

## 5.06

## Global Occurrence of Major Elements in Rivers

M. Meybeck

*University of Paris VI, CNRS, Paris, France*

5.06.1	INTRODUCTION	000
5.06.2	SOURCES OF DATA	000
5.06.3	GLOBAL RANGE OF PRISTINE RIVER CHEMISTRY	000
5.06.4	SOURCES, SINKS, AND CONTROLS OF RIVER-DISSOLVED MATERIAL	000
5.06.4.1	<i>Influence of Lithology on River Chemistry</i>	000
5.06.4.2	<i>Carbon Species Carried by Rivers</i>	000
5.06.4.3	<i>Influence of Climate on River Chemistry</i>	000
5.06.5	IDEALIZED MODEL OF RIVER CHEMISTRY	000
5.06.6	DISTRIBUTION OF WEATHERING INTENSITIES AT THE GLOBAL SCALE	000
5.06.7	GLOBAL BUDGET OF RIVERINE FLUXES	000
5.06.8	HUMAN ALTERATION OF RIVER CHEMISTRY	000
5.06.9	CONCLUSIONS	000
	REFERENCES	000

## S0005 5.06.1 INTRODUCTION

P0005 Major dissolved ions ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$ ) and dissolved silica ( $\text{SiO}_2$ ) 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  $\text{mg L}^{-1}$ ; they are also reported in  $\text{meq L}^{-1}$  or  $\mu\text{eq L}^{-1}$ , which permits a check of the ionic balance of an analysis: the sum of cations ( $\Sigma^+$  in  $\text{eq L}^{-1}$ ) should equal the sum of anions ( $\Sigma^-$  in  $\text{eq L}^{-1}$ ). Dissolved silica is generally not ionized at pH values commonly found in rivers; its concentration is usually expressed in  $\text{mg L}^{-1}$  or in  $\mu\text{mol L}^{-1}$ . Ionic contents can also be expressed as percent of  $\Sigma^+$  or  $\Sigma^-$  ( $\%C_i$ ), which simplifies the determination of ionic types. Ionic ratios ( $C_i/C_j$ ) in  $\text{eq eq}^{-1}$  are also often tabulated ( $\text{Na}^+/\text{Cl}^-$ ,  $\text{Ca}^{2+}/\text{Mg}^{2+}$ ,  $\text{Cl}^-/\text{SO}_4^{2-}$ , 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  $\text{meq L}^{-1}$ )). The export rate of ions and silica, or the yield ( $Y_{\text{Ca}^{2+}}$ ,  $Y_{\text{SiO}_2}$ ) 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  $\text{eq m}^{-2} \text{yr}^{-1}$ .

P0010

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  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$ ; 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  $10^4 \text{ km}^2$ . 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 ( $\Sigma^+$ ) of PRISRI rivers have been split into classes based on annual runoff ( $q$  in  $\text{mm yr}^{-1}$ ) and  $\Sigma^+$  ( $\text{meq L}^{-1}$ ). 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  $\text{Na}^+/\text{K}^+$  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).