Effects of Acidification on Metal Availability to Aquatic Biota, with Special Reference to Filamentous Algae

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A survey of 34 shield lakes in Ontario and Quebec, pH 4.4 to 7.1, was made to evaluate which metals should be considered of concern as a risk to aquatic biota or consumers when lakes are acid stressed. A set of predictions, concerning the mobilization by man, the mobility, the chemical speciation, and the toxicity or bioaccumulation of metals in acid-stressed waters, were used as a basis for designing the study and organizing the results. Attached algae were used as biomonitors to assess metal bioavailability.

The study concluded that zinc, lead, aluminum, and mercury were of concern in acid-stressed lakes, while the situation for manganese was unresolved, and cadmium was not studied. Nickel and copper were of concern only when a point source was involved. The study also concluded that the attached algal community had some value as a biomonitor, for metals in acid-stressed as well as metal-polluted surface waters.

Introduction

The acidification of aquatic and terrestrial ecosystems, whether by natural processes, acid deposition, or experimental manipulation, has a number of potentially profound effects on the biota of the affected systems. Mechanisms of these effects are undoubtedly complex, involving not only the direct effect of the hydrogen ion but also the effects of other elements and compounds in solution which change qualitatively and quantitatively with changes in pH. Furthermore, one anticipates higher order effects resulting from alterations in populations of competing species, predators, or prey, respectively.

Changes in the concentration and speciation of some metals in response to depression of pH are variously documented from field studies. The sources of the metals may be internal to the system (i.e., from soils, bedrock, or sediment) or from net additions by deposition resulting from short or long range transport in the atmosphere. The effects on biota may involve acute or chronic toxicity, which will change community composition directly or indirectly, or may be manifest in increased body burden of metals without any apparent toxic symptoms. In a recent attempt to document or predict changes in biogeochemical cycling of elements resulting from acidic deposition, Campbell et al. (1) have used a number of criteria to identify metals of concern in this context. Table 1 summarizes their results.

The metals which were considered to be of concern by Campbell et al. formed the basis of a field study in 1982, in which 34 softwater lakes ranging in pH from 4.4 to 7.1 in Ontario and Quebec were sampled twice during the ice-free season. The availability of the metals was estimated by measuring the metal burden of a specific community: the attached algae, often referred to as periphyton or "aufwuchs." In an earlier publication by Bailey and Stokes (2), a multivariate approach was used to evaluate factors which were correlated with metal mobility and availability. In the present study, the results are presented for individual metals and discussed in the context of factors controlling the behavior of each metal in the aquatic system. The potential for risk to biota from the metals is evaluated. At the same time, the practical value of the algal community as a biomonitor is considered.

Rationale and Hypothesis

For a number of metals, a correlation has been demonstrated between pH of surface water and metal (total) concentration (3,4). These metals include aluminum, manganese, cadmium, zinc, and lead, all of which were shown to be inversely correlated with pH in surface waters. Of these, only aluminum has been implicated in
Table 1. Metals of concern in relation to acidification of surface waters.*

| Metal | Atmosphere control | Over the range pH 4–7 | Toxicity | Bioaccumulation observed |
|-------|--------------------|------------------------|----------|-------------------------|
|       | Anthropogenic      | Increased total        | Speciation change | Inherent | Observed in acid lakes | |
|       |                    | concentration          | Calculated | Observed |               |               |
| Ag** | +                  | +                      | +          | +         | +              | +              |
| Al*  | +                  | +                      | +          | +         | —              | +              |
| As   | +                  | +                      | +          | +         | —              | +              |
| Be   | +                  | +                      | +          | +         | —              | +              |
| Cd** | +                  | +                      | +          | +         | +              | +              |
| Co*  | +                  | +                      | +          | +         | +              | +              |
| Cu*  | +                  | +                      | +          | +         | +              | +              |
| Hg*  | +                  | +                      | +          | +         | +              | +              |
| Mn*  | +                  | +                      | +          | +         | —              | +              |
| Mo   | +                  | +                      | +          | +         | —              | +              |
| Ni** | +                  | +                      | +          | +         | +              | +              |
| Pb   | +                  | +                      | +          | +         | +              | +              |
| Se*  | +                  | +                      | +          | +         | +              | +              |
| Te   | +                  | +                      | +          | +         | +              | +              |
| Ti†  | +                  | +                      | +          | +         | +              | +              |
| V†  | +                  | +                      | +          | +         | +              | +              |
| Zn*  | +                  | +                      | +          | +         | +              | +              |

* Data of Campbell et al. (1).

** Symbols: * denotes sufficient evidence to warrant concern; † denotes insufficient evidence; no symbol denotes evidence suggests no problem in the context of acidification.

Toxic responses of biota (5). In addition to these five metals, mercury is of concern in the context of acidification, since a correlation has been demonstrated between mercury in fish tissue and decreasing pH of surface water (6–11). Based on theoretical considerations, copper may also be of concern, since its solubility and its speciation are pH-dependent (1).

Even if the concentration of a metal in surface water increases with acidification, this is not sufficient to warrant its implication as a risk to biota. In order to establish if a risk factor exists, it is necessary to demonstrate that metal concentrations are approaching levels which would be toxic to biota, and/or that biota are accumulating metals such that metal burden is related to acidification. This latter phenomenon clearly has implications for human health and wildlife if food items are contaminated.

In the present study, filamentous algae, which grow well in acidic lakes (12) and which produce a large amount of biomass on artificial substrates (2) were evaluated as monitors of available metal in a survey of 34 softwater lakes in Ontario and Quebec (Fig. 1). Since a number of physical and chemical factors other than pH are known to influence metal uptake by biota (Fig. 2), we also determined on a site-specific basis the major nutrients and metal ions in water and sediments (Table 2). Detailed values for the metals and other environmental variables are presented elsewhere (2). The present account attempts to summarize trends and patterns.

It was hypothesized that algal metals would reflect the availability of metals and that while pH would be a major controlling variable, other factors such as major ions and dissolved organic carbon would also influence metal uptake.

Methods and Data Analysis

Details of the site characteristics and field and analytical methods are provided elsewhere (2). Data were subjected to bivariate correlation analysis and also to multivariate analysis. The latter are reported in the earlier publication (2), and the former are reported here.

In the present paper, the results are presented on a metal-by-metal basis, with predictions based on the theoretical and actual behavior of the metals (1) followed by the observations and results for the present study. It should be noted that for some of the most acidic sites there was a complicating factor in that they were close to the Sudbury, Ontario, copper-nickel smelting complex, and thus had a direct point source of copper and nickel. A number of the correlations and analyses were run for the entire data set and then re-run with the omission of the lake sites close to Sudbury.

Results and Discussion

Copper

Predictions and Background Information. Predictions are that copper deposition is increased by hu-
human activities; that copper is moderately mobile in the terrestrial system; there is evidence for release from sediments in response to acidification. Copper solubility is theoretically increased as pH decreases. The total Cu concentration in water is not changed as lakes acidify (except where smelters are implicated). Speciation is strongly pH-dependent over the range pH 4–7. Copper is moderately toxic (13).

**Results.** It was found that Cu concentration in lakes is not pH-dependent (except for smelter sites) and is below the toxic threshold (except for smelter sites) (Table 3). Copper was found to bioaccumulate in algae. Algal copper is correlated with dissolved organic carbon (−), all sites; pH (−), and dissolved Cu (+) only if smelter sites were included.

The data therefore support the prediction that copper concentrations in acid lakes are elevated only if there is a local input such as a smelter. In our study, accumulation of copper by algae decreased with increases of organic carbon, presumably because of the complexation and decrease of free metal as organic carbon increased.

There were significant increases in algal copper with increase in dissolved copper and decrease in pH, but this relationship was lost if the smelter sites were removed. No other environmental variables showed significant correlations with algal copper.

**Nickel**

**Predictions and Background Information.** Nickel deposition is predicted to be increased by human activities. Ni is moderately mobile in the terrestrial system; there is evidence for release from sediments in response to acidification. Solubility is theoretically not increased as pH decreases. Total Ni concentration in water is not expected to change as lakes acidify (except where smelters are implicated). Speciation is not pH-dependent over the range pH 4–7. Nickel is moderately toxic (13).

**Results.** It was found that Ni concentration in lakes is pH-dependent, (Fig. 3) but remains below the toxic threshold (except for smelter sites) (Fig. 4). Ni bioaccumulates in algae. Algal nickel is correlated with dissolved Ni(+) dissolved organic carbon and with pH (−); the pH correlation held only if smelter sites are included (Fig. 4).

Nickel resembles copper in several of the predictions; however its solubility and speciation are not expected to be pH-dependent. For our survey, nickel concentrations in water were pH-dependent, even if the lakes
Figure 2. Pathways of metals to algae: factors influencing transfer. Data of Bailey and Stokes (2).

Table 3. Range of dissolved metals in study lakes and toxic thresholds for aquatic biota.

| Metal    | Background water levels, ppb | Our range, ppb* | Threshold, ppb | Reference |
|----------|------------------------------|-----------------|----------------|-----------|
| Aluminum | <30                          | 46–372          | 100 (fish)     | (5)       |
| Cadmium  | 0.07                         | <1              | 0.2 (zooplankton) | (15)     |
| Copper   | 1.8                          | <1–17–69(s)     | 50 (algae)     | (16)     |
| Lead     | 0.2                          | <2–11           | 30 (zooplankton) | (7)      |
| Manganese| <5                           | <5–276          |                |           |
| Nickel   | 0.3                          | <2–6–247(s)     | 30 (zooplankton) | (5)      |
| Zinc     | 10                           | <2–44           | 15 (zooplankton) | (15)     |

*For copper and nickel, ranges excluding and including Sudbury Lakes are given.

Close to the smelter were removed from the calculation. There is a possible confounding effect, however, in that the most acidic lakes surveyed, even excluding those close to the smelter, were in the Killarney region (Fig. 1) and those may still have been under the influence of the Sudbury smelters (18,19). Nickel is clearly more mobile than copper (20). However, none of the lakes outside the immediate influence of the smelter had potentially toxic levels of nickel.

Algal nickel, like algal copper, increased as dissolved carbon decreased and was also positively correlated with dissolved nickel. The negative correlation between algal nickel and pH was significant only when the smelter sites were included.
Zinc

Predictions and Background Information  It was predicted that Zn deposition would be increased by human activities. Zn is highly mobile in the terrestrial system. The solubility is theoretically not increased as pH decreases. Total Zn concentration in water is expected to increase as lakes acidify (field and experimental evidence). Speciation is theoretically not pH-dependent over the range pH 4–7. Zn is moderately toxic (13).

Results. The concentration of Zn in lakes was found to be pH-dependent (Fig. 5). Zn concentration in acidic lakes was approaching toxic levels (Table 3). Zn bioaccumulates in algae. Algal Zn correlated with pH (+) (Fig. 6) and correlated weakly with P, N (−).

Zinc is likely to be released from internal sources by desorption from soils and sediments in response to acidification; it is also deposited as a result of long-range transport (1). Our survey showed a significant increase in dissolved zinc with a decrease in pH, presumably as a result of both of the above processes. Unlike copper and nickel, zinc does not have a discrete point source in the smelter complex. Its concentration in the more acidic lakes was 30 to 44 μg/L, at which concentration it has been demonstrated to have toxic effects to zooplankton (15).

The relationship between algal zinc and pH showed a positive correlation, even though the zinc concentrations in water showed the opposite trend. This can be explained by the fact that neither solubility not speciation of zinc is expected to change over the pH range under consideration, so zinc is mainly in the cationic form. The hydrogen ion is able to compete with the zinc at the cell surface, so other things being equal, at lower pH the uptake of zinc is less than at pH close to neutrality. If this is a widespread occurrence, it will have a mediating effect on the potentially toxic levels of zinc in acidified lakes.

Lead

Predictions and Background Information. Lead deposition is predicted to be increased by human activities. It has low mobility in terrestrial system. The solubility is theoretically not pH-dependent over the range pH 4–7. The concentration of Pb is possibly increased as lakes acidify, but this has not been verified experimentally. Speciation is predicted to be strongly pH-dependent over the range pH 4–7. Pb is moderately toxic (13). Bioaccumulation in fish is increased in acid lakes.

Results  It was found that Pb concentration in lakes is not pH-dependent (Fig. 7). The Pb concentration in
lakes is below the toxic threshold (Table 3). Pb bioaccumulates in algae. Algal lead correlated with P, N (−) and correlated weakly with dissolved organic carbon (−) and pH (−) (Fig. 8).

Lead concentration in surface waters is not expected to increase with decreased pH except at very low pH (21) because of its low mobility and low solubility. Data from other areas, notably in Scandinavia (3), have however shown that in a given geographic area, lead in water is negatively correlated with pH. In our data there is no such relationship, and in no case was there lead concentration high enough to indicate potential toxicity to biota. Lead did accumulate in algae; it was not related to dissolved lead but was negatively correlated with pH and dissolved carbon, indicating an increased availability at low pH. The same relationship has been shown for fish, (K. Sun, personal communication). There was also a positive correlation between algal lead and dissolved phosphorus and nitrogen for which there is no clear interpretation at this time.

Manganese

Predictions and Background Information. It was predicted that deposition was not controlled by human activities. Mn was expected to be highly mobile in the terrestrial system. Mn solubility is predicted to increase as pH decreases. Total Mn concentration in water is increased as lakes acidify. Speciation is not expected to be pH-dependent over the range pH 4–7. Mn has very low toxicity (13). Bioaccumulation in fish centra increases in acid lakes (22).

Results. Concentration in lakes was found to be pH-dependent (Fig. 9) but was not toxic (Table 3). Mn bioaccumulation was found in algae. No significant correlations of algal manganese with environmental variables were found, but there was a trend to increased algal manganese at low pH (Fig. 10).

Manganese, as expected, increased with decreased pH but was below potentially toxic concentrations in the lakes surveyed. Although the algal concentrations were very high (2), they showed no significant relationship with any of the environmental variables, with the possible exception of pH. There was a suggestion of a trend to increased algal manganese at lower pH, but this was not significant. The interest in manganese is currently in the context of bioavailability being an indicator of acidification; it may subsequently be shown to have toxic effects, or ameliorative effects in combination with other metals, but at present its significance to biota in acid lakes is unknown.

Aluminum

Predictions and Background Information. It was predicted that Al deposition is not controlled by human activities. Al is highly mobile in the terrestrial system,
and its solubility increases as pH decreases. Total Al concentration in water is expected to increase as lakes acidify. Al speciation is pH-dependent over the range pH 4–7. Al is of low toxicity (13).

**Results.** Al concentration in lakes was pH-dependent and toxic (Table 3). Al was found to bioaccumulate in algae. No significant correlations of algal aluminum with environmental variables were found.

Aside from supporting the prediction that decreasing pH results in increased aluminum which gives rise to potentially toxic concentration in lakes, the data do not provide any further insight into the importance of mechanism of aluminum bioaccumulation. Whereas fish are already known to be adversely affected by concentrations of aluminum which occur in acidic lakes (23), the effects of these elevated levels of aluminum on other aquatic biota is not documented except for experimental studies. Like manganese, aluminum reached extremely high concentrations in the algae in acidic lakes (2), but its accumulation showed no pattern. One explanation for this, and one which is being investigated, is that the apparent metal burden of the algae included metal external to the cell or cell wall proper, which was precipitated, coprecipitated or complexed outside the cell due to localized changes in pH in the vicinity of the algal cells.

**Mercury**

**Predictions and Background Information.** Hg deposition is expected to be increased by human activities. Mobility in the terrestrial system is unknown. Hg solubility is theoretically not increased as pH decreases. The total concentration of Hg in water possibly increases as lakes acidify but this has not been verified experimentally. Speciation is theoretically strongly pH-dependent over the range pH 4–7. Hg is highly toxic (13). Hg bioaccumulation in fish is increased in acidic lakes.

**Results.** It was found that Hg concentration in lakes is not pH-dependent and is below the toxic threshold (Table 3). Hg bioaccumulates in algae. Algal Hg is correlated with dissolved organic carbon (+), conductivity (−), in organic ions (−), P and N (−), and fish Hg (+). Some of these data for mercury have been described elsewhere (24). Levels in water are orders of magnitude lower than those of other metals. Nevertheless, because of its tendency to bioaccumulate in fish in acidic lakes, and because of its extreme toxicity, it is of perhaps greater concern than most other metals. The explanation whether increased deposition or simply mobilization, for the increased fish mercury in acidic lakes is still the subject of discussion although Lindqvist et al. (26) suggest that both factors are important.

The present study established that algae could bioaccumulate mercury to relatively high levels and that this was largely methylmercury (24). Algal mercury was positively correlated with dissolved organic carbon, presumably because methylation is stimulated by organic
matter, and negatively correlated with conductivity, inorganic ions and nutrients. This is in agreement with the observation that most oligotrophic lakes promote more mercury uptake by biota (27). Most interesting from a practical as well as a mechanistic viewpoint was the positive correlation between mercury in algae and mercury in yearling perch (25) from the same lakes.

Summary and Conclusions

In the context of acidification, the change in the concentrations in water and bioavailability of metals can be predicted relatively successfully. Zinc, manganese and aluminum increased as pH decreased; zinc and aluminum have reached potentially toxic concentrations in the surface waters surveyed, while manganese which is much less toxic has not. Zinc accumulation in algae decreased at low pH, even though the concentration of zinc increased, while manganese in algae showed a trend towards increasing at low pH. Aluminum in algae did not follow any pattern, but there may be technical problems.

Copper and nickel in water increased as pH decreased, and algal copper and nickel both increased as pH decreased or metal increased. These relationships were, however, driven by the factor of local loadings of nickel and copper from a smelter complex. The smelter also enhanced acidification; such confounding effects should be taken into account in studies of acidic lakes.

Lead in water showed no relationship with pH, but algal lead tended to increase as pH decreased. Mercury was low to undetectable in surface waters, yet algal mercury showed a number of significant correlations, notably with dissolved ions (negative), dissolved carbon (positive), and fish mercury (positive).

It is proposed that the attached algal community can provide a useful monitor for nickel and copper in polluted situations, and for zinc, lead and mercury in acid stressed lakes.

Metals of concern to biota in the context of acidification, omitting point sources of metals, are zinc, lead, aluminum and mercury. The situation for manganese is still unclear. The predictions (1) also included cadmium, but this metal was excluded from the present survey because of the very low to undetectable cadmium concentrations in most of the compartments and components measured.

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