

Introduction

The acidity of water is a function of the concentration or, more correctly, the activity of free hydrogen ions (H^+). Since the molar concentration of these ions is normally very small, it is usually expressed as pH, the negative base-10 logarithm of the hydrogen ion concentration in mol l^{-1} :

$$pH = -\log_{10}[H^+]$$

with a range from 1 (highly acidic) through 7 (neutral) to 14 (highly basic). Temperature has a small influence on pH, *e.g.*, the pH of neutral water at 30°C is approximately 6.9, whereas at 0°C it is typically 7.5.

The pH of surface water forms part of a dynamic system controlled by a range of buffering reactions occurring in solution and at the solid–solution interface, which produce or consume H^+ . Most natural water falls in the pH range 5 to 9 but, in stream water, considerable short-term variations in pH, up to a full pH unit, are likely to occur as a result of changes in stream-flow conditions (Neal *et al.* 1997).

The pH of rainwater is an important control on surface water pH, and this shows considerable spatial and temporal variation. In the absence of pollutants, and strong acid anions such as sulphate and nitrate, the pH of rainwater is naturally acidic (pH 5.65 to 5.7), equivalent to pure water in equilibrium with atmospheric levels of CO_2 (Hem 1992). Acidity from inorganic sources is higher in winter as a result of the higher atmospheric total solute load (Barbieri and Mosello 2000). This can promote cation exchange reactions that liberate H^+ (Heath *et al.* 1992). If rainwater also contains marine aerosols, high levels of Na^+ in rain may result in cation-exchange reactions, releasing H^+ into stream water.

Further controls on surface water pH include the abundance of base cations and other neutralising components in bedrock and overburden, how easily such components are leached, and the nature of their mediation through soil and vegetation. The highest pH values are

associated with carbonate-rich bedrock. Biochemical reactions in soil and streams, particularly during the summer, result in increased acidity in the form of organic acids, *e.g.*, humic and fulvic acids. The dissociation constants of many organic acids lie between pH 4.0 and 4.5; pH levels in this range are typical of streams draining peat bogs. Other important natural controls include the hydrolysis reactions of Al and Fe and the oxidation of sulphides.

Land use can be an important influence on the pH of surface water. Low pH values in surface water are commonly associated with ‘acid mine drainage’ - metal-rich water produced by the chemical reaction between water and rocks containing sulphur-bearing minerals. The resulting runoff is usually highly acidic and frequently occurs in areas where metal ore or coal mining activities have exposed rocks containing pyrite, although metal-rich drainage can also occur in mineralised areas that have not been mined. The planting of coniferous forests typically results, under storm-flow conditions, in H^+ concentrations 1.5 times higher than normal (Stoner and Gee 1985, Ormerod *et al.* 1989). This is caused by tree roots reducing the buffering capacity of soil through the uptake of base cations (Reuss and Johnson 1986). The natural acidity of rainwater is increased by the presence of sulphur dioxide (SO_2) and nitrogen oxides (NO_x), which are atmospheric pollutants originating mainly from fossil fuel combustion. These compounds are likely to be carried by wind over long distances from urban, mining, thermo-electric power plants and industrial emission sources. During rainfall the acidic pollutants are washed out as sulphuric and nitric acids over vast areas and may affect pristine areas located hundreds or even thousands of kilometres away from pollutant sources. Areas affected by acidified water are usually characterised by a major decrease in biological density and diversity.

Table 53 compares the median concentrations of pH in the FOREGS samples and in some reference datasets.

Table 53. Median concentrations of pH in the FOREGS samples and in some reference data sets.

Acidity (pH)	Origin – Source	Number of samples	Size fraction mm	Extraction	Median
Subsoil	FOREGS	763	<2.0	0.01 M CaCl ₂ leach	5.79
Topsoil	FOREGS	818	<2.0	0.01 M CaCl ₂ leach	5.51
Soil ²⁾	World	19 299	<2.0	Water leach	6.3
Soil ³⁾	Barents Region	1342	<2.0	Water leach	5.91
Water	FOREGS	800			7.7
Water ³⁾	Barents Region	1361			7.3

¹⁾Rudnick & Gao 2004, ²⁾Batjes 1995, ³⁾Salminen *et al.* 2004,

pH (acidity) in soil

In soil, pH was measured in the laboratory in a 0.01 M CaCl₂ leach. The median pH value is 5.79 in subsoils and 5.51 in topsoil, with a range varying from 2.89 to 7.86 in subsoils and 3.38 to 7.55 in topsoil. Subsoil and topsoil pH maps are very similar, and the average ratio topsoil/subsoil is 0.94, expressing a slight shift towards more acidic topsoil.

The pH distribution maps, of both subsoil and topsoil, show acidic values over Fennoscandia, Scotland, Wales, northern Ireland, Portugal and western Spain, Brittany, the Central Massif, the central and eastern Alps, Switzerland and southern Germany, the Bohemian Massif, southern Poland, Slovakia (except south-west part), and northern Croatia. The rest of the map shows near neutral or alkaline values. In France, near neutral pH (6.5 to 7.5) in soil are characteristic for the carbonate basins, whereas soil over basement areas have slightly acid pH (4.5 to 6.6).

Acidity in soil in Fennoscandia and Scotland is related to climate, in combination with the absence of carbonate rocks. In the western Iberian peninsula, the Massif Central, the central Alps and Bohemia, acidic pH is related to bedrock geology consisting of granitoid crystalline rocks or Variscan carbonate-poor detrital sediments. In central Europe, especially the Czech Republic, acidity is exacerbated by acid rain.

Large regions with alkaline soil pH, which generally coincide with a calcareous lithology, include the Baltic states and north-eastern Poland, the Paris Basin, the western Alps, the Poitou region between Brittany and the Central Massif,

southern France, the eastern part of the Iberian Peninsula, central and southern Italy, coastal Croatia and Greece, where alkaline pH values occur also over different lithologies, such as ultramafic, felsic, metamorphic and sedimentary rocks.

The good positive correlation of pH with CaO (0.52 in subsoil and 0.49 in topsoil) does not correspond to a gradual increase in both values, but to a sharp boundary at around pH 6.6 between acidic low-Ca soils and neutral to slightly alkaline Ca-bearing soil, as can be seen in the scattergrams (Figure 9 subsoil and Figure 35 topsoil). There is also a negative correlation of soil pH with SiO₂ (-0.39 in subsoil and -0.35 in topsoil), Na₂O (-0.42

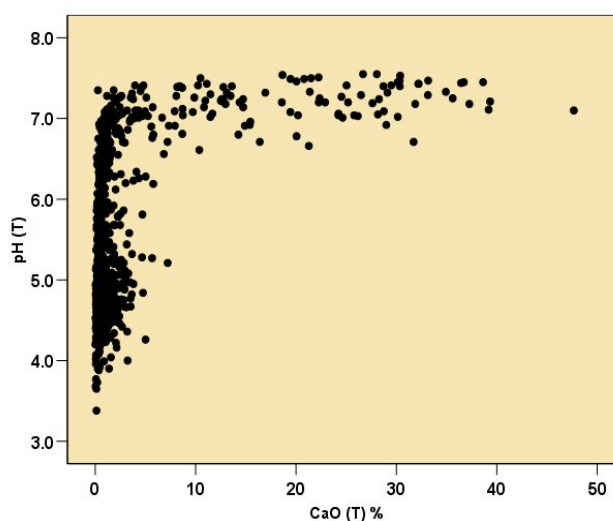


Figure 35. Scattergram of pH and CaO values in topsoil.

for both) and Ba (-0.32 and -0.26). For Na and Ba, the correlation is based on feldspar-rich (thus

Na- and Ba-rich) Fennoscandia, which also happens to show a climate-related acidity in soil.

pH in stream water

pH in stream water was measured in the field with a pH meter (Salminen, Tarvainen *et al.* 1998). The polyethylene decanter marked for pH measurements was rinsed twice with stream water and subsequently filled with stream water. The pH electrode was placed in the decanter and the pH value was noted with one decimal figure on the field observation sheet.

Stream water pH values range over almost five pH units, from 4.5 to 9.1, (excluding two outliers below 4.5 and one of 9.8), with a median value of 7.7.

Acid stream water (pH<7) is predominantly found throughout Fennoscandia, northern Denmark, northern Ireland, Brittany, over the Massif Central in France, and north-west of the Iberian Peninsula. These regions have base-poor buffering capacity, because of their geology, but the low pH is also controlled by acid buffering effects with dissolved organic species, particularly over parts of Fennoscandia, Denmark and Northern Ireland. Low pH values in southern Italy are related to volcanic rocks. One anomalously low pH value of 2.2 is found in Germany in eastern Bavaria in the western part of the Bohemian Massif within the Osser granite complex; it can be explained by high acid rainfall and the absence of natural buffering capacity.

The most basic stream water (pH>8.1) is found throughout the eastern and northern Iberian Peninsula, central Britain, Austria and in many areas adjacent to the Mediterranean. The pH in these areas is predominantly controlled by the carbonate geology. In Extremadura and the Iberian Pyrite Belt in southern Spain, in comparison to slightly acidic topsoil (pH 5 to 6),

stream water is slightly alkaline (pH 8); this may be caused by a sampling bias: small streams were sampled outside the zone of influence of massive sulphide deposits, where acid drainage is of great concern; also stream water has a high salinity in this area, and DOC and Ca in stream water form a good buffer leading to neutral or alkaline water.

Most near-neutral pH stream water values (from 6.7 to 7.7) are found within central Europe and in the Baltic states, Slovenia and Croatia. A highly anomalous alkaline pH value in southern Poland lies in the vicinity of a chemical plant producing sodium hydroxide and sodium lime. One isolated highly anomalous pH value of 8.9 in northern Germany shows high DOC in stream water and is close to the North Sea.

The acidity pattern in stream water, one of the important parameters controlling the behaviour of elemental species in water, is itself controlled by climate: precipitation and temperature control the rate of weathering and the continental zonality of vegetation types. In addition, geological factors are important, *e.g.*, in Fennoscandia crystalline rocks with low buffering capacity cause acid stream water, whereas in central and southern Europe widely exposed carbonate rocks cause alkaline stream water. The pH acidity distribution shows a similarity with the REEs and related element patterns (inverse relation with pH value).

A more detailed description on the influence of pH on the speciation of some metals and solubility of certain minerals in stream water is given in Annex 1 in this volume by Ander *et al.* (2006), where the thematic interpretation of stream water chemistry is discussed.

pH comparison between sample media

The stream water pH and topsoil and subsoil pH maps have broadly similar distributions, with most acid pH values found throughout Fennoscandia, western Iberian Peninsula and over

the Massif Central in France. The soil pH data tend to be slightly less acidic over Scandinavia compared to stream water pH.