

Gibbs (1970) used the concentrations of ions in major world rivers to suggest the origins of their dissolved constituents and their waters. Rivers dominated by precipitation show low concentrations of dissolved substances, and a high ratio of Cl to the total of  $\text{Cl} + \text{HCO}_3$ , reflecting the importance of Cl from rainfall (Zone A in Fig. 8.7). Rivers in which the

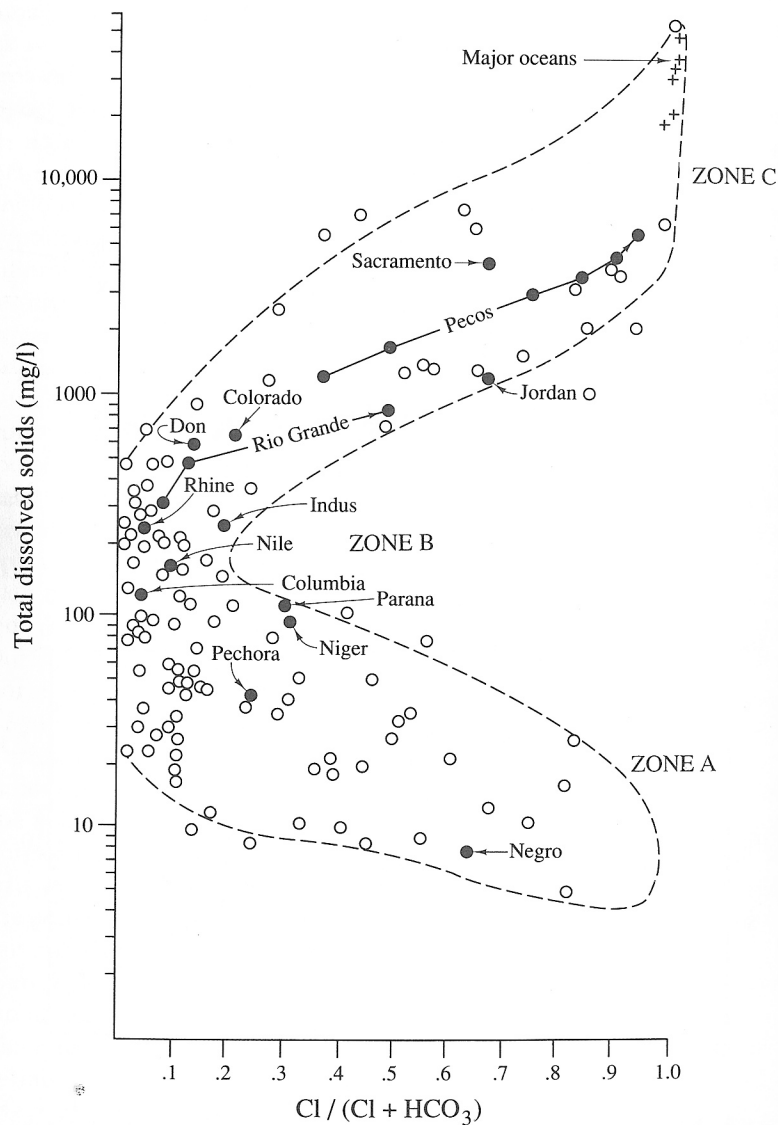


Figure 8.7 Variation in the total dissolved solids in rivers and lakes as a function of the ratio  $\text{Cl}/(\text{Cl} + \text{HCO}_3)$  in their waters. From Gibbs (1970).

dissolved load is largely derived from chemical weathering show higher concentrations of dissolved substances, and  $\text{HCO}_3$  is the dominant anion (Zone B), reflecting the importance of carbonation weathering in most soils (Chapter 4). Rivers that pass through arid regions lose a significant amount of water to evaporation before reaching the ocean. These rivers (Zone C) show the greatest concentrations of dissolved ions and high ratios of  $\text{Cl}/(\text{Cl} + \text{HCO}_3)$ , because  $\text{HCO}_3$  has been removed by the chemical precipitation of minerals such as  $\text{CaCO}_3$  on the streambed (Holland 1978). In this scheme, seawater represents the endpoint of the evaporative concentration of river waters. These relationships are also seen when Na and Ca are used to scale the X axis, with the relative concentration of Na as an index of rainfall and Ca as an index of chemical weathering.

The composition of "average" riverwater was calculated by Livingstone (1963) from measurements on a large number of rivers (Table 8.5). His estimate of total dissolved transport,  $37.6 \times 10^{14}$  g/yr, is confirmed by more recent work (e.g., see also Tables 4.7 and 9.1). Not all dissolved substances in rivers are derived from rock weathering. A significant fraction of the Na, Cl, and  $\text{SO}_4$  in riverflow is derived from marine aerosols ("cyclic salts," Chapter 3) that are deposited on land,<sup>1</sup> and humans have enhanced the atmospheric deposition of  $\text{NO}_3$  and  $\text{SO}_4$ , accounting for the relatively high concentrations of these ions in the runoff from industrialized continents (Table 8.5). Reflecting the importance of carbonation weathering (Chapter 4), about  $\frac{2}{3}$  of the  $\text{HCO}_3$  in rivers is derived from the atmosphere, either directly from  $\text{CO}_2$  or indirectly via organic decomposition and root respiration that contribute  $\text{CO}_2$  to the soil profile (Holland 1978, Meybeck 1987).

Nearly all the Ca, Mg, and K in river water is derived from rock weathering (Table 8.6). Weathering of carbonates is the dominant source for Ca, while silicates are the dominant source for Mg and K (Holland 1978). At least some Na is also derived from weathering, since its content in river water is in excess of the molar equivalent of Cl, which would be expected if seasalt were the sole source. The composition of individual streams may differ strongly from these averages depending upon local conditions. For instance, streams draining areas of carbonate terrain are dominated by Ca and  $\text{HCO}_3$  (e.g., Laudelout and Robert 1994), and streamwaters may contain high concentrations of Na, Cl, and  $\text{SO}_4$  where evaporite minerals are exposed (e.g., Stallard and Edmond 1983). The river transport of some dissolved ions is also enhanced by human activities, such as mining, which

<sup>1</sup> The amount of Cl in rivers that is derived from the atmosphere is the subject of some controversy (Berner and Berner 1987). Some budgets (e.g., Table 8.6) suggest that a relatively small amount of Cl is "cyclic," based on the observations by Stallard and Edmond (1981, 1983) in the Amazon basin. Other workers have assumed that a larger fraction of the Cl in global riverflow is derived from the sea, with values ranging from 85% (Dobrovolsky 1994, p. 83) to nearly 100% (Möller 1990).