

## Introduction

Alkalinity is a measure of the buffering capacity of a stream water, i.e., the ability of water to resist changes in pH. Stream water with relative high alkalinities has a greater ability to neutralise acidic pollution from rainfall or wastewater, and is able to resist major shifts in pH. Water with low alkalinity is very susceptible to changes in pH. The buffering species that constitute alkalinity are primarily the base anions bicarbonate ( $\text{HCO}_3^-$ ) and carbonate ( $\text{CO}_3^{2-}$ ), although hydroxide ( $\text{OH}^-$ ), borates, silicates, phosphates, ammonium, sulphides and organic ligands may also contribute. Alkalinity not only helps regulate the pH of a water body, but also the metal content. Bicarbonate and carbonate ions in water can remove toxic metals, such as lead and cadmium, by precipitating the metals out of solution.

Alkalinity in most natural surface and groundwater is mainly derived from the dissolution of carbonate minerals, and from  $\text{CO}_2$  present in the atmosphere and in soil above the water table. Three carbonate species ( $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ ) contribute to total alkalinity, their relative proportions being dependent on pH and temperature. At near-neutral values of pH, dissolved bicarbonate ( $\text{HCO}_3^-$ ) is the dominant ion. A significant contribution from  $\text{CO}_3^{2-}$ , and other anions, emerges only at pH levels greater than approximately 9.0. In more acidic streams, a greater proportion of dissolved  $\text{CO}_2$  is present as  $\text{H}_2\text{CO}_3$ . Carbon dioxide species are important participants in reactions that control the pH of natural water. The attainment of equilibria between the three carbonate species and the pH-related species ( $\text{H}^+$  and  $\text{OH}^-$ ) is relatively rapid. However, rates of reaction between solutes in stream water and gaseous  $\text{CO}_2$  in the atmosphere are slower and equilibrium may not exist at all times. When soil water enters streams, excess free  $\text{CO}_2$  may be gradually released to the atmosphere as the water equilibrates with the atmospheric concentration of  $\text{CO}_2$  - the outgassing effect. Thus, low-order streams are likely to have greater dissolved  $\text{CO}_2$  concentrations than high-

order streams.

Carbonate-rich sedimentary rocks, principally formed from deposition of biogenic marine materials (Wedepohl 1978), are by far the most common geogenic source of alkalinity in stream water. Limestone contains predominantly calcite  $\text{CaCO}_3$ , the commonest carbonate mineral, and Mg calcite  $(\text{Ca,Mg})\text{CO}_3$  with trace amounts of aragonite, a polymorph of  $\text{CaCO}_3$ . Diagenetic alteration of calcite, involving substitution of Mg for Ca, forms dolomite  $\text{CaMg}(\text{CO}_3)_2$ , another major source of carbonate. Magmatic and volcanic rocks are relatively insignificant sources of carbonate compared to sedimentary rock types. Khitarov and Rengarten (1956) quote values ranging from 200 to 900  $\text{mg kg}^{-1} \text{CO}_2$  in granite, the carbonate being sourced from melt derived carbon dioxide. Intermediate rocks display very similar values to those of granite, although basaltic rock types have been quoted to contain as much as 5800  $\text{mg kg}^{-1} \text{CO}_2$  (Wedepohl 1978).

The  $\text{CO}_2$  content of the atmosphere is nearly 0.03% by volume, but the soil atmosphere can be significantly enriched in  $\text{CO}_2$  through respiration by plants and soil organisms and from the oxidation of organic matter. Dissolved  $\text{CO}_2$  becomes hydrated to form carbonic acid ( $\text{H}_2\text{CO}_3$ ), which undergoes two stages of dissociation, producing  $\text{HCO}_3^-$  and then  $\text{CO}_3^{2-}$ . The presence of  $\text{CO}_2$  in solution enables percolating water to dissolve calcite, and other carbonate minerals from rocks and soils, thus adding to the total  $\text{HCO}_3^-$  in solution.

Anthropogenic sources of alkalinity include limestone applied to fields to increase soil pH, or to poorly buffered lakes to remediate acidification. The effluent from wastewater treatment plants can also add alkalinity to a stream as the wastewater from industry, and domestic uses, contains carbonate and bicarbonate from cleaning agents and food residues.

Table 33 compares the median concentrations of  $\text{HCO}_3^-$  in the FOREGS samples and in the Barents region.

Table 33. Median concentrations of  $\text{HCO}_3^-$  in the FOREGS samples and in the Barents region

<i>Bicarbonate (<math>\text{HCO}_3^-</math>)</i>	<i>Origin – Source</i>	<i>Number of samples</i>	<i>Size fraction</i>	<i>Extraction</i>	<i>Median <math>\text{mg kg}^{-1}</math></i>
Water	FOREGS	808			126 ( $\text{mg l}^{-1}$ )
Water <sup>1)</sup>	Barents region	1346			28.0 ( $\text{mg l}^{-1}$ )

<sup>1)</sup>Salminen *et al.* 2004

### Alkalinity in stream water

Bicarbonate values in stream water range over more than two orders of magnitude, from  $<5$  to  $730 \text{ mg l}^{-1}$  (excluding an outlier of  $1804 \text{ mg l}^{-1}$ ), with a median value of  $126.4 \text{ mg l}^{-1}$ . The pH data indicate that whilst the majority of the alkalinity is due to the presence of bicarbonate, some stream water, particularly those in southern Europe, would also be expected to contain carbonate. Alkalinity data correlate very closely with calcium and, to a lesser extent, with pH and conductivity.

Lowest alkalinities in stream water ( $<42 \text{ mg l}^{-1}$ ) are found throughout Fennoscandia and northern Denmark, northern Britain, Wales and north-west Ireland, north-west Iberian Peninsula, Brittany, over the Massif Central and in eastern Switzerland. The low values are predominantly associated with felsic igneous and with metamorphic rocks.

Enhanced alkalinities in stream water ( $>263 \text{ mg l}^{-1}$ ) are found in the Baltic states, south-east Britain and western Ireland on limestones, throughout much of France (except Brittany and the Massif Central), southern Germany, southern and eastern Iberian Peninsula, Hungary and adjacent areas in Austria, Slovakia and Croatia, as well as parts of central Italy with Sicily and on the carbonate rocks in parts of Greece. These data are for stream water generally derived from calcareous rocks (mainly calcitic sandstone, limestone, chalk and marble). In Britain, anomalously high alkalinity values on the east

coast are related to the presence of calcitic sandstone, mudstone, thin limestone and chalk; high values may also be related to intense agricultural practices in these areas. A highly anomalous bicarbonate value ( $471 \text{ mg l}^{-1}$ ) in south Poland near the Czech border occurs in a stream draining Quaternary loess.

Bicarbonate is the most abundant anion, and ionic species generally, in stream water, and therefore has a dominating role in electrical conductivity. It is closely correlated with many other major ions, and especially with the Ca cation. The distribution pattern is controlled by climate and carbonate rocks distribution, and tends to illustrate climate zonality in northern Europe only, with a zone of very low values in Fennoscandia and Scotland. South of Fennoscandia, the patterns are determined mainly by the geological substrate, crystalline massifs and older mountainous fold belts showing lower alkalinity. The alkalinity is inversely distributed to the REEs and associated elements patterns, both in its geological component and in its climatic component.

A more detailed description on the chemistry of bicarbonate in stream waters is given in Annex 1 of this volume by Ander *et al.* (2006), where the thematic interpretation of stream water chemistry is discussed (see sections on anion predominance and calcite solubility).