pH, the CO$_2$ system and freshwater science

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Abstract

Appreciation of pH as an ecological index has varied considerably over its past history, influenced by perceptions of chemical rigour, ease or difficulty of measurement, and multiple chemical and biological correlations. These factors, and especially the last, are considered in relation to the extensive range of pH in inland waters. Emphasis is placed upon the role of the CO$_2$ system, the components of which are subject to biological metabolism (photosynthesis, respiration) and are extensively determined by products from rocks (e.g. limestone) and soils.

Titration alkalinity, or acid neutralising capacity, is a most valuable summarising and reference measure. For this, and CO$_2$ variables, potentiometric Gran titration opens new possibilities – including the definition of negative alkalinity (acidity). The relationship of pH and titration alkalinity is close and semi-logarithmic for waters in equilibrium with atmospheric CO$_2$. Very high pH, above 10, can develop from the photosynthetic depletion of CO$_2$ and by the evaporative concentration of bicarbonate-carbonate waters in closed basins. Very low pH, below 4.5, results from the introduction of strong acids by volcanic emissions, pyrite oxidation, ‘acid rain’ and cation exchange; here the CO$_2$ system lacks influence, biological diversity is reduced, and ionic aluminium often exerts toxic biological effects.

Situations of pH excursion are discussed and illustrated; they operate over day–night, seasonal and long-term time-scales. A summer rise of pH is widespread in productive near-surface waters. There is also a seasonal pH rise in the anoxic deep water of many lakes, as a consequence of the interaction of acid–base and oxidation-reduction systems. These can be regarded as two ‘master systems’ of environmental chemistry and – dating from pioneer studies of wetland soils and waters – of much freshwater ecology.

Keywords: acidifuge; alkalinity; acid neutralising capacity; bicarbonate; buffering; carbonate; carbon dioxide; hydrogen ion; pH; potentiometric titration; redox.
**Introduction**

No chemical concept, dependent upon a mathematical twist, has been received more enthusiastically by ecologists than pH. Few chemists are aware that its value as a convenient variable was originally promoted by a botanist, the Dane Sørensen. It is generally perceived as the exponent expressing the logarithm (base 10) of the hydrogen ion concentration in moles per litre, with its sign reversed. If heavy isotopes are discounted, the hydrogen ion is an elementary particle, the proton. The chemical species involved in its exchange, as donors or acceptors of protons, are protolytes.

This simplicity neglects two considerations: quantitatively, the chemically effective quantity is related to activity rather than concentration; qualitatively, the hydrogen ion H\(^+\) in aqueous solution is largely associated with a water molecule H\(_2\)O as the hydroxonium ion, H\(_3\)O\(^+\). The volumetric basis introduces a small temperature-dependency via water density, and a larger one comes from the temperature-sensitivity of the dissociation constant of water (\(K_w\)). The latter, like [H\(^+\)] concentration, can be represented by its negative logarithm p\(K_w\). Consequently, as Hutchinson (1957) explains, the pH of pure water is estimated as 7.00 at 25 °C, but 6.77 at 40 °C. In natural waters other pK factors also determine a variable temperature-dependence of pH, generally of the order of -0.1 unit per 10 °C rise.

Here emphasis is given to the interrelationship of many components, illustrated mainly by examples from my own experience.

**Ecological appreciation and prejudice**

Botanical influence behind pH perhaps presaged a welcome among biologists and ecologists of a quantity regarded as rigorous and fundamentally entrenched in chemistry. It was early perceived as having wide ecological associations and this generated a less than critical enthusiasm. An anecdote of this era – that of Shelford- influenced ecology – is recounted by Allee et al. (1949). It centred on a supposed useful supremacy of pH-measuring equipment among the apparatus of ecologists on a small boat greeted in an American harbour. It will later be shown that although associations are indeed numerous, they are often the result of indirect and non-rigorous correlation.

*Fig. 1.* Examples of the depth-distribution of pH measured in two English lakes, dissimilar in depth and planktonic production, illustrating the range encountered seasonally under varied conditions of stratification and algal abundance. Small arrows indicate the approximate pH of surface water at atmospheric equilibrium. For one depth-profile, estimates are also given of total CO\(_2\) (C\(_t\)) and its relation to alkalinity (A). From Talling (2006 Fig. 6).
A later swing to a more critical – at times over-critical – approach prevailed in the 1950s and 1960s. This centred on imperfections of measuring methods and equipment – including colorimetric standards unsupported by standard buffers, and ‘pH papers’ with appreciable intrinsic buffering. The widely used measurement via electrical potential, with a reference electrode, suitable offsets and scaling, usually depended on a glass electrode whose high resistance introduced problems of electrical measurement – especially in more dilute natural waters. Examples, instanced by Schindler, occurred in early work on the Experimental Lakes on the Precambrian Shield of Canada. There was similar experience in the English Lake District; this led to certain astonishingly high records of pH obtained by a bacteriologist being discounted by some chemical and botanical colleagues. They were later found to have a basis in reality (Talling, 1976, 1985; Maberly, 1996; examples in Fig. 1) among some of the most remarkable chemical behaviour of the English Lakes! Problems of potentiometric measurement in this phase were reduced by improvement in measuring equipment. Nevertheless, a really critical recognition of potential errors in pH in electrometric measurement, as by Covington et al. (1985a, b) and Davison (1990), was – and is – often not applied in practice. The chemical significance of measurements to hundredths of a pH unit – electrically feasible – may be uncertain to tenths of a unit. Nor is it generally appreciated that pH is a temperature-dependent quantity, as is implied by the temperature-dependence of relevant dissociation constants, and that it can be altered by exposure of a water sample to atmospheric CO₂. Precautions when sampling may therefore be advisable (Mackereth et al., 1989). Continuous recording in situ is also possible (e.g. Maberly, 1996).

Some relevant chemical background

In ascending the pH scale from 0 to 14, one moves from an acidic region of predominant proton (H⁺) donors to one of predominant proton acceptors. In most natural waters, and notably present-day sea water after its remarkably near-balanced evolutionary interaction or ‘titration’ to circum-neutral salts (Sillén, 1961), the free forms of strong acids and strong bases are insignificant. Instead, pH is usually determined by the ionised forms and derivatives of weak acids and weak bases. Here the concentrations, and so activities, of components of the CO₂-system related to H₂CO₃ generally predominate:

\[
\begin{align*}
\text{CO}_2 + \text{H}_2\text{O} &= \text{H}_2\text{CO}_₃ \\
\text{H}_2\text{CO}_₃ &= \text{H}⁺ + \text{HCO}_₃⁻ \\
\text{HCO}_₃⁻ &= \text{H}⁺ + \text{CO}_₃^{2⁻}
\end{align*}
\]

with the dissociation of water

\[
\text{H}_₂\text{O} = \text{H}⁺ + \text{OH}⁻
\]

and sometimes gain or loss of \( \text{CO}_₂^{2⁻} \) and \( \text{HCO}_₃⁻ \) to or from calcium carbonate of limited solubility.

The importance of this system is contributed by

1. the major involvement of CO₂ – a pH depressant – as a metabolic input and product
2. the abundance of sedimentary carbonates – potentially soluble in water – in the earth’s crust
3. the existence of a major atmospheric reservoir of gaseous CO₂
4. the magnitude of relevant dissociation constants \( (K) \), yielding pK values and hence large changes in the chemical species within the common pH range of 4 to 10. In ascending this span, the predominant form of dissolved inorganic carbon changes from CO₂ to \( \text{HCO}_₃⁻ \) to \( \text{CO}_₃^{2⁻} \), as shown in the relative Buch diagram reproduced in many textbooks.

Outside the CO₂-system, there are in natural waters other weak inorganic acids – notably boric acid and silicic acid – whose molecules and their ionic derivatives act as proton-donors and acceptors and so influence pH. Concentrations of borate are significant in sea water (e.g. Hill, 1963). Those of silicic acid – Si(OH)₄, for which the substitution of fictitious SiO₂ is unfortunately common – are appreciable in most fresh waters and exceed 0.5 mmol L⁻¹ in many tropical examples. However, its ionisation – first
to SiO(OH)$_3$ – is appreciable only above pH 9. It has been usual to neglect an influence of this, and of organic acids at lower pH values, although detectable effects can exist (e.g., Talling, 1973) and need more study. At the other end of the pH scale, below pH 4.5, there is a potential mobilisation of ionic species of aluminium that influence pH and exert a biological toxicity (see, e.g., contributions in Mason, 1990).

Besides the CO$_2$ system, one should recognise the following chemical agencies as influencing pH in natural waters. First, there is the introduction of strong acids, most universally in atmospheric precipitation bearing products of combustion (especially compounds of sulphur and nitrogen). In this way the pH of rainwater is often reduced from c. 5.0 to c. 4.3. Also widespread is a mineral origin of sulphuric acid, as by the oxidation of pyrite FeS$_2$. Examples are described in Geller et al. (1998). Second, there are the less readily resolved effects of weak organic acids (discussed in Perdue & Gjessing, 1990 and by Tipping, 2002) that often originate in the catchment. Third, there is ion-exchange involving base cations. Fourth, there can be influence from co-existing oxidation-reduction (redox) reactions in the aquatic medium. In the wider sense, these can include aspects of carbon and nitrogen metabolism. Broad quantitative discussion of factor interaction, as affecting pH in lakes, is given by Psenner & Catalan (1994).

A measure of capacity in proton exchange has long been used in limnology. It was originally known as one form of titration alkalinity, and latterly also (and more expressively) as acid neutralisation capacity (ANC) or the German Säurebindungvermögen (SBV). It represents the capacity to neutralise strong acid added to the bicarbonate endpoint, and can be expressed in milli- or micro-equivalents (meq or μeq) per L. Strictly it is a difference, not a concentration, and has negative values in acidic solutions. A former and misleading expression used mg L$^{-1}$ units of fictitious CaCO$_3$ (1 meq L$^{-1}$ = 50.05 mg L$^{-1}$ CaCO$_3$). This alkalinity is not to be confused with an alkaline reaction as high pH. The endpoint was classically approximated using methyl orange indicator, and later mixed indicators, with endpoint at pH 5 approximately; a small correction of c. 0.01 meq L$^{-1}$ was often applicable (e.g., Sutcliffe et al., 1982). More accurate determination is possible by potentiometric titration (Gran titration: Gran, 1952), originally applied to sea water (Dyrssen, 1965; Dyrssen & Sillén, 1967; Edmond, 1970) and then introduced to fresh waters (Talling, 1973). It involves an antilogarithmic conversion of pH values met during the titration. Two successive conversions – one in a higher band of pH – can in a closed system yield a measure of total (i.e. free + ionic) CO$_2$ between the endpoints which they indicate (Edmond, 1970).

Several chemical species are potentially involved in the acid neutralising capacity. Normally the bicarbonate and carbonate ions are far predominant, but formally allowance is required for presence in the samples of pH-dependent OH$^-$ and H$^+$ ions and possibly anions of other weak acids (A$^-$) such as SiO(OH)$_3$ from silicic acid:

alkalinity (or ANC) = [HCO$_3^-$] + 2[CO$_2^-$] + [OH$^-$] + [A$^-$] - [H$^+$]

(5)

It is consequently a mixed sum of concentrations that is best expressed (as above) in units of milli-equivalents or micro-equivalents L$^{-1}$ (displaced in much modern chemistry) rather than the corresponding molar units (represented by terms in brackets above) – although components other than HCO$_3^-$ are typically negligible over the common pH range of 6.0 to 8.5. All these component quantities, like those of ‘free CO$_2'$ that conventionally deals with the aggregate CO$_2$ + H$_2$CO$_3$ (denoted H$_2$ CO$_3^\ast$), tend to change logarithmically over the pH scale whether expressed in equivalents or molar units. The latter are shown in Fig. 2 for a water of alkalinity 0.40 meq L$^{-1}$, similar to that of the English lake Esthwaite Water, with pH varied by the addition or depletion of CO$_2$. 

Alkalinity also sets an upper (and temperature-sensitive) limit to pH-rise induced by the removal of CO$_2$. If that is complete, and the quantity A$^-$ is small or negligible as often assumed, then alkalinity is largely made up of OH$^-$ and approximates its concentration, that in turn – by the known dissociation constant of water $K_w$ – determines pH. At this point all CO$_2$- related quantities – free CO$_2$, HCO$_3^-$, CO$_3^-$ – are extinguished. This situation is shown in Fig. 2 and was approached in some experimental exposures, ‘pH-drifts’, with the cyanoprokaryote (cyanobacterium, cyanophyte, ‘blue-green’) Microcystis aeruginosa as an
effective photosynthetic remover of CO$_2$ (Talling, 1976). Upper limiting values of pH, so engendered, could exceed 11.0, but – as also found by Maberly et al. (2009) for less effective CO$_2$ removers limited by H$_2$CO$_3^*$ depletion – varied with the initial alkalinity and so concentrations of exchangeable CO$_2$. They are also markedly temperature-dependent. This has implications for an assessment of accentuated limiting pH in warm tropical waters, for which a high pH implies more CO$_2$-depletion than in colder waters.

The capacity for removal, and hence CO$_2$ depletion with raised pH, varies widely in different groups and species of algae and macrophytes. Differences were formerly ascribed to the presence or absence of an ability to directly utilise bicarbonate as C-source (e.g. Ruttner, 1947), later linked more widely to the possession of carbon-concentrating mechanisms (e.g. Maberly & Madsen, 2002). There is limited capacity in chrysophytes, related to their absence from the more alkaline waters (Saxby-Rouen et al., 1999) and the probable lack of a carbon-concentrating mechanism (Maberly et al., 2009). Diatoms show very variable capacity.

It was found to be low in Aulacoseira subarctica Haworth (formerly Melosira italica subsp. subarctica O. Müll.) (Talling, 1976), and may contribute to growth restriction of the related A. granulata at elevated pH (9.0+) generated by growth of phytoplankton in the Nile (Talling et al., 2009).

In my opinion, alkalinity is the best single measure for interpreting the wider ‘ecological’ meaning of a pH measurement on a water sample. In part this is because alkalinity is an unaltered or ‘conservative’ property regarding the addition or the removal of CO$_2$, which respectively depress or raise pH in natural waters subject to biological activity. It could, for example, resolve the meaning of a high pH such as 10, which might result from CO$_2$ depletion in a productive water of low alkalinity or from high alkalinity in a saline soda lake. It is temperature-independent (cf. Dyrssen & Sillén, 1967). It also represents ions, and especially bicarbonate, that make up most of the total anion concentration of many inland waters. These and other correlations, soon to be discussed, once led an experienced limnologist (C.H. Mortimer) to remark in my hearing that if he had to choose a single chemical measure of a fresh water he would take alkalinity.

Buffer intensity ($\beta$) is another chemical property of note. It indicates the resistance to pH change induced by unit addition of CO$_2$ acid, or alkali. The first is most prevalent in ecological situations, where buffer intensity with respect to CO$_2$ change can be calculated (e.g. in mmol CO$_2$ per pH unit) from parameters of the CO$_2$ system (e.g. Talling, 1973). In this system, buffer intensity varies very non-linearly with pH, and is low in a pH region – slightly temperature-dependent around pH 8.1 to pH 8.3 – where induced molar changes in HCO$_3^-$ and CO$_3^{2-}$ concentrations over the pH scale are minimal. At much lower and higher pH it is raised.

**Fig. 2.** Logarithmic and temperature-sensitive distributions with pH, varied by CO$_2$ change, of chemical components active in operation of the CO$_2$ system. This system is modelled for a fresh water of low ionic strength (0.001), alkalinity (0.40 meq L$^{-1}$) and non-carbonate alkalinity ($A^-$), showing extinction of CO$_2$-system components (free CO$_2$ = H$_2$CO$_3^*$, HCO$_3^-$, CO$_3^{2-}$) at high pH with OH$^-$ domination of alkalinity. Modified from Talling (1985 Fig. 1),

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by exponential increase in H\(^+\) and OH\(^-\) concentrations and possibly by other chemical species, such as ionic forms of aluminium below pH 5. Saline inland waters of low alkalinity exist but are not necessarily more strongly buffered than much more dilute fresh waters. Waters of moderate alkalinity (e.g. 1 – 2 meq L\(^{-1}\)) tend to have pH values near the point of minimum buffer intensity, and are in consequence prone to upward shift of pH when CO\(_2\) is consumed in photosynthesis, and fall of pH when CO\(_2\) accumulation results from decomposition and respiration. Incidentally, animal ecologists have only rarely taken episodes of the former rise into account (as by Dunn, 1967).

Salinity has but little direct influence on pH insofar as it is mainly contributed by neutral salts of strong acids and bases. Sea water, with high concentrations of Na\(^+\) and Cl\(^-\), is the commonest example. Here, as in most fresh waters, the magnitude of titration alkalinity (circa 2.3 meq L\(^{-1}\) in oceanic water) is of most significance. However, salinity has a small systematic effect by altering ionic strength, a characteristic that widens the gap between concentration and chemical activity of dissolved constituents; it thereby alters the values of effective or apparent dissociation constants (K'), reducing their pK' (negative logarithmic) values. Means of calculating this effect on CO\(_2\)-related quantities in fresh waters are set out by Mackereth et al. (1989). In general, critical treatments of the variable CO\(_2\) system in fresh waters (e.g. Howard et al., 1984) have been fewer than the corresponding studies on sea water.

**Excursions of pH over time**

The susceptibility of pH to free CO\(_2\) content is obviously liable to promote its changes in time, as natural waters are subject to biological influence from CO\(_2\) consumption (photosynthesis) and CO\(_2\) production (respiration, decomposition). In fact, changes in pH were formerly used as a method for assessing aquatic photosynthesis and production (Verduin, 1956; Byers & Odum, 1959; Byers, 1970). Photosynthesis follows the day–night (diel) cycle of solar radiation, and is often very localised over depth. Diel cycles of pH, elevated by day, are consequently near-universal in waters productive of aquatic macrophytes or phytoplankton. The latter situation is illustrated in Fig. 3, which shows the distribution of temperature, dissolved oxygen and pH in a Nile reservoir that is seasonally rich in phytoplankton. Here the density stratification imposed by daytime rise of water temperature stamps similar depth-time patterns on the chemical variables. The daytime or diurnal rise of pH is reversed by a largely nocturnal re-distribution of CO\(_2\) from depth and net production in respiration, and by its slow re-entry from the atmospheric reservoir. In general,
the rate of such re-entry is limited by the small atmospheric proportion, and hence partial pressure, of CO₂, although there is stimulation by chemical reactivity to waters above pH 9 (Emerson, 1975). For these situations of diurnal excursion involving pH, the limitations of atmospheric replenishment are clear. There are relatively few examples in which the changing content of total CO₂ has been measured by direct chemical methods (e.g. Schindler & Fee, 1973).

The annual cycle in most fresh waters involves changes in the same variables. Those of pH are again most generally linked with net consumption and production of CO₂; elevated pH may be correlated with a lower rate of photosynthesis per unit biomass (e.g. in Loch Leven: Bindloss, 1974). There are often depth-differences of pH associated with temperature-density stratification and the distribution of biological activity. Figure 4 illustrates such patterns of seasonal change in two English lakes. Windermere South Basin shows, in summer, elevation of pH in the upper layers and its depression in the lower – which respectively correspond to net depletion and accumulation of CO₂. Even wider changes (e.g. with pH range 10.35 to 6.47 in 1971–72) occur in the more productive Esthwaite Water, but here another chemical system – of oxidation-reduction or redox – also intervenes to modify pH in deep water. There the deep pH decline is reversed to pH rise in late summer, and is accompanied – and partly induced – by a major increase in alkalinity. These extra changes are a consequence of final deoxygenation at depth, that induces several chemical reductions (e.g. Fe³⁺ to Fe²⁺) in which electron transfer also leads to proton transfer (Heaney et al., 1986; Talling, 2006), and previously free CO₂ is incorporated in bicarbonate. Bacterial reductions are implicated (Kelly et al., 1982). Interaction between the two systems also influences reaction kinetics, as is manifest in strong pH-sensitivity of the rate of Fe²⁺ oxidation (Davison & Seed, 1983).

Some other pH trends, often longer-term, do not depend on changes in CO₂. Some aquatic macrophytes, notably species of the bog-moss Sphagnum, induce acidification by processes of ion-exchange (e.g. Clymo, 1963). Inputs of strong acids – including H₂SO₄ – from ‘acid rain’ influenced by industry, are another now-familiar source of long-term acidification (e.g. Mason, 1990). Prospects of freshwater susceptibility, and recovery (e.g. Tipping et al., 1998), depend critically upon sources of alkalinity to a water-body from the catchment and in the water-body itself. The latter may exceed the former (Psenner & Catalan, 1994). The internally derived alkalinity may modify biological production, and be itself augmented by experimental stimulation of that production (e.g. Kelly et al., 1982; George & Davison, 1998).

**Ecological and environmental correlations**

Acidophile and acidophobe species have long been distinguished by freshwater and terrestrial ecologists, from floristic and faunistic surveys. In fresh waters the species itself rarely generates the associated condition, although abundant

Fig. 4. Seasonal changes during 1967 in the magnitude and depth-distribution of temperature, dissolved oxygen and pH in two English lake basins, illustrating upward shifts of pH due to photosynthetic CO₂ depletion above and interaction with redox shifts induced by anoxia below. Adapted from Talling (2006 Fig. 4).
phytoplankters and acidophile species of *Sphagnum* (already mentioned) are conspicuous exceptions. More usually the pH condition arises passively, and often from other chemical correlations of pH. One is that with calcicoles and calciphytes species influenced by exposure to calcium carbonate, abundant as marine residues in limestone and chalk and subject to weathering to yield waters with elevated levels of both calcium and alkalinity. These waters are generally of moderately high pH as pH rises near-linearly with the logarithm of alkalinity when the concentration of free CO$_2$ is near that at equilibrium with that of the atmospheric reservoir. An approximation under current conditions, excluding saline waters and those at high altitude, is derived by Psenner & Catalan (1994) as

$$\text{pH}_{\text{equilibrium}} = 11.3 + \log [\text{HCO}_3^-] = 11.3 + \log [\text{alkalinity}]$$

for the pH range 6 to 9 and alkalinity (measured in eq L$^{-1}$) below $10^2$ eq L$^{-1}$ (i.e. 10 meq L$^{-1}$). Temperature-influence exists but is minor; it has effects on the solubility of gaseous CO$_2$ (Bohr coefficient) and on relevant dissociation constants (K values). A recent long-term trend to higher concentrations of atmospheric CO$_2$ is not without a small but significant effect on the pH of oceanic waters (Raven, 2005). Altitude is influential via atmospheric pressure and hence the partial pressure of atmospheric CO$_2$.

Figure 5 illustrates the semi-logarithmic relationship for a wide range of lake waters, with some large individual deviations from linearity mainly associated with extreme
natural excursions of free CO$_2$ concentration. Remarkably, Windermere, a lake of low alkalinity, has been found to have occasionally a pH of more than 10 in surface water. Although pH elevation by CO$_2$ depletion is here more extensive than pH depression by CO$_2$ accumulation, the latter condition is more predominant year-round in this and many other lakes, and most running waters (e.g. Rebsdorf et al., 1991), with implications for the overall balance of metabolism affected by external inputs of sources of CO$_2$ (e.g. Cole et al., 1994; Maberly, 1996). Higher alkalinity, shown in Fig. 5 from selected African lakes, is there closely correlated with salinity as the HCO$_3^-$ + CO$_3^{2-}$ pair generally predominates among anions, as does Na among cations. Consecutively evaporation in closed basins results in a range of saline ‘soda lakes’, of high pH and low content of Ca$^{2+}$ and Mg$^{2+}$ (Talling & Talling, 1965; Wood & Talling, 1988). Such development to high alkalinity, and correlatively high pH, would be impossible from CaCO$_3$-based marl lakes – water-bodies recently reviewed by Pentecost (2009). In these the low solubility of CaCO$_3$ is combined with its frequent deposition, in part biogenic. One such lake, the upland Malham Tarn in Yorkshire, UK, had in 1985–87 a seasonal range of alkalinity of 1.0 to 2.4 meq L$^{-1}$, and, in antiphase, a pH range in surface water of 7.7 to 8.7 (Talling & Parker, 2003). Much of the variation of alkalinity was caused by the seasonal abstraction of CaCO$_3$ by a stonewort (Chara sp.; Pentecost, 1984). Here and beside Sunbiggin Tarn, another upland water in Cumbria (Holdgate, 1955), there is wide local variation of calcicole and calcifuge plants in peripheral waters and soils, influenced by adjacent limestone and upward building of acid raised bog. These influences apart, soil-water typically has a high content of free CO$_2$, which can fall by an order of magnitude upon exit to surface waters with opportunity for atmospheric equilibration and associated rise in pH.

Both alkalinity and pH are characteristics that often have close correlations with the distribution of species of algae, most notably desmids and diatoms. Desmids often reach remarkably high diversities in waters of low alkalinity and low pH. However, high pH induced by CO$_2$ uptake in low alkalinity waters is not excluded; evidence includes that of Reynolds (1986) for Staurastrum pingue above pH 10.0 in an experimental enclosure and a maximum of S. cingulum at pH 10.2 in Windermere South Basin (Maberly, personal communication). Physiological work (Spijkerman et al., 2005) has shown that planktonic desmids include species with diverse capacity for CO$_2$ uptake, not all restricted to free CO$_2$ as the source. Examples of alkalinity as a prime factor in the distribution of diatoms have been demonstrated by Hustedt (1949), Richardson (1968), Gasse et al. (1983) and Wood & Talling (1988) in African lakes, and by Knudson (1954) in the English Lakes. Still more widely studied have been the pH-preferences of diatoms. Diatoms have been a popular source of recoverable indicator species and associations, widely used to trace past conditions on the pH scale (e.g. Battarbee et al., 1990) rather than the correlated scale of alkalinity. Exceptionally, both scales have been used (Catalan et al., 2009). On the short time-scale of a few hours, population activity and growth can be extinguished by CO$_2$ depletion rather than correlated increase of pH – as was evident in pH-drift experiments involving pH shifts recorded in illuminated algal suspensions with variable alkalinity.

![Fig. 6. Continuous record of a 'pH drift' over time during photosynthetic uptake of CO$_2$ by a dense suspension of the dinoflagellate Ceratium hirundinella, in an initial lake-water medium with alkalinity values (inserted above, in µeq L$^{-1}$) successively altered by additions of HCl and Na$_2$CO$_3$. Adapted from Talling (1976 Fig. 17c).](image-url)
northern Europe is divisible into two groups, separable by their response to prolonged exposure to pH less than 5.7. This is broadly borne out by the natural distribution with pH of numerous species surveyed by Psenner & Catalan (1994), who suggest that there is a corresponding minimum HCO$_3^-$ requirement of about 20 µeq L$^{-1}$. Additionally, tolerance of low pH appears to be reduced in waters of low salt content via adverse balance between ion (e.g. Na$^+$, K$^+$) loss and uptake. Examples appear in experimental work on crustaceans (Potts & Fryer, 1979) and in patterns of their geographical distribution in Yorkshire. In this topographically varied county there is a strongly bimodal frequency distribution of pH in standing fresh waters, with maxima near pH 7.6 (mostly lowland) and 4.0 (mostly upland), the latter marked by a reduced occurrence of many species. Nevertheless, there is an appreciable occurrence of small crustaceans – including the near omnipresent Chydorus sphaericus – in very acid waters of pH 3 to 4 (Fryer, 1980, 1993a, b).

Another factor behind the elimination of acidifuges is susceptibility to toxicity of ionic aluminium, especially Al$^{3+}$, abruptly mobilised from other insoluble forms at pH below 5 with zero to negative alkalinity. This additional toxicity factor at low pH, 'beyond the CO$_2$ system', has recently engaged much attention in relation to episodic and long-term acidification of surface waters (examples in Mason, 1990).

Figure 7 summarises the incidence of these and other transitions on the overall pH scale. Looking at the pH 0–14 scale as a whole, there is some symmetry of opposites in the associated rise of [H$^+$] or [OH$^-$] concentrations at the two ends – exceeding 1 mmol L$^{-1}$ at approximately pH 3

**Fig. 7.** The pH scale, showing distribution of components and situations discussed in the text.
and pH 11 respectively. Asymmetry in natural waters appears in the main influence of labile CO$_2$ exchange over a largely alkaline to slightly acidic band, and of cation exchange over a decidedly acid band. Other than in these processes, input of strong acid dominates the lower end, and evaporative concentration of pre-existing carbonate the upper, with typically long-persistent consequences.

### General comments

The historical after-view would suggest that an original hope, that pH might represent a uniquely rewarding factor embracing many ecological relationships, has been fulfilled only partially. One reason (both for and against) is the multiplicity of variably cross-correlated properties (e.g. pH, alkalinity, Ca$^{2+}$); another is the influence, and frequent dominance, of the relatively labile CO$_2$ system of relationships. In the words of Fryer (1993a), "just as pH is no philosopher’s stone, even a complex of several physico-chemical factors may not fulfil this function either". One relation to habitat productivity might be induced by photosynthesis; another by ion-speciation – e.g. of H$_2$S–HS$^-$–S$^2-$, and of H$_2$PO$_4^-$–HPO$_4^{2-}$–PO$_4^{3-}$ – sensitive to pH and influencing the mobility of phosphate in base-poor (Mortimer, 1941–42; Drake & Heaney, 1987) and base-rich (Golterman, 1984) situations.

It seems to me that two developments in the 1930s were especially notable. First, there was the systematic study by Jenkin (1936) of a series of Kenyan rift lakes of high-ascending alkalinity and pH. This benefitted from the influence of earlier basic work at Cambridge by Saunders (1926) on the pH–CO$_2$ system of relationships and of his and Jenkin’s work on the ciliate Spirostomum (Jenkin, 1927). These investigations once led G.E. Hutchinson (formerly a pupil of Saunders) to cite this ciliate as providing perhaps the best established instance of a pH relationship in aquatic ecology. Second, co-action between the acid–base and oxidation-reduction (redox) systems were investigated by Pearsall (1938) in relation to soil, fen and bog water (see Fig. 8) and extended to lake sediments by him and Mortimer (Pearsall & Mortimer, 1939; Mortimer, 1941–42). Later Sillén (1967) and others considered the two realms centring on proton and electron transfers, here portrayed...
within a lake setting in Fig. 9, as major ‘master systems’ (i.e. primary systems with multiple consequences approachable by quantitative deductions; e.g. Stumm & Morgan, 1970). These master systems not only underlie aquatic chemistry but also – one might add – much aquatic ecology.

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**Author Profile**

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