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Lack of Bioaccumulation of Metals by *Elliptio complanata* (Bivalvia) During Acidic Snowmelt in Three South-Central Ontario Streams

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Episodic depression of stream pH coincidental with spring melt of acidic snow has been reported from most areas of the world receiving atmospheric deposition of anthropogenic acids (Overrein et al. 1980; Harvey et al. 1981). Associated with short-term depression of pH is a rapid increase in the concentration of metals, particularly aluminum and/or a shift in metal speciation (Driscoll et al. 1980; LaZerte 1984), primarily to more bioavailable inorganic forms (Borgman 1983). This rapid fluctuation of pH and/or metals (concentration and/or speciation) may impact biota before long-term gradual acidification is even detectable. Fish kills during the spring of 1979-81 in Plastic Lake, Ontario have been attributed to reduced pH and the associated elevated aluminum concentrations during snowmelt (Harvey and Lee 1982).

Depression of pH and elevation of metals during spring snowmelt may be widespread. However, because of the episodic nature of these events they are very difficult to measure or even detect. Sampling of snowmelt at regular intervals of only a few days, may not be adequate to detect short-term variations in pH and metal concentrations. The objective of the present study was to determine the feasibility of using biomonitoring to detect short-term changes in concentration or bioavailabilty of metals (Al, Zn, Cd) during spring snowmelt. Unionid clams, (*Elliptio complanata*) were held in three south-central Ontario streams during the spring snowmelt period of 1982. The gill tissues accumulate metals more readily than other tissues and thus are better biomonitors of available metals than whole body concentrations of these elements (V.-Balogh and Salanki 1984). Therefore, the concentration of metals in soft tissues (gill, body, foot) were compared separately to the stream water chemistry during snowmelt.

MATERIALS AND METHODS

Three streams in south-central Ontario were selected based on data collected in 1980-81 (P. Dillon, unpub. data): Harp Lake outflow,

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little or no pH depression; Plastic Lake inflow, a severe pH depression; Plastic Lake outflow, an intermediate pH depression. Fish kills during spring snowmelt have been reported in Plastic Lake between 1979 and 1981 (Harvey and Lee 1982). The location and characteristics of each watershed are described by LaZerte and Dillon (1984).

Elliptio complanata (Lightfoot) from 51.0-72.7 mm total length were collected on March 26, 1982 from Lake of Bays at Dorset, Ontario, (pH 6.2-6.8, spring 1982) using an Eckman dredge. Clams were collected from Lake of Bays because relatively large numbers were easily accessible in 2-4 m of water. Although *E. complanata* is common in most of central Ontario, it is not found in Plastic Lake and is found only in low numbers in Harp Lake (Rooke and Mackie 1984). On March 27, 20 clams were transferred to fiberglass mesh cages (0.6 x 0.3 x 0.3 m) held on the sediment in small pools in each stream. Five clams collected from Lake of Bays on March 27 and from each stream on April 21 (peak discharge) and May 20, were immediately frozen. Each clam was later separated from the shell and dissected into gill, foot and body (remaining soft tissue).

Whole soft tissue samples were freeze-dried, weighed then digested with 1 mL of perchloric acid and 3 mL of nitric acid. The nitric acid was evaporated off, cooled and the sample volume adjusted to 10 mL with deionized water. Samples were analyzed for total Al (D.C. emission spectrometry, Spectrospan 3B Spectrometrics; detection limit 2 ug/g), Zn and Cd (flame atomic absorption spectrometry, Varian AA-975; detection limit 1 ug/g). National Bureau of Standards, citrus leaves, standard material 1572 (92±15 ug/g) were determined to be 93.8 ug/g for Al. Tissue concentrations of each metal were compared ($P=0.05$) within and among dates (protected LSD procedure) using analysis of variance (Steel and Torrie 1980). Chemical analyses of water are described by Ontario Ministry of the Environment (1981) and the determination of the speciation of Al is described by LaZerte (1984).

RESULTS AND DISCUSSION

During snowmelt the pH in Plastic Lake outflow dropped rapidly from pH 5.8 to 4.8 within several days. Depression of pH lasted much longer in Plastic Lake inflow, such that the pH fell (from 4.8) to below 4.5 for several weeks while Harp Lake outflow had little or no depression of pH during snowmelt (Fig. 1A). The total Al concentration of water remained relatively constant, although at different levels, among the three streams, rising slightly only in Plastic Lake outflow during snowmelt (Fig 1C). Speciation of Al, however, shifted quickly from organic to inorganic monomeric forms during the peak of the pH depression in both Plastic Lake inflow and Plastic Lake outflow (Fig. 1D). The pH depression and increase in inorganic Al in both Plastic Lake outflow and Plastic Lake inflow corresponds closely with the peak discharge (April 18-20) in these streams (Lazerte 1984). Both Zn and Cd remained at or below the detection limits (2 ug/L) during snowmelt in all

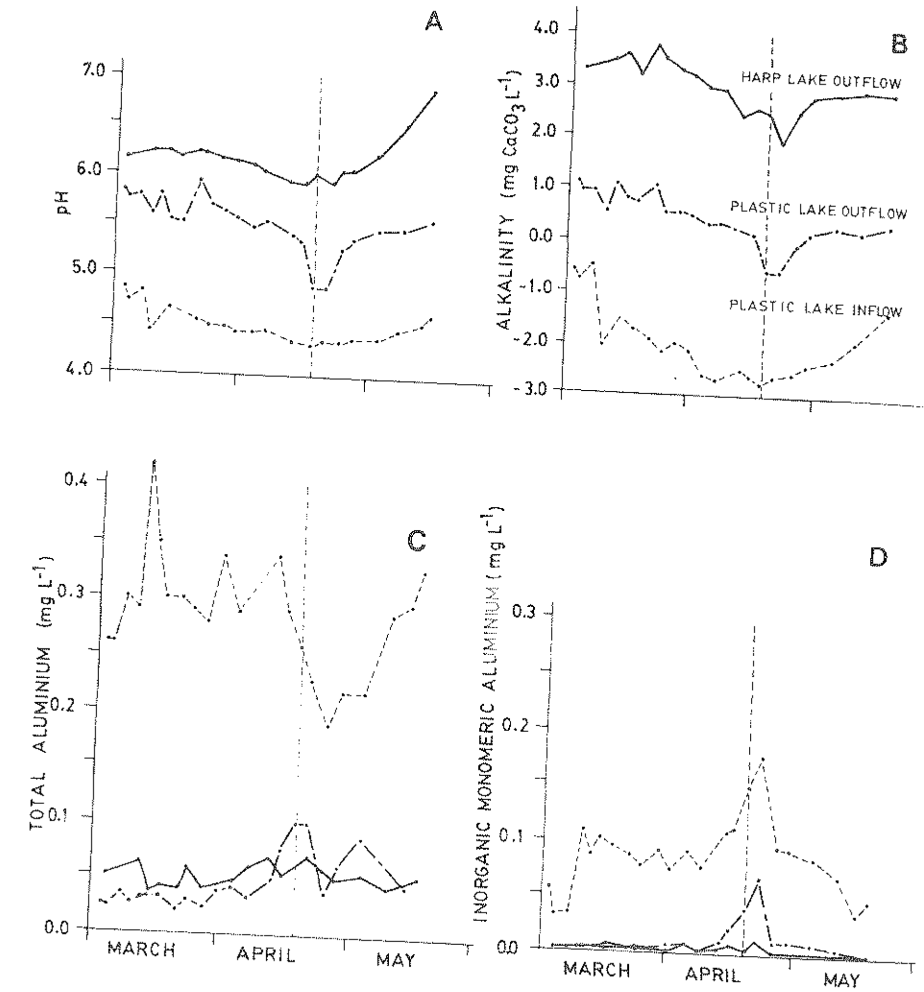
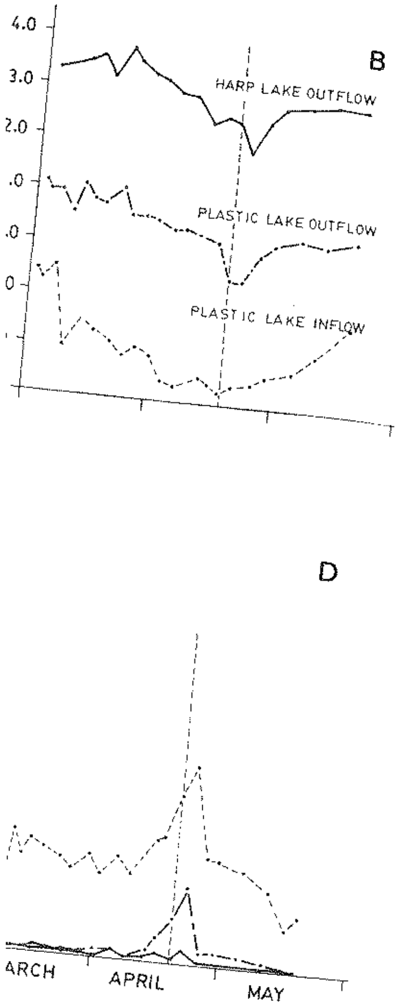


Figure 1. The pH (A), alkalinity (B), total aluminum (C), and total inorganic monomeric aluminum (D) in three south-central Ontario streams during spring snowmelt of 1982 (P. Dillon and B. LaZerte, unpub. data). Vertical lines represent April 18, 1982.

three streams.

The shift in speciation of Al to the inorganic monomeric forms (primarily aluminum fluoride complexes; LaZerte 1984), was not reflected in the concentration of Al in the soft tissues of Elliptio complanata. There was no increase in the concentration of metals (Al, Zn, Cd) in either gill or body tissues in any of the streams over time (Fig. 2). Although both Al and Cd concentrations in the foot tissue increased ($P<0.05$) with time, the concentrations of Al and Cd were not different between streams on



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any date sampled (Fig. 2). The tissue concentrations (gill, body, foot) of all three metals in Plastic Lake inflow or Plastic Lake outflow were equal to or less than Harp Lake outflow on all dates. The Al concentration in the body tissue was lower ($p<0.05$) in Plastic Lake inflow than in either Plastic Lake outflow or Harp Lake outflow on both April 21 and May 20. The Zn concentration in the body tissue on April 21 and in the gill tissue on May 20 in both Plastic Lake inflow and Plastic Lake outflow was lower ($p<0.05$) than in Harp Lake outflow (Fig. 2).

Most metals, including Al, are more bioavailable or toxic in the inorganic form, especially the free (hydrated) ion (Borgman 1983; Graney et al. 1984). Harvey and Lee (1982) attributed fish kills in Plastic Lake during spring snowmelt (1979-1981) to the combined toxicity of metals and reduced pH. Gills of dead or dying fish in Plastic Lake had elevated Al concentrations (H. Harvey, University of Toronto, Toronto, personal communication). However, clams in the present study, held in Plastic Lake inflow or Plastic Lake outflow, which reflected the water chemistry of the near shore areas of the lake, did not have increased Al in the gills or other tissues (Fig. 2).

Long-term acidification has resulted in increases in Zn and Cd in acidic lakes (Harvey et al. 1981). Short-term acidification could also result in similar mobilization of these metals. However, water concentrations of both Zn and Cd were below the detection limits during this study. Because bivalves can bioaccumulate both Zn and Cd, they could detect a shift in concentration or speciation of metals which was below detection limits for water. However, the concentrations of metals in the soft tissues of *E. complanata* in this study do not indicate a shift in the bioavailability of either of these metals during spring snowmelt.

The tissue metal concentrations in the reference clams collected from Lake of Bays were low or similar to other reported values for freshwater bivalves (Forester 1980; Jones and Walker 1979; Tessier et al. 1984). The initial concentrations of metals in the clams used in this study should not have limited or obscured uptake of metals during snowmelt. However, Jones and Walker (1979) found that the freshwater unionid clam, *Velesunio ambiguus*, was not a good short-term monitor of those metals naturally found in large permanent stores (i.e., Fe, Mn, Zn). Naturally occuring high initial concentrations of both Al and Zn (i.e., 100-500 ug/g) may obscure any small changes in concentration resulting from short-term exposure to elevated metal concentrations in the water during snowmelt. Although reduced pH may result in the mobilization and altered speciation of metals, the increase in H^+ concentration may reduce uptake and toxicity of metal ions (Graney et al. 1984; Borgman 1983; Campbell and Stokes 1985). Hydrogen ions may compete for a limited number of active binding sites on the outer gill membranes, therefore reducing the uptake of metals. Unless the concentration of available metals is increased sufficiently by mobilization or speciation, the decreased pH may actually lead to reduced metal concentations in biota. Low pH may

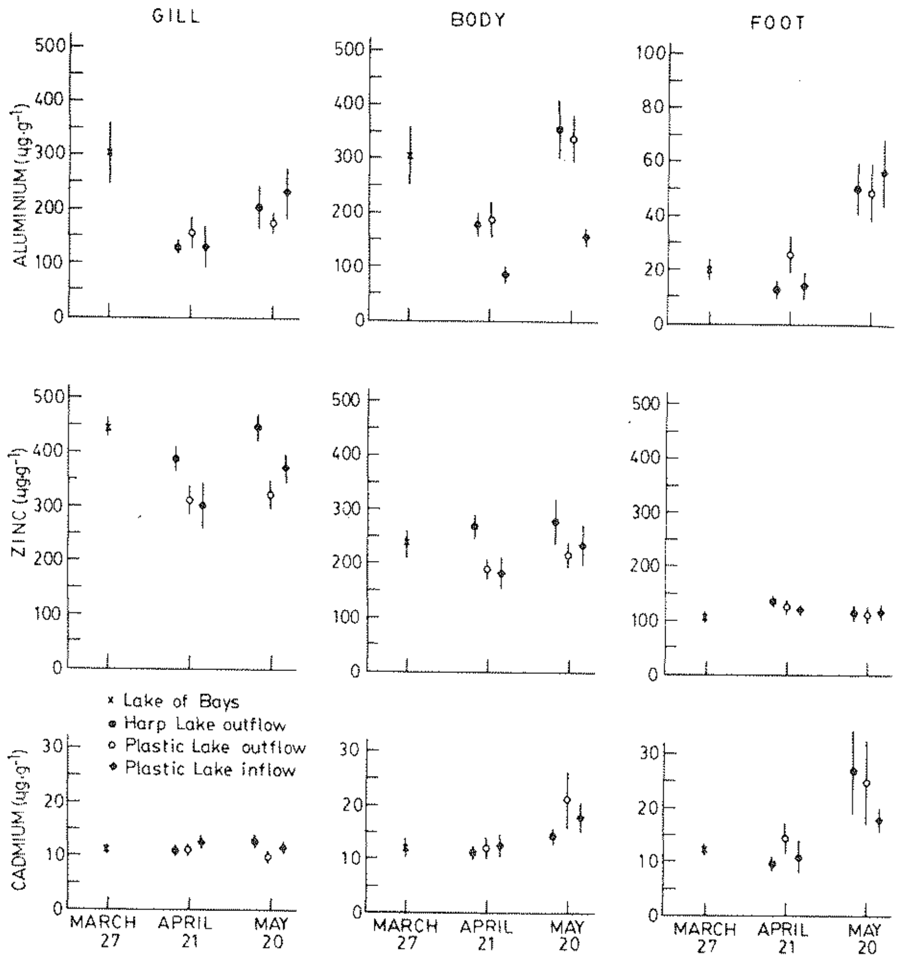
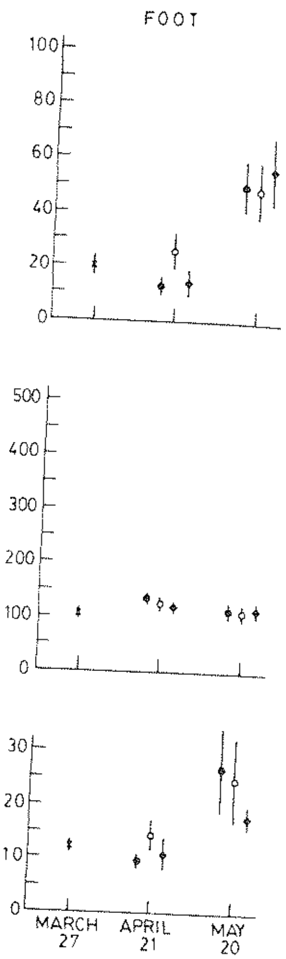


Figure 2. The mean concentration (dry weight) ± standard error of Al, Zn and Cd in soft tissues of <u>Elliptio</u> <u>complanata</u>. N=5 clams per sample.

also have a negative physiological effect (e.g., reduced respiration rates) on the organism resulting in reduced uptake of metals. This may partially explain the lower concentration of Al in the gill and body tissues in Plastic Lake inflow which had a pH below 5.0 over the course of this study.

Although clams were active in all three streams, low temperatures during snowmelt (0-4^{o}C) may also have limited bioaccumulation (Fig. 3). Low temperature reduces the metabolic activity and filtering rates of molluscs (Cairns <u>et al</u>. 1975) possibly reducing the uptake and toxicity of metals (Graney <u>et al</u>. 1984) <u>Elliptio</u>



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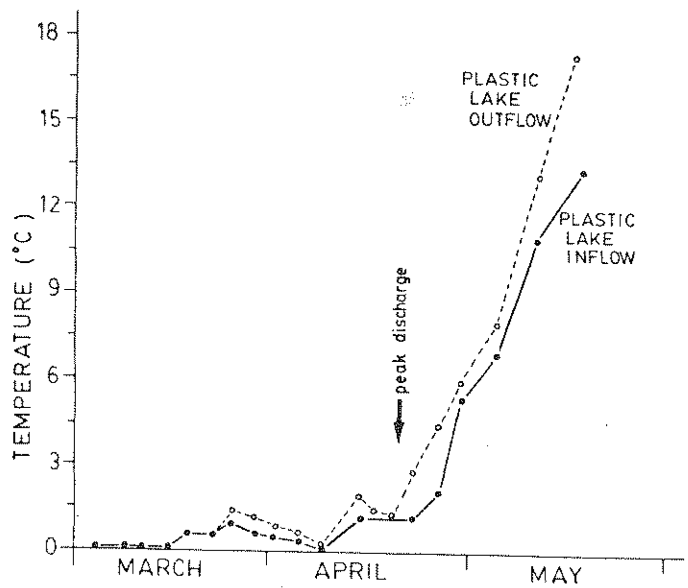

Figure 3. Temperature (mid day) in Plastic Lake outflow and Plastic Lake inflow during the spring of 1982.

complanata may also be inefficient at accumulating metals at low temperature and may therefore be poor indicators of short-term fluctuations of available metals during snowmelt.

Elliptio complanata and other unionid clams are very effective monitors of contamination of aquatic environments when exposed for longer periods of time, especially in association with sediments (Forester 1980; Tessier et al. 1984). Bivalves may be useful to monitor and integrate the biological availability of metals in acidifying lakes over extended periods of time. In this study E. complanata did not differentially bioaccumulate Al, Zn, or Cd in soft tissues from any of the three streams. Therefore, E. complanata did not provide a practical tool to monitor the concentration or speciation of Al (Zn or Cd) during these episodic events.

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