Water-Quality Principles
QW1022–TEL

Lesson 5, Part 2: Field-Measured Properties and Major Ions: Major Ions and Their Cycles

Source: Berner, E.K., and Berner, R.A., 1966, Global environment: Water, air, and geochemical cycles: North Haven, Conn., Prentice-Hall, Inc., p. 215–218. Electronically reproduced with permission of the authors.

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pollution from fertilizer sulfur (7%). In the central European Elbe River Basin, Paces (1985) studied an acidic river (pH 4.9) draining a forested mountain basin where part of the conifer forest has died and which faces an industrial area. The mountain basin receives acid rain (pH 4.2), but more important, because the air concentration of SO_2 is very high, about 10 times as much acid comes from SO_2 dry deposition as from the rain. Thus, the combined effects of dry deposition and acid rain would be equal to a pH 3.2 rain. The river has very high sulfate concentrations and high Ca and silica in addition to being acidic.

In coal-mining areas, natural pyrite weathering is greatly accelerated by the exposure of relatively large amounts of pyrite contained in the coal and by increased water circulation due to mining. If the groundwater circulating through the pyrite-rich coal beds does not contain sufficient HCO_3^- (from previous carbonate weathering) to neutralize the sulfuric acid being produced, extremely acid water (pH < 3) results, which can seep into nearby streams. This acid production via pyrite oxidation is greatly accelerated by bacteria (e.g., Kleinmann and Crerar 1979). Moshannon Creek (see Table 5.14), a tributary of the West Branch of the Susquehanna River in a coal-mining area of Pennsylvania, is an example of a mine-drainage river with a very high sulfate concentration (300 ppm) and low pH (2.9) (Lewis 1976). Further evidence of river sulfate pollution from coal mining is shown by increases in SO_4^{2-} from 1974 to 1981 in a number of midwestern U.S. rivers which were associated with increased surface coal production via strip mining (Smith et al. 1987).

Natural weathering of pyrite-rich black shales can produce high sulfate concentrations and quite acid streamwater because the pyrite is oxidized to sulfuric acid (see Chapter 4). An extreme example is the Ichilo River in the Madeira River drainage of the Amazon Basin (Stallard 1980) (see Table 5.14 and Figure 5.5), which has a very high sulfate concentration (on a mole basis, more than double the Ca concentration), and a pH of 5.28.

Organic Matter (Organic Carbon)

Organic matter is present in rivers in both dissolved and particulate forms. The concentration of dissolved organic matter in rivers is usually expressed in terms of dissolved organic carbon (DOC). The average amount of dissolved organic carbon in rivers is about 5.3 mg C/l, equivalent to a global transport flux of 200 Tg DOC/yr (Meybeck 1993), but there is considerable variation depending on climatic conditions (Meybeck 1988). High median concentrations of DOC are found in taiga (subarctic) rivers, which average 7 mg/l DOC, and in humid tropical rivers, which have about 8 mg/l DOC. Low concentrations are found in arctic and alpine rivers (2 mg/l DOC). Rivers draining swampy areas (such as the Satilla River in Georgia, which we shall discuss below) have the highest concentrations (~25 mg/l DOC). Most rivers show a flushing effect, with DOC concentrations increasing with increasing discharge, and showing a dominant soil and plant organic matter source of the DOC (Spitzy and Leenheer 1991).

In addition to dissolved organic carbon, there is also considerable transport of organic matter in the form of particulate organic carbon (POC) associated with the suspended load. Meybeck (1993) estimates the POC river load at 172 Tg/yr, while Ittekot (1988) estimates 231 Tg POC/yr. As the river suspended sediment load increases, the POC content decreases as a percentage of the total sediment solids (Meybeck 1982, 1988). This is due to dilution by increased erosion of rock and less biological activity in turbid water. On average, about 1% of the suspended sediment load is POC. Meybeck (1993) divides his total river load of POC into 55% young eroded soil POC and 45% fossil rock POC. Of the river POC, Ittekhot (1988) estimates

that only 35% is labile, or degradable, and likely to be metabolized in rivers, estuaries, or the ocean, with the rest being highly degraded and nonreactive. Degens et al. (1991) estimate the global river flux of total organic carbon or TOC (= DOC + POC) (excluding Australia) as 330 $\times 10^6$ t/yr, similar to Meybeck's (1993) estimate of a natural load of 370 Tg TOC/yr (198 Tg DOC + 172 Tg POC). Meybeck estimates an additional pollutional flux of 100 Tg TOC/yr.

Because the average ratio of dissolved organic carbon to total (inorganic) dissolved solids in rivers is low (DOC:TDS = 1:19), chemical associations between organic matter and major inorganic ions do not have a large relative effect on the overall chemistry of most rivers. (By contrast, the behavior of trace metal ions is strongly affected.) However, in rivers with low total dissolved solids and large DOC concentrations, organic matter can dominate the river chemistry (see Table 5.14). An example is the Coastal Plain rivers of southeastern Georgia, particularly the Satilla River, which drains a swampy area, has a low pH (4.3), and a ratio of dissolved organic carbon (24 mg/l) to total dissolved (inorganic) solids (20 mg/l) of roughly 1:1 (Beck et al. 1974). It is not the absolute amount of dissolved organic carbon in the Satilla (which, however, is very high) that is so important, but rather its very high ratio to dissolved inorganic solids.

The dissolved organic matter which dominates the chemistry of organic-rich rivers such as the Satilla consists mainly of a mixture of humic and fulvic acids. Both substances are mixtures of complex (and poorly understood) high-molecular-weight organic polymers, which contain carboxyl groups and phenolic groups. (Humic acids are defined as being insoluble in strong acid, while fulvic acids are acid soluble.) The low pH of the Satilla River (3.8–5.0) results from the dissociation of the humic and fulvic acidic carboxyl groups (—COOH). The organic acids (R—COOH) lose a hydrogen ion and become $(R—COO)^-$ with a net negative charge:

$$\underset{\text{organic acid}}{(R—COOH)} \rightarrow \underset{\text{organic anion}}{(R—COO)^-} + H^+$$

The river has little or no bicarbonate (HCO_3^-), because any bicarbonate is used up in neutralizing the H^+ from the organic acid dissociation:

$$HCO_3^- + H^+ \rightarrow H_2O + CO_2$$

Thus, the overall reaction of HCO_3^- with organic acids is

$$(R—COOH) + HCO_3^- \rightarrow (R—COO)^- + H_2O + CO_2$$

As more HCO_3^- ions are added by carbonate-draining tributaries downstream, the hydrogen ions produced by organic acid dissociation are neutralized and the river pH goes up, producing large concentrations of organic anions.

This leads to the other major characteristic of rivers such as the Satilla: The sum of the charge on the major inorganic cations (equivalents per liter of Na^+, Mg^{2+}, K^+, Ca^{2+}, H^+) is greater than the sum of the charge on the major inorganic anions (equivalents of Cl^-, SO_4^{2-}, HCO_3^-, NO_3^-), leading to an apparent deficiency of inorganic anion charge. However, since there must be electrical balance in the river, the excess inorganic cation charge is balanced by organic anions, which result, as discussed above, from the dissociation of organic acid carboxyl groups. Thus, the overall charge balance in an organic-dominated river is

$$\sum \text{inorg. cations} = \sum \text{inorg. anions} + \sum \text{org. anions}$$

Another characteristic of organic-rich rivers is their large concentration of "dissolved" iron and aluminum relative to other rivers. Fe and Al form dissolved organic complexes or colloidal oxyhydroxides mixed with organic matter, and this leads to the mobilization and transport of Fe and Al, which are otherwise immobile and insoluble.

The major characteristics of the organic-dominated Satilla River (Beck et al. 1974), which might be used as criteria in identifying other rivers whose chemistry is dominated by organic matter, are as follows: (1) The ratio of the concentrations of dissolved organic matter (DOC) to dissolved inorganic matter (TDS) is high (here about 1:1); (2) there is an excess of total inorganic cation charge relative to total inorganic anion charge that is presumably balanced by organic anion charge; and (3) the river tends to be acid (although many acid rivers are not organic—see Table 5.14).

Some of the Amazon tributaries are chemically dominated by organic matter. The Negro River in the Amazon Basin, named for its typically organic-rich black color, is an example. Stallard (1980) gives the concentrations of major dissolved inorganic ions for the Upper Negro River (pH 4.6–4.8) and the Negro River (pH 4.95–5.4) (see Table 5.14). Both of these rivers have considerably greater inorganic cation charge than inorganic anion charge. The DOC concentration in the Upper Negro (Leenheer 1980) is 12 mg/l, and TDS is 5 mg/l. Thus, the ratio of DOC:TDS in the Upper Negro River is 2.4:1, fitting the criteria for an organic-dominated river. Similarly, the DOC:TDS ratio for the Negro River is 1.7:1. The Matari River, another Amazon tributory, with low TDS (4.8) and low pH (4.7), also has considerably greater inorganic cation charge than inorganic anion charge, and its dark color (Stallard 1980) suggests a large concentration of organic matter.

There has been considerable discussion about whether some of the effects in rivers and lakes attributed to pollutive sulfuric (and nitric) acid rain might rather be natural due to high concentrations of organic matter (e.g., Krug and Frink 1983). The criteria set forward above for recognizing organic rivers can be used to test whether or not a given acidic river or lake is naturally acidic due to high DOC content. For example, Hubbard Brook (which we discussed above as being affected by sulfuric acid rain) has a DOC:TDS ratio of 1:20 (less than world average river water) and an essential balance between inorganic cation charge and inorganic anion charge, and thus would not seem to be organic controlled. This agrees with the general observation that in subalpine northeastern forests, 75% of the charge balance in soil and groundwater is accomplished by sulfate (from acid rain) and not organic anions (Cronan et al. 1978).

The Pine Barrens rivers in New Jersey (Yuretich et al. 1981; Crerar et al. 1981) have a low pH (4.5), brown water, a fairly high concentration of organic matter (2.2 mg/l), a low TDS (20 mg/l), and a high concentration of SO_4 (6.4 mg/ l). The ratio of DOC:TDS is 1:10, which is about twice as organic rich as world average river water but nowhere near the 1:1 ratio of organic-rich rivers discussed above, and there is charge balance. Thus the low pH of the Pine Barrens rivers is due more to very high sulfate concentrations than to the presence of natural dissolved organic matter. This agrees with the work of Johnson (1979), who finds an increase in the acidity of several Pine Barrens streams from 1963 to 1978 which is attributed to acid rain. However, there is reason to suspect that the groundwater, and possibly the river, were already moderately acid, due to organic acids, before the advent of acid rain, as attested to by the presence of bog iron ores. (The iron most likely was transported in association with organic matter.)

Lowering of the pH of a river can also occur due to increases in the concentration of CO_2 from excessive microbial breakdown of organic matter. This occurs in the lower Rhine, where

pollution provides nutrients, particularly phosphate, that greatly increase organic matter production (Buhl et al. 1991; Kempe 1988).