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The pH regime of sediments underlying acidified waters

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Abstract. The pH of sediments underlying acidified lake waters does not necessarily reflect the acidification of the water. Profiles of sediments in Lake Anna, Virginia showed interstitial pH values between 6.0 and 7.0 within the top 4 cm, even though the sediments are constantly exposed to overlying waters with pH values as low as 3.5. The amount of acidity neutralized by sediment processes is 2 orders of magnitude greater than previously reported observations. The results indicate that caution must be used in drawing conclusions about sediment biogeochemical processes based on the pH of overlying waters.

Introduction

Sediments and sediment microorganisms play a crucial role in decomposition and nutrient cycling in lakes. Concern has been expressed that lake acidification will slow down the recycling processes in water (Rao and Dutka, 1983) and sediments (Rao et al., 1984), leading in extreme cases to oligotrophication (Grahn et al., 1974). Effects of acidification on sediment processes have been examined by artificially lowering the sediment pH to the lake water pH (Andersson et al., 1978; Baker et al., 1983). However, data from the experimental water-column acidification of Lake 223 showed that sediment pH rapidly reached 6.5 in the top 3 cm below the pH 5.0 lake water (Kelly and Rudd, 1984). The present study corroborates those findings and extends them by examining pH profiles in a southeastern impoundment with chronic pH values as low as 3.0.

Lake Anna is a mesotrophic impoundment in central Virginia (Figure 1) that receives acid mine drainage from Contrary Creek (pH = 2.5–3.5). Sediment pH was measured at 4 stations to observe the relationships of the acidic lake water with the interstitial pH. The results showed that the sediment pH was always circumneutral (pH = 6–7) even when overlain by lake water with a pH as low as 3.5. We conclude that buffering mechanisms previously attributed to sediments may, under appropriate conditions, greatly exceed any thus far reported and that consideration of the pH regime in the sediments is critical in evaluating the potential impact of acidification on the biogeochemical processes that occur there.

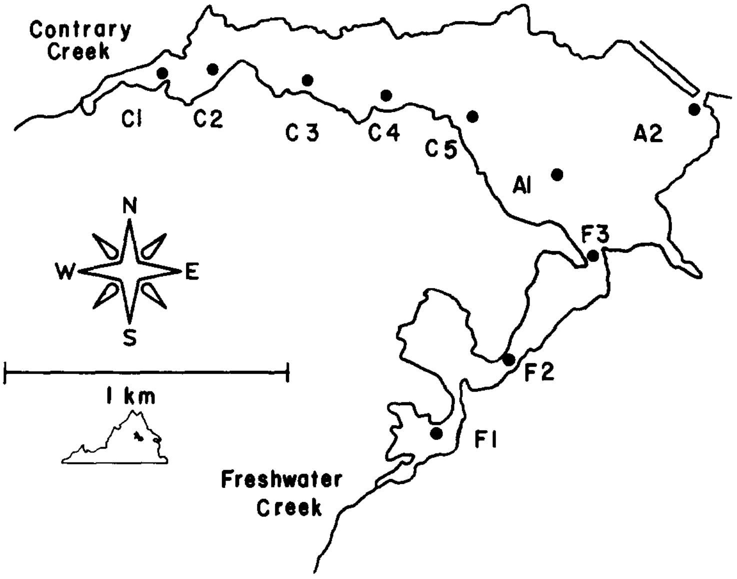

Figure 1. Location of stations in the Contrary Creek arm of Lake Anna, Virginia, showing the relative proximity to the mouth of the acid mine stream.

Methods

Sediment pH profiles were determined at stations C2, C5, A2 and F1 (a station in an unpolluted arm of the lake, Figure 1). Interstitial water for pH analysis was obtained with plexiglass membrane-equilibrators similar in design to those of Hesslein (1976) as modified by Herlihy and Mills (1985). The equilibrators had nine rows of wells, at 4 cm vertical intervals. The equilibrators were soaked in 95% ethanol, rinsed and filled with sterile water and the face was covered with a sheet of sterile, 0.2 μm pore size Versapore (Gelman) membrane filter. The equilibrators were deployed by *SCUBA* divers leaving one row of wells slightly above the sediment surface. Accurate depth placement of the equilibrators was difficult because of poor visibility, but the presence of a bright orange band of iron sesquioxide on the equilibrator clearly marked the position of the sediment surface so that accurate measurement of the distance between the sediment surface and the wells could be made. After two weeks the equilibrators were removed. Immediately on emersion the equilibrator face was rinsed with deionized water, blotted dry and a Sensorex pH probe was inserted through a slit cut in the filter. The pH was read using a Leeds and Northrup pH meter (two point calibration in the field, pH 7.00 and 4.01).

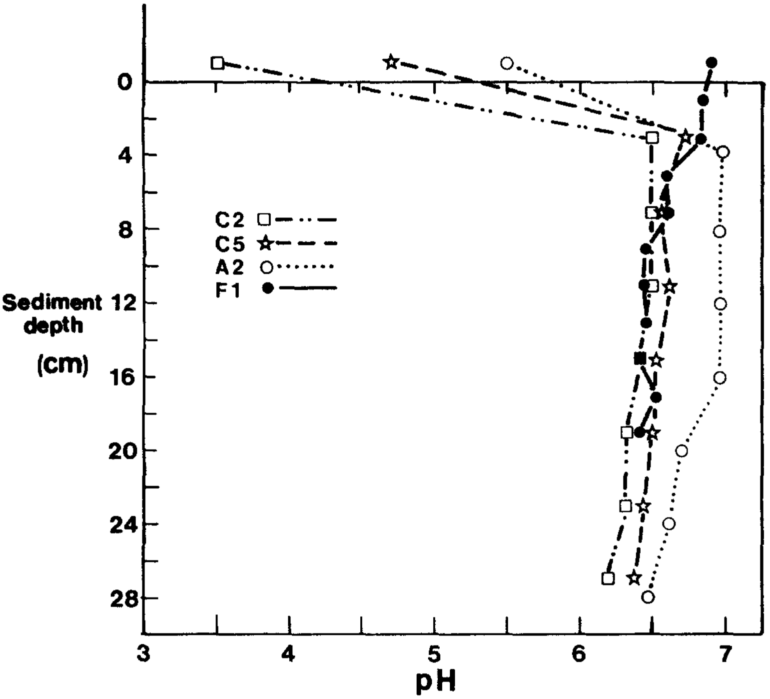

Figure 2. Profiles of interstitial pH in sediments of Lake Anna. The data presented are for May 1983, although the pattern has been replicated in all seasons of the year. Values above the line represent the pH of the water column at a distance of 1–3 cm above the sediment surface.

Results and discussion

The gradient in bottom water pH (Figure 2) from station C2 (pH = 3.5) to station A2 (pH = 5.5) demonstrates the effect of dilution and removal of the acid mine drainage pollutants with distance from Contrary Creek as described by Herlihy and Mills (1985). However, the observed interstitial pH values were always circumneutral (pH = 6–7), even just 3 cm below the pH 3.5, C2 bottom water. At all stations, the topmost sediment well showed a rapid departure from the surface acidic conditions. Profiles such as shown in Figure 2 have been obtained in each of 8 samplings. Because of the differences in depth placement of the equilibrator, the position of the topmost well varied slightly. The wells were two centimeters in diameter and therefore integrated the average pH over that depth. The topmost well in the sediment was taken as the first well completely below the orange line marking the sediment water interface and in no case extended below 4 cm. In some cases, the topmost well in the sediment was barely below the orange line, thus representing an integration of pH in the 0–2 cm depth range. Even in these cases the pH measurement intervals may show that the neutralization zone is much shallower. While water column microbial processes are inhibited by acidification, a similar inhibition may not be observed in sediments, especially in mesotrophic or eutrophic lakes. Suitable measurement of the pH of interstitial waters in sediments is critical to understanding the impact of lake acidification on the biological processes in the sediments; extrapolation of the bottom water pH of 3.5, pH 7 at depth and a diffusion coefficient (D_{sed}) of 4.5×10^{-5} cm^2 sec^{-1} (calculated for Pacific red clay [Li and Gregory, 1974]). Thus if there were no neutralization mechanism the sediments would be rapidly acidified.

Previous work at Lake Anna attributed the observed neutralization to alkalinity generated by bacterial sulfate reduction in the sediment (Mills and Herlihy, 1985), a conclusion consistent with work from other sites (Schindler et al., 1980; Kelly et al., 1982; Kelly and Rudd, 1984). Other mechanisms may contribute to the neutralization; for example, ion exchange is likely to be important immediately after large amounts of sediment and acidity are deposited by major storm events. The rocks of the Piedmont region are very low in $CaCO_3$ (the study site is located in the Chopawamsic Formation dominated by sericitic granitic schists), thus neutralization by mineral derived carbonates is presumed to be minimal. Because of the high concentrations of iron in the water and sediments (3–7 mM Fe^{2+} in sediment pore water), reduction of iron may play an important role in proton consumption. This process is intimately associated with sulfate reduction and constitutes part of the biological buffering mechanism. Measured rates of sulfate reduction account for generation of more alkalinity than needed to produce the observed changes in pH in both the water and sediment (Herlihy and Mills, 1985).

The rapid neutralization of acidity in the sediments has important implications in the study of effects of lake acidification. It would be erroneous to assume that the sediments are acidic just because the lake water has a low pH. Due to high organic matter availability to the sulfate, nitrate and iron reducing bacteria, generalizations of this report may be most relevant to mesotrophic or euthrophic lakes (like Lake Anna). However, similar pH profiles were observed in the experimental acidification of Lake 223 (Experimental Lakes Area) where the pH changed from 5.0–5.5 in the bottom water to 6.7–6.9 at 2 cm depth (Kelly and Rudd, 1984). Furthermore, organic matter decomposition rates in Lake 223 sediments appeared unaffected by the lake acidification (Kelly et al., 1984). Andersson et al., (1978) measured pH in a Swedish lake by directly inserting a pH electrode into sediment cores overlain with experimentally acidified pH 4.7 lake water and found a rapid return to circumneutrality (pH = 6.8) within the top 3–5 cm of sediment. The Lake Anna work demonstrates that acid from waters with pH values as low as 3.5 is capable of being rapidly neutralized within the surficial sediments.

The data from Lake Anna and other acidified lakes indicate that sediment pH returns to circumneutrality within the top 1–4 cm of sediment, but finer measured was never below 6.0. While close-interval measurements (such as obtained with microelectrodes [Howarth and Jørgensen, 1984]) would be desirable, they would not negate the conservative conclusion that the pH of the interstitial water reaches circumneutrality within the top 2–3 cm of the sediment.

Diffusion calculations using Fick's law indicate that after 100 days the pH at 10 cm sediment depth would be 3.6 given initial boundary conditions of a water column pH is not a suitable surrogate for appropriate sediment measurements.

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