% of the PRISRI data set; they contribute much less than 1% of runoff but ~7% of the ionic fluxes.

5.06.7 GLOBAL BUDGET OF RIVERINE FLUXES

The unglaciated land surface of the present Earth amounts to ~133 Mkm². Excluding land below a 3 mm yr⁻¹ runoff threshold (at a 0.5° resolution), ~50 Mkm² can be considered as nonexposed to surface water weathering (arheic, where $q < 3 \text{ mm yr}^{-1}$), whether draining to the ocean (exorheic) or draining internally such as the Caspian Sea basin (endorheic) (Table 6). The land area effectively exposed to weathering by meteoric water is estimated to be ~82.8 Mkm² (rheic regions); this, in turn, has to be divided into exorheic regions (76.1 Mkm²) and endorheic regions (6.7 Mkm²). Since the weathering intensity in the rheic regions is highly variable (see above), three main groupings have been made on the basis of weathering intensity or runoff: the least active or oligorheic regions (36.4 Mkm²), the regions of medium activity or mesorheic (42.3 Mkm²), and the most active or hyperrheic regions (4.1 Mkm²). The corresponding ionic fluxes can be computed on the basis of the PRISRI database. The hyperrheic regions, which are exclusively found in land that drains externally, represent 37% of all DIC fluxes for only 2.75% of the land area; the mesorheic regions (28.3% of land area) contribute 55% of the DIC fluxes, and the oligorheic regions (24.4% of land area) contribute only 8% of these fluxes (Table 6). If a finer spatial distribution of these fluxes is extracted from the PRISRI data, 1% of the land surface (carbonate rocks in very wet regions) contributes 10% of the river DIC fluxes. Similar figures are found for all other ions.

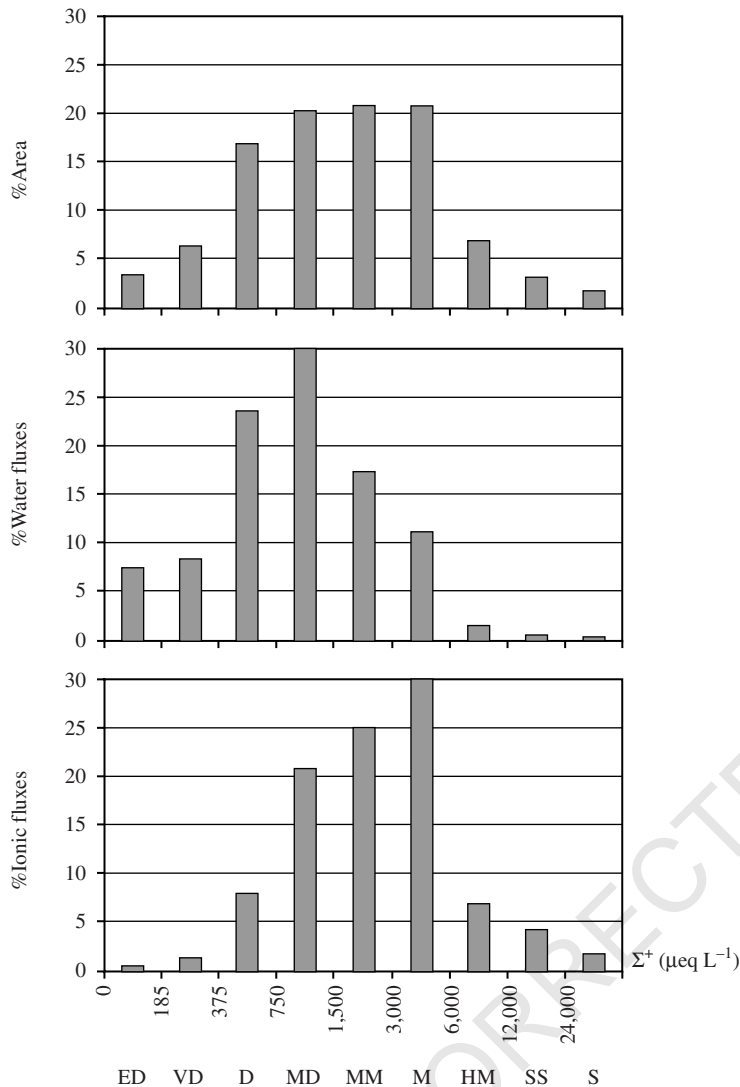
Although we have drawn attention to the extreme variability of ionic and silica concentrations, ionic proportions, ionic ratios, ionic and silica yields throughout this chapter, two sets of global averages are proposed here (Table 7). The world spatial median values (WSM) of the medium-sized PRISRI data set (3,200–200,000 km² endorheic and exorheic basins) correspond to the river water chemistry most commonly found on continents at this resolution. The world weighted average (WWA) has been computed by summing the individual ionic fluxes of the largest 680 basins, including endorheic basins (Aral, Caspian, Titicaca, Great Basin, Chad basins), in the PRISRI set. The runoff values in both averages are different, although very close considering the global range. The WSM lists higher concentrations than the WWA because the dry and very dry regions are more common in the database than the very humid regions. Ionic ratios are more similar between the two averages. The composition of river inputs to the oceans is not stable: (i) it has varied since the Late Glacial Maximum and during the geological past (Kump and Arthur, 1997); (ii) present-day river chemistry is much altered by human activities. Four estimates of average exorheic rivers are presented in Table 7: considering the natural variations of river chemistry, these averages are relatively close to each other and to WWA and WSM, the differences are due to the nature of the data sets and to the inclusion or exclusion of presently altered rivers. A re-estimation of the pristine inputs (under

These budgets can also be broken down into classes on the basis of ionic contents (Figure 8), assuming the PRISRI database to be fully

Table 6 Distribution of global land area (Mkm²) exposed to chemical weathering and to river transfer of soluble material. A: percent of land area (nonglaciated area also contains alpine glaciers). B: percent of weathering generated fluxes (e.g., DIC flux). C: percent of river fluxes to oceans.

		A % land area	B % weath. flux	C % flux to ocean
Total land 149 Mkm ²	Glaciated 16 Mkm ²	10.7	0.1 ?	0.1 ?
	Nonglaciated 133 Mkm ²			
	Arheic 50.2 Mkm ²	Endorheic ^a	0	0
		Exorheic ^a		
	Rheic 82.8 Mkm ²	Oligorheic { Endorheic	3.4	1
		{ Exorheic	21	7
		Mesorheic { Endorheic	1.1	2
	Hyperrheic	{ Exorheic	27.3	53
		Exorheic	2.75	37

^a Potentially.



F0040 **Figure 8** Distribution of global river attributes from the PRISRI database for classes of increasing total cations (Σ^+) based on PRISRI rivers (rheic regions). ED: extremely dilute waters, VD: very dilute, D: dilute, MD: medium dilute, MM: medium mineralized, HM: highly mineralized, SS: subsaline, S: saline.

present-day climatic conditions) should now be done with the new data, although human impacts are difficult to quantify.

S0055 5.06.8 HUMAN ALTERATION OF RIVER CHEMISTRY

P0230 River chemistry is very sensitive to alteration by many human activities, particularly mining and the chemical industries, but also to urbanization as urban wastewaters are much more concentrated than rural streams, and to agriculture through the use of fertilizers (Table 2) (Meybeck *et al.*, 1989; Flintrop *et al.*, 1996). New sinks are also created such as reservoirs (calcite and silica trapping; enhanced evaporation) and irrigated soils,

which may retain soluble elements if they are poorly drained. New controls correspond to these anthropogenic influences, such as mining and industrial production, rate of urbanization and population density, fertilization rate, irrigation rate and practices, and construction and operation of reservoirs. Wastewater treatment and/or recycling can be effective as a control on major ions originating from mines (petroleum and gas exploitation, coal and lignite, pyritic ores, potash and salt mines) and industries, yet their effects are seldom established. Urban wastewater treatment does not generally affect the major ions. Human impacts on silica are still poorly studied apart from retention in reservoirs. At the pH values common in surface waters, silica concentration is limited and

Table 7 WWA ionic concentrations (C_i^* in $\mu\text{eq L}^{-1}$, and $\mu\text{mol L}^{-1}$ for silica) and yields (Y_d^* in $\text{g m}^{-2} \text{yr}^{-1}$, Y_i^* in $\text{meq m}^{-2} \text{yr}^{-1}$, and $\text{mmol m}^{-2} \text{yr}^{-1}$ for silica), ionic ratios (C_i/C_j^* in eq eq^{-1}) and relative ionic proportion ($\%C_i^*$). Same variables for the WSM determined for mesobasins ($3,000\text{--}200,000 \text{ km}^2$) $\text{Na}^\# = \text{Na-Cl}$; q = global average runoff (mm yr^{-1}).

	SiO_2	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	SO_4^{2-}	HCO_3^-	Σ^+	Σ^-	q	
<i>World river inputs to oceans</i>												
Clarke (1924) C_i	161	843	231	208	45	132	208	969	1,327	1,309	(320)	
Livingstone (1963) C_i	217	748	337	274	59	220	233	958	1,418	1,411	314	
Meybeck (1979) pristine C_i	174	669	276	224	33	162	172	853	1,202	1,187	374	
1970 C_i	174	733	300	313	36	233	239	869	1,382	1,341	374	
<i>World weighted average (endorheic + exorheic)</i>											340	
C_i^*	145	594	245	240	44	167	175	798	1,125	1,139		
Y_d^*	2.98	4.04	1.01	1.88	0.60	2.0	2.87	16.54				
Y_i^*		202	83.3	81.8	15.3	56.8	59.7	271.3	382	388		
$\%C_i^*$		52.2	21.5	23	3.3	14.7	15.4	69.9	100	100		
<i>World spatial median (endorheic + exorheic)</i>											222	
C_{i50}	134	1000	375	148	25.5	96	219	1256	1,548	1,571		
Y_{d50}	1.82	3.78	0.91	1.31	0.29	0.95	2.66	13.3				
Y_{i50}		188	75	57	7.4	22	55	278	327	300		
$\%C_{i50}$		64.6	24.1	9.6	1.7	6.1	13.9	80				
	$\frac{\text{Ca}^{2+}}{\text{Mg}^{2+}}$	$\frac{\text{Ca}^{2+}}{\text{Na}^+}$	$\frac{\text{Na}^+}{\text{K}^+}$	$\frac{\text{Na}^+}{\text{Cl}^-}$	$\frac{\text{Ca}^{2+}}{\text{SO}_4^{2-}}$	$\frac{\text{Mg}^{2+}}{\text{Na}^+}$	$\frac{\text{Cl}^-}{\text{SO}_4^{2-}}$	$\frac{\text{SO}_4^{2-}}{\text{HCO}_3^-}$	$\frac{\text{Na}^\#}{\text{K}^+}$	$\frac{\text{Ca}^{2+}}{\text{Na}^\#}$	$\frac{\text{Mg}^{2+}}{\text{Na}^\#}$	$\frac{\text{SiO}_2}{\Sigma^+}$
WWA ($C_i C_j$) [*]	2.42	2.47	5.5	1.43	3.39	1.02	0.95	0.22	1.65	8.1	3.35	0.13
WSM ($C_i C_j$) ₅₀	2.32	2.54	6.55	2.27	2.97	1.14	0.48	0.26	3.0	4.3	1.9	0.12

evidence of marked excess silica in rivers due to urban or industrial wastes has not been observed by this author. The gradual alteration of river chemistry was noted very early, for example, for SO_4^{2-} (Bernier, 1971) and Cl^- (Weiler and Chawla, 1968) in the Mississippi and the Saint Lawrence systems. Regular surveys made since the 1960's and comparisons with river water analyses performed a hundred years ago reveal a worldwide increase in Na^+ , Cl^- , and SO_4^{2-} concentrations, whereas Ca^{2+} , Mg^{2+} , and HCO_3^- concentrations are more stable (Meybeck *et al.*, 1989; Kimstach *et al.*, 1998). Some rivers affected by mining (Rhine, Weser, Vistula, Don) may be much more altered than rivers affected by urbanization and industrialization only (Mississippi, Volga, Seine) (Figure 9). When river water is diverted and used for irrigation, there is a gradual increase of ionic content, particularly Na^+ , K^+ , Cl^- , and SO_4^{2-} as for the Colorado, Murray, Amu Darya (Figure 9). Salinization may also result from agriculture as for the Neman River (Figure 9). Salinization is discussed in detail by Vengosh (see Chapter 9.09)

It is difficult to assess the different anthropogenic sources of major ions which depend on the factors mentioned above. These human factors also vary in time for a given society and reflect the

different environmental concerns of these societies, resulting in multiple types of river-society relationships (Meybeck, 2002). In the developed regions of the northern temperate zone it is now difficult to find a medium-sized basin that is not significantly impacted by human activities. In industrialized countries, each person generates dissolved salt loadings that eventually reach river systems (Table 8).

These anthropogenic loads are higher for Na^+ , Cl^- , and SO_4^{2-} relative to natural loads. This partially explains the higher sensitivity of river chemistry to human development. At a certain population density in impacted river basins the anthropogenic loads equal (Na^+ , K^+ , Cl^- , SO_4^{2-}) or greatly exceed the natural ones (NO_3^- , PO_4^{2-}), defining a new era, the Anthropocene (Meybeck, 2002) when humans control geochemical cycles.

The silica trend in world rivers has recently attracted attention: dissolved silica is decreasing in impounded and/or eutrophied rivers, at the same time as nitrate is increasing in agricultural basins. As a result the Si : N ratio, which was generally well above 10 a hundred years ago, has dropped below 1.0 g g^{-1} in rivers such as the Mississippi, resulting in a major shift in the coastal algal assemblages (Rabalais and Turner, 2001), leading to dystrophic coastal areas. This trend, which is also observed for other river

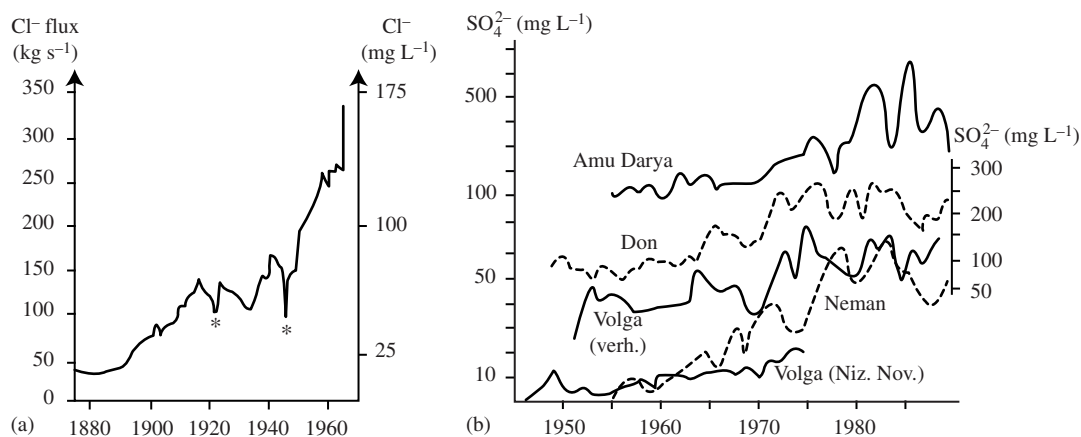
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F0045 **Figure 9** (a): Chloride evolution (fluxes, concentrations) in the Rhine River at mouth from 1,875 to 1,970 (ICPR). (b) Sulfate evolution in selected rivers of the former USSR, Volga at Nizhny Novgorod and Verhnelebyazhye, Don at Aksai, Neman at Sovetsk, Amu Darya at Kzyl Djar (Tsikurnov in Kimstach *et al.*, 1998). * reduced mining activity in the Rhine Basin due to crisis and conflicts.

T0040 **Table 8** Excess loads of major elements normalized to basin population in industrialized regions (kg cap⁻¹ yr⁻¹).

	SiO ₂	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	Period
<i>Per capita loads in residential urban sewage (kg cap⁻¹ yr⁻¹)</i>									
Montreal	ND	3.2	0.65	6.6	1.0	8.2	13.5	24	1970s
US sewer	2.4	3	1.5	14	2	15	6	20	1960s
Brussels	1.2	2.6	ND	9.5	1.6	8.4	5.8	14.7	1980s
Paris	0.2	1.2	0.7	6.4	1.5	6.3	11.0	14.5	1990s
<i>Evolution of rivers^a (kg cap⁻¹ yr⁻¹)</i>									
	ND	51	17	85	6	100	136	ND	1900–1970
<i>Estimated anthropogenic input to ocean (10⁶ t w⁻¹)</i>									
	ND	47	10.5	78	5	93	124	100	1970

Sources: Meybeck (1979) and Meybeck *et al.* (1998).

^aMississippi, St. Lawrence, Seine, Rhine, Odra, Wisla.

systems (Seine, Danube), could expand in the next decades due to increased fertilizer use and to increased reservoir construction.

S0060 5.06.9 CONCLUSIONS

P0250 Riverine chemistry is naturally highly variable at the global scale, which confirms the observation made by (the former) Soviet geochemists on a 20 Mkm² subset of land area (Alekin and Brazhnikova, 1964) and the conclusions of Clarke (1924) and Livingstone (1963). Ionic concentrations and yields (weathering rates) commonly vary over two to three orders of magnitude: only a fraction of the surface of the continents is actively exposed to weathering by meteoric water. The related river water types are multiple. There are at least a dozen types depending on surficial rock exposed to weathering, the water balance, and atmospheric inputs. Gibbs' (1970) global scheme

for water chemistry holds for ~80% of river waters but is oversimplified for the remaining 20%. In very dilute waters (cation sum < 0.185 μeq L⁻¹) water chemistry is probably controlled by vegetation. In these areas water chemistry is likely to be very sensitive to climate change and to forest cutting, although the related ionic fluxes are small. Each major ion and silica should be considered individually, since its sources, sinks and controls, both natural and anthropogenic, are different.

In the northern temperate regions of the world from North America to East Asia, the human impacts should be carefully filtered from the natural influence: the study of pristine river geochemistry will be more and more limited to the subarctic regions, to some remaining undeveloped tropical regions, and to small temperate areas of the southern hemisphere such as South Chile and New Zealand. There is a global-scale increase of riverine Na⁺, K⁺, Cl⁻, and SO₄²⁻. HCO₃⁻ is still

very stable. Impacts of riverine changes on the Earth System (Li, 1981) should be further addressed.

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