GEOCHEMICAL AND LITHOLOGICAL FACTORS IN ACID PRECIPITATION

JAMES R. KRAMER, Department of Geology, McMaster University,
Hamilton, Ontario, Canada, L8S 4M1.

ABSTRACT

Acid precipitation is altered by interaction with rocks, sediment and soil. A calcareous region buffers even the most intense loading at pH ∿8; an alumino silicate region with unconsolidated sediment buffers acid loadings at pH ∿6.5; alumino silicate outcrops are generally acidified. Either FeOOH or alumino silicates are probable H^+ ion sinks in non-calcareous sediments. Glacially derived sediment is more important than bedrock in assimilation of acid precipitation in Shield areas. Toxic metal concentrations are dependent upon sediment metal concentrations and the pH of water.

INTRODUCTION

The pH of precipitation has been measured as low as 3.5 over various parts of the world and commonly approaches 4 (Cogbill and Likens, 1974; Granat, 1972; Oden, 1971), whereas the expected pH of unpolluted atmospheres from the CO_2-H_2O equilibria is about 5.7. Low pH appears to be the most common toxic factor for biomass, although Cd and Cu concentrations are commonly significant factors. A pH of 5-5.5, Cd concentration of 0.01-1 mg/l and Cu concentration of 0.1-0.5 mg/l are considered threshold conditions for toxicity to fish and invertebrates, although combinations of metals and pH may lower the threshold value by an order of magnitude (Arthur D. Little, 1971).

Precipitation may have metal and pH values which infer toxic conditions, but there is always a tendency for increase in pH and decrease in soluble metal concentrations when precipitation reacts with the lithology. It is the purpose of this paper to define interactions of soils and rocks with acid precipitation and associated metals in order to predict the resulting water quality.

1. pH - ALKALINITY

The main variables in the system are H^+ ion, alkalinity, and soluble metal ions. Alkalinity is the concentration measure of any possible sink for H^+ and includes carbonate alkalinity, sorption on colloidal metal oxides including FeOOH, alumino silicates, $Al(OH)_3$ and ionizable organic acids. Figure 1 is a typical pH-alkalinity curve obtained for lakes in Canada and Switzerland. (See also Oden, 1973; Figure 12.) The general shape of the curve is apparently universal. An alkalinity of about 2 meq/l and a pH of 8 is indicative of a calcareous sediment. The pH-alkalinity relationship is defined by the equilibrium of $CaCO_3$ and/or $CaMg(CO_3)_2$:

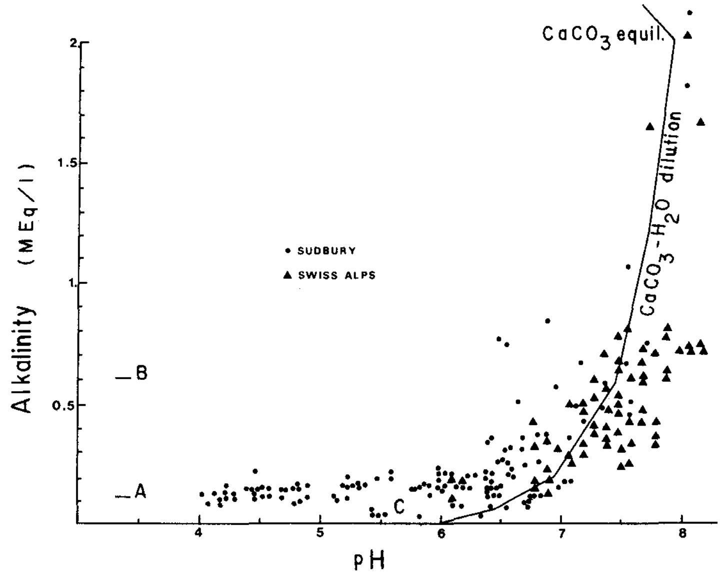

Figure 1. pH-alkalinity relationship for lakes in the Canadian Shield and Swiss Alps. The solid line represents the dilution of water equilibrated with $CaCO_3$ at 2 meq/l carbonate alkalinity. A and B represent pH boundary values for alumino silicate control whereas C represents the alkalinity pH obtained from $FeOOH-H_2O-CO_2$ (atm) equilibrium.

$$CaCO_3 + H^+ = Ca^{+2} + HCO_3^-$$

or

$$CaMg(CO_3)_2 + 2H^+ = Ca^{+2} + Mg^{+2} + 2HCO_3^-$$

In this case, the alkalinity is entirely carbonate alkalinity. Furthermore, this system has an almost infinite H^+ ion assimilation capacity if the carbonate mineral content is large. Lower alkalinity waters are found which represent a simple dilution of the equilibrium $CaCO_3$-H_2O system as shown in Figure 1. Carbonate alkalinity is less than 0.01 meq/l at a pH of about 6, yet measured alkalinities between pH 4-6 are almost constant, ranging between 0.1-0.2 meq/l. This alkalinity can be due to interactions of cation alumino silicates such as

$$1.5\ H_2O + KAl_3Si_3O_{10}(OH)_2 + H^+ = 1.5\ Al_2Si_2O_5(OH)_4 + K^+$$

OR

$$4.5\ H_2O + KAlSi_3O_8 + H^+ = 0.5\ Al_2Si_2O_5(OH)_4 + K^+ + 2\ H_4SiO_4$$

which are noted on Figure 1 by A and B. There are numerous other alumino silicate reactions that give results between A and B.

Fe commonly occurs in oxidized portions of the earth's crust as colloidal FeOOH as small as 100Å (Lengweiler et al., 1961), and these particles can impart a large H^+ ion buffering capacity. FeOOH gives a pH of about 5.7, which is analagous to the CO_2-H_2O system.

Alumino-silicates and FeOOH are singled out as H^+ ion sinks, only because they represent the most abundant oxides on the surface of the earth. There are other less abundant metal oxides that can act as H^+ sinks. FeOOH is probably a more common buffer because it tends to occur in very fine particle sizes, allowing a large specific surface for reaction. Alumino-silicates tend to occur in larger sizes and they tend to equilibrate very rapidly in water (Houston, 1972; Wollast, 1967).

In addition to metal oxides, it is possible that soluble organic acids that have a dissociation constant of about 10^{-4} to 10^{-5} can assimilate H^+ ion at low pH and account for the alkalinity noted. Although there are many organic acids with the proper dissociation constant, few natural waters of pH 4-6 have high enough soluble organic carbon concentrations to exhibit the pH control.

More knowledge on the nature of the alkalinity of a water body below 6.5 is required in order to assess the H^+ ion assimilation capacity of acid rain. Particularly, the detailed knowledge of detritus is required. Commonly lakes of low pH are very transparent (Secchi depth ∿20m) and this transparency may be due to the total dissolution of the fine colloidal buffer; or the transparency may be due to the lack of organic detritus caused by negligible biological production.

In summary, a classification of H^+ ion assimilation of sediment and rock in decreasing order is:

Kind	Alkalinity	pH	Capacity re: acid rain
Calcareous rock and soil	2 meq/l	8	Very large
Fine-grained non-calcareous soil and sediment	0.2-1 meq/l	6-7	Can be altered
Non-calcareous rock outcrop	0.1 meq/l	4-7	Is altered by acid rain

The detailed mineralogy of the unconsolidated post-glacial cover is the most important parameter in assessing the H^+ ion assimilation of acid precipitation in non-calcareous terrain, and this information cannot be obtained from general geological maps. Furthermore, knowledge of the complete surficial and subsurface hydrology is required as lower soil horizons may be calcareous, whereas surface deposits may be non-calcareous. This situation exists quite commonly on the Canadian Shield.

A useful indicator of the pH-alkalinity relationship can be expressed by the calcite saturation index (CSI), which is the logarithm of the degree of saturation of a water body with respect to $CaCO_3$ (Conroy et al., 1974).

The CSI is defined by:

$$CSI = p(Ca^{+2}) + p(Alk) - p(H) + pK$$

where $p(X) = -\log_{10}(X)$, $pK = +2$, $(Ca^{+2}) = mol/l$, $(Alk) = eq/l$, and $(H^+) = eq/l$.

If a body of water is saturated, with respect to $CaCO_3$, the CSI = 0; if supersaturated, the CSI < 0, and if undersaturated, the CSI > 0. A body of water with a CSI ≤ 3 is generally stable relative to acid precipitation. Bodies of water with a CSI from 4-6 are unstable relative to acid loading and are typically non-productive (Conroy et al., 1974).

2. METAL SORPTION

Assume that soluble metals are sorbed onto surfaces of bonding of the type either Me-O or Me-OH. One can derive an exchange reaction of the form:

$$\log_{10}Me(aq) = \log_{10}Me(sed) + pK - pH$$

where $\log_{10}Me(aq)$ is the soluble metal concentration (μg/l), Me(sed) is the detrital sediment metal concentration (ppm) and pK = 2.6, 3.9, 4.75, 4.5 for Fe(+3), Cu(+2), Ni(+2) and Zn(+2) respectively. The values of pK have been calculated from lake data for the Canadian Shield with pH ranges 4-8 and metal concentrations varying over 3 orders of magnitude.

Using the above sorption relationship, values of trace metals in igneous and calcareous rocks for the earth's crust (Horn and Adams, 1966), and corrections for OH, HCO_3 and CO_3 ligands, the soluble trace metal concentration can be calculated. Table 1 gives the estimates from the calculation for Fe(+3), Cu(+2), Ni(+2) and Zn(+2) in calcareous terrain (pH ∿ 8.1), igneous rock terrain (pH ∿ 6.4) and acid lake environments (pH ∿ 4.5), using average values of metals for the earth's crust. The effect of going from pH 8.1 to 4.5 and from calcareous to non-calcareous sediment is very large on soluble trace metal concentrations. The change in trace metal concentrations and resultant concentrations in acidified lakes, due primarily to the decrease in pH, compares with estimates of threshold concentrations for toxicity effects. Therefore, one should expect not only toxicity effects due to a decrease in pH, but also toxicity effects from increased soluble metal concentrations. In a buffered calcareous terrain, however, there would be very little chance of large soluble trace metals concentrations.

Table 1. Predicted soluble metals in an average crustal rock for calcareous, igneous and acidified water bodies. Metal values are in µg/l.

Total Soluble Metal	pH 8.1 calcareous	pH 6.4 igneous	pH 4.5 acidified
Fe(+3)	.03	7	500
Cu(+2)	.0003	.3	25
Ni(+2)	.006	2	170
Zn(+2)	.004	1	80

3. SUDBURY LAKES REGION

There exist calcareous and non-calcareous lakes to the NE of the Sudbury, Ontario, smelting operations. Lakes vary from a pH of 4-8, with total soluble Ni, Cu, Fe and Zn varying from <0.1 to 200 µg/l. The area is generally covered by igneous and metamorphic rocks typical of Precambrian Shield areas, but there is also an ample cover of post-glacial sediment.

The unconsolidated sediment is the key factor regarding the acidity and resultant production of lakes in the region, and the lithological control completely overshadows the acid precipitation loading. Acid precipitation contours (as well as SO_4, Fe, Cu and Ni) decrease NE-SW away from Sudbury, paralleling major wind directions (Figure 2). But acid lakes lie in quartzite rocks which have little or no unconsolidated sediment (Beamish and Harvey, 1972). The NE-SW trend of the calcite saturation index (CSI) parallels the glacial movement direction (Figure 3). Thus glacial scouring eroded some regions in a NE-SW direction and filled other regions with fine sediment. The CSI value of 0, reflecting a calcareous regime in the middle of igneous and metamorphic rocks, occurs in lakes that have a large subsurface flow, suggesting that unconsolidated sediments at depth are calcareous.

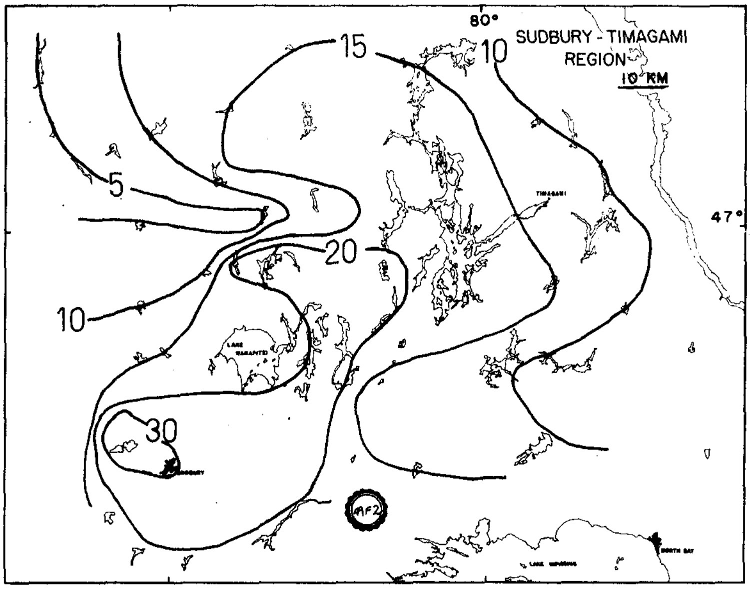

Figure 2. Concentrations of SO_4 (mg/l) in lake waters derived from smelter emissions in the Sudbury, Ontario region. Natural background is about 2 mg/l SO_4. Lakes outlined are those sampled.

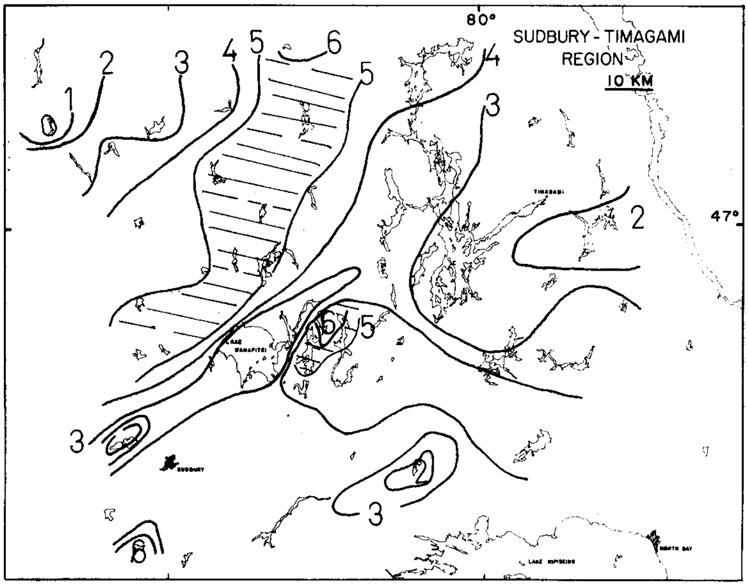

Figure 3. The calcite saturation index (see text) calculated for lakes in the Sudbury area. Those lakes below pH 5 are in the area hatched. Compare with loadings as shown by SO_4 in Figure 2.

REFERENCES

1. Lengweiler, H., W. Buser and W. Feitknecht. 1961. Die Ermittlung der Löslichkeit von Eilsen (III)-hydroxiden mit ^{59}Fe I, HELV. CHIM. ACTA 44, 796-805.

2. Wollast, R. 1967. Kinetics of the Alteration of K-feldspar in Buffered Solutions at Low Temperature, GEOCHIM. COSMOCHIM. ACTA 31, 635-648.

3. Little, Arthur D. 1971. INORGANIC CHEMICAL POLLUTION OF FRESHWATER, U.S. Environ. Protection Agency, Water Quality Criteria Data Book 2, No. 18010DPV07/71, 280 p.

4. Oden, S. 1971. Acidification by Atmospheric Precipitation--A General Threat to the Ecosystem *in* Mysterud, I. (ed.), Acidification of the Biologic Environment, 63-98 (trans. from the Swedish).

5. Beamish, R. J. and H. H. Harvey. 1972. Acidification of the La Cloche Mountain Lakes, Ontario, and Resultant Fish Mortalities, J. FISH. RES. BD. CANADA 29, 1131.

6. Granat, L. 1972. On the Relation between pH and the Chemical Composition in Atmospheric Precipitation, TELLUS 24, 550-560.

7. Houston, W. N. 1972. THE SURFACE CHEMISTRY AND GEOCHEMISTRY OF FELDSPAR WEATHERING, thesis, McMaster University, 126 p.

8. Cogbill, C. V. and G. E. Likens. 1974. Acid Precipitation in the Northeastern United States, WATER RESOURCES RESEARCH 10, 1133-1137.

9. Conroy, N., D. S. Jeffries and J. R. Kramer. 1974. Acid Shield Lakes in The Sudbury, Ontario Region, PROC. 9th CANADIAN SYMP. WATER POLL. RES. CANADA 9, 45-61.