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A Biomonitor for Tracking Changes in the Availability of Lakewater Cadmium over Space and Time

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ABSTRACT

Determining the exposure of organisms to contaminants is a key component of Ecological Risk Assessments (ERAs). Effective estimates of exposure consider not only the total concentrations of contaminants in an organism's surroundings but also the availability of the contaminants to organisms. Contaminant availability can be inferred from mechanistic models and verified by measurements of contaminant concentrations in organisms. We evaluated the widespread lake-dwelling insect *Chaoborus* as a potential biomonitor for use in exposure assessments for three metals: cadmium (Cd), copper (Cu), and zinc (Zn). We show that larvae of this midge maintain constant their concentrations of the essential metals Cu and Zn and thus cannot be used to monitor them. In contrast, larval Cd concentrations varied widely both among lakes and in a given lake over time. We were able to relate these variations in biomonitor Cd to changes in lakewater Cd and pH using the Free Ion Activity Model (FIAM). Our results suggest that *Chaoborus* larvae could be used as an effective tool for estimating the Cd exposure of organisms in lakes for the purposes of ERAs.

Key Words: metal, Cd, bioaccumulation, biomonitor, ERA, lakes.

INTRODUCTION

A key goal of Ecological Risk Assessments (ERAs) is to evaluate the exposure of organisms to contaminants (Chapman *et al.* 2003; Campbell *et al.* 2006). In lakes, exposure is often evaluated by measuring the total concentration of a contaminant in sediment or water, in spite of the fact that only a portion of this total is available for uptake by organisms (Hare *et al.* 2003). A more direct way to evaluate exposure is to measure contaminants in organisms, that is, to use them as biomonitors (Phillips and Rainbow 1993).

The ideal biomonitor should be tolerant to metals, acidity, and other physicochemical variables so that it can be collected from the widest possible range of lakes,

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Figure 1. The aquatic larva (uppermost) of *Chaoborus*, in which the insect spends the majority of its life, and the aquatic pupal stage (lower right) during which larval tissues are reorganized to create the sexually mature aerial male adult (lower left). Redrawn from Johannsen 1937 (larva and pupa) and Cook 1981 (adult).

including those that are heavily contaminated. Among the myriad of lake-dwelling organisms, the phantom midge *Chaoborus* (Figure 1) fits this requirement well. Larvae of this non-biting fly can be found in lakes that encompass a wide range of hardness ([Ca] of 30–2000 μ mol L⁻¹), temperature (4–32°C), and metal concentrations (total dissolved (nmol L⁻¹) [Cd] 0.1–20, [Cu] 5–1700, [Zn] 1–5000) (Hare and Carter 1987; Croteau *et al.* 1998). Especially noteworthy is the wide range in pH (4–9) that is tolerated by *Chaoborus* larvae, both because metal-contaminated emissions are often very acidic and because many potential biomonitors (mollusks, crustaceans and fish) are absent from highly acidic waters (Økland and Økland 1986).

An ideal biomonitor should also be widespread, easy to collect, large enough to allow contaminant measurements, and identifiable to species. *Chaoborus* larvae meet these criteria well because: they are found on all continents except Antarctica; they are easy to collect, either in the sediment during the day (migratory species) or in the water column at night (Croteau *et al.* 2003a); they are large enough to permit metal measurements on individuals (Croteau *et al.* 2002c); and they are easily identified to the species level (Saether 1972), which is not the case for most aquatic insect larvae but which is important because species differences in contaminant accumulation could confound exposure evaluations (Croteau *et al.* 2003a; Buchwalter and Luoma 2005). Lastly, an ideal biomonitor should have a limited capacity to regulate the uptake and loss of metals (Rainbow 2002), such that its metal concentrations vary in a predictable way with those in its surroundings (*e.g.*, water, sediment, or food particles).

We set out to determine if the insect *Chaoborus* can be used as a biomonitor to estimate metal exposure in lakewater for the purposes of ERAs. Specifically, we collected *Chaoborus* larvae and water from a series of lakes and used the precepts of the Free Ion Activity Model (FIAM) to determine if we could relate Cd, Cu, and Zn concentrations in this insect to those of the free ions of these metals in lakewater. The FIAM states that the concentration of unbound metal (the free metal ion) is a better predictor of metal bioaccumulation and toxicity than is the total concentration of the metal to which an organism is exposed (Campbell 1995). Although this model has been tested with success in simple laboratory media, the goal of ERAs is to estimate contaminant exposure in the field. We ask if the FIAM can be used to predict metal exposure in the complexity of nature. We used the chemical speciation code WHAM (Windermere Humic Aqueous Model; Tipping 1994, 2002) along with measurements of total dissolved metals, pH and ligands in lakewater to estimate free metal ion concentrations in lakewater; at present, there are few proven methods for measuring free metal ion concentrations at natural levels in lakewater.

METHODS

We collected water samples and larvae of *Chaoborus* from lakes in Ontario and Québec, Canada, from year 1987 to 2000. A complete list of the lakes, their chemical characteristics and sampling dates are given in Hare and Tessier (1996, 1998) and Croteau *et al.* (1998, 2002b). Lakes near Sudbury (Ontario) and Rouyn-Noranda (Québec) have historically been contaminated by acidic and metal-rich atmospheric emissions from nearby smelters, although design changes in the late 1900s have led to dramatic reductions in the quantity of contaminants that they emit to the atmosphere (Gunn 1995; Croteau *et al.* 2002b). Lakes in areas distant from these mining activities were influenced only by weathering processes, local domestic sources (cottages), and long range atmospheric transport.

Chaoborus larvae were collected from each of the lakes at about the same time of year (in late May or early June, shortly after ice-off) to minimize possible differences in their age and metal-exposure history. For example, Cd concentrations in final instar Chaoborus punctipennis larvae are reported to be higher by a factor of ≈ 2 in summer than in winter (Hare and Campbell 1992). Larvae were collected either during the daytime, from littoral sediments (using an Ekman grab), or shortly after sunset, from the water column (using a plankton net). Collecting larvae in the water column has the advantage that larvae do not need to be sorted from sediments. In the laboratory, living larvae were sorted according to species (Saether 1972) and instar (Carter and Kwik 1977). We chose only fourth (final) instar larvae for study in order to minimize age and size related differences and to maximize the size of larvae for metal measurements. For samples collected prior to 1998, we held larvae in lake water for ≈ 1 d to defecate their gut contents. However, because gut contents were found to have no measurable influence on larval metal concentrations (Croteau et al. 2001), we abandoned this procedure in subsequent years. To minimize inadvertent metal contamination, we soaked all labware in 15% nitric acid and then rinsed it repeatedly with ultrapure water prior to use. Individuals of a given species were pooled and placed on a piece of acid-washed Teflon sheet for drying and weighing.

Because our goal was to study lake to lake variations rather than individual larval differences, we generally pooled up to 20 individuals for a single sample and made 3 to 5 such replicates of each *Chaoborus* species for each lake.

Lakewater was collected at each sampling site in PlexiglasTM diffusion samplers (Croteau *et al.* 1998) filled with ultrapure water and separated from lake water by a 0.2 μ m nominal pore-size polysulfone membrane (Gelman HT-200). Samplers were fixed in place either by anchoring them in the sediment (for 2 weeks) or by suspending them in the water column (for 3 days) near the collection site for larvae in each lake. Samplers were retrieved and water was removed for the measurement of pH, inorganic and organic carbon, major ions and trace metals following the procedures described in Croteau *et al.* (1998) and Hare and Tessier (1998). Values for each lake are generally the means for 10–15 water samples.

We measured total dissolved trace metal concentrations by flameless atomicabsorption spectrophotometry (AAS) (THGA graphite tube atomiser, Perkin-Elmer model SIMAA 6000). Certified reference riverine water samples (National Research Council of Canada -NRCC; SLRS-4, 1643d) were analyzed during each analytical run and measured trace metal concentrations were within the certified range. Detection limits for Cd and Zn were ≈ 1 nmol L⁻¹, whereas those for Cu were ≈ 15 nmol L⁻¹. We measured major cations by flame AAS (Varian model Spectra AA-20), major anions by ion chromatography (Dionex AutoIon, system DX300), dissolved inorganic carbon by gas chromatography (Hewlett-Packard GC 5890 Series 2), and dissolved organic carbon using a total organic carbon analyser (Shimadzu, TOC-5000A) by the combustion-infrared method. Concentrations of free metal ions, [M²⁺], were estimated using the above measurements and the Windermere Humic Aqueous Model version 1.0 (Tipping 1994) with the assumptions discussed in Croteau *et al.* (1998).

Dried insects were digested in concentrated nitric acid (100 μ L acid per mg sample dry weight). Digestions were carried out either in Teflon bombs in a microwave oven (pre-1998) or at room temperature in 4-mL high-density polyethylene vials for 7 d (post-1998). In the latter case, hydrogen peroxide (40 μ L mg⁻¹ dw) was added 24 h prior to final dilution with ultrapure water (860 μ L mg⁻¹ dw). Cooled, digested samples were diluted to volume with ultrapure water. We submitted samples of similar weight of a certified reference material (lobster hepatopancreas, Tort 1, National Research Council of Canada, Ottawa, ON) to the same digestion procedure during each run; values were comparable for the two methods used. Cadmium and copper concentrations in animals were measured by flameless AAS (Varian model Spectra AA-30). Zinc in animals was measured by flame AAS (Varian model Spectra AA-20). Trace metal concentrations measured in the reference material were within the certified range and the recovery of metals in spiked samples was within 10% of the amounts added.

RESULTS AND DISCUSSION

Copper and zinc are components of several metallo-enzymes, such as cytochromec oxidase (Cu) and carbonic anhydrase (Zn). Although these metals can be toxic when in excess, their concentrations in cytoplasm tend to be tightly controlled because they are essential (Rainbow 2002). As shown in Figure 2, concentrations of



Figure 2. Mean $(\pm$ SD) concentrations of the essential elements Cu and Zn in larvae of *Chaoborus punctipennis* versus those of the free ions of these metals in water collected from a series of eastern Canadian lakes.

these metals in *Chaoborus* were similar across a wide range of Cu and Zn concentrations in lakewater. Thus, this insect cannot be used to monitor Cu and Zn concentrations in lakewater. Similar results have been reported for some freshwater crustaceans (Amyot *et al.* 1994; Borgmann 1998), but there is evidence that some freshwater plants (Campbell *et al.* 1985; Holding *et al.* 2003), mollusks (Tessier *et al.* 1984; Pyatt *et al.* 2003), and other insects (Bervoets *et al.* 1996; Tochimoto *et al.* 2003) do not maintain their whole body concentrations of Cu and Zn constant and thus have potential as biomonitors for these metals. These differences among organisms likely result from the manner in which a given species manages metals, that is, either by controlling their uptake or loss (or both) or by storing excess metal in detoxified forms such as granules (Hare 1992; Rainbow 2002; Campbell *et al.* 2005).

In contrast to Cu and Zn, concentrations of the non-essential metal Cd varied by more than an order of magnitude among *C. punctipennis* larvae from the various lakes (from 0.2 to 13.3 μ g g⁻¹, Figure 3). This capacity of *Chaoborus* larvae to accumulate Cd in contaminated lakes, and yet survive, is likely due to its ability to produce the metal-binding protein metallothionein. Indeed, there is a direct relationship between Cd concentrations in this insect and those of metallothionein-like metalbinding proteins in its cells, which suggests that Cd induces this protein's synthesis beyond the concentrations required for normal metabolic use (Croteau *et al.* 2002a). The wide range in Cd concentrations measured in *C. punctipennis* suggests that this insect could be used to monitor Cd in lakewater. However, to determine if this is so we need to demonstrate that Cd concentrations in *Chaoborus* are related in a predictable way to those in its surroundings rather than being the result of factors intrinsic to the insect.



Figure 3. Mean (\pm SD) concentrations of the non-essential metal Cd in larvae of *Chaoborus punctipennis* versus those of the free Cd ion (upper panel) or the free-Cd ion corrected for competition with H⁺ at biological uptake sites (middle panel). In the lower panel, the data for *C. punctipennis* (middle panel) are augmented by adding those for 3 other *Chaoborus* species. Open symbols represent lakes having a pH > 5.5, whereas closed symbols refer to lakes of pH < 5.5.

We first compared Cd concentrations in *Chaoborus* to those in sediment (data not shown) because this is the place where migratory *Chaoborus* species spend the daylight hours to avoid predation by fish. Of the four species that we collected (Figure 3), only *Chaoborus americanus* does not take refuge in sediment since it lives in lakes lacking fish (Croteau *et al.* 2003a). We found no significant correlations between Cd concentrations in sediment and those of any *Chaoborus* species (Hare and Tessier 1998). This lack of a relationship is likely explained by the fact that while in sediment *Chaoborus* larvae remain immobile below the oxic-anoxic boundary (Gosselin and Hare 2003) and do not feed (Croteau *et al.* 2003a). In fact, because they take up Cd only from prey in the water column (Munger and Hare 1997; Munger *et al.* 1999) it is not surprising that their Cd concentrations are not correlated with those in sediment.

Because all *Chaoborus* species spend some of their time in the water column, we then compared Cd concentrations in *C. punctipennis* to those of the free Cd ion in

lakewater (upper panel in Figure 3). There is no significant correlation (p > .05) between these two variables for the whole of the dataset. However, when lakes are discriminated according to their pH, there is a very strong ($r^2 = 0.92$) and significant (p < .001) relationship for *C. punctipennis* collected from the circum-neutral lakes (pH > 5.5, open symbols in the upper panel of Figure 3). Thus, knowing Cd concentrations in this insect would allow us to rank circum-neutral lakes according to their Cd exposure level. To predict free Cd ion concentrations in lakewater for comparison with other species and biological endpoints, we can use Cd concentrations measured in the biomonitor in a model based on the FIAM and derived from our data set;

$$Cd]_{Chaoborus punctipennis} = F_{Cd}[Cd^{2+}]$$
(1)

where F_{Cd} is a proportionality constant between the concentrations of Cd in *C.* punctipennis ([Cd]_{Chaoborus punctipennis}, $\mu g g^{-1}$) and those of the free Cd ion ([Cd²⁺], nmol L⁻¹). The value of F_{Cd} (\pm SE) for the circum-neutral lakes in our dataset is the slope of the relationship between the two variables, that is, $\approx 7.7 \pm 0.5 \ \mu g g^{-1} L$ nmol⁻¹ (the y intercept is not significantly different from 0).

We expanded Equation (1) to include highly acidic lakes, which are common in areas subject to industrial inputs (Gunn 1995), by assuming that H ions are able to out-compete Cd ions at Cd-uptake sites on organisms, which leads to the low Cd concentrations measured in *C. punctipennis* (Croteau *et al.* 2003a,b; Orvoine *et al.* 2006) from highly acidic lakes (Figure 3, upper panel, closed symbols). A series of assumptions (summarised in Croteau *et al.* 1998) yields Equation (2),

$$[Cd]_{Chaoborus \cdot punctipennis} = F_{Cd-H} \frac{[Cd^{2+}]}{[H^+] + K_a}$$
(2)

where K_a is equilibrium constant for the reaction of H ions at Cd-uptake sites and F_{Cd-H} is a proportionality constant. Using our data for lakes of all pHs in Equation (2), we found that Cd concentrations in *C. punctipennis* were strongly correlated with $[Cd^{2+}] / ([H^+] + K_a)$ (Figure 3, middle panel; $r^2 = 0.78$, p < .001) where the value of F_{Cd-H} (the slope) is $18,000 \pm 1,700 \ \mu g \ g^{-1}$ and that of K_a is 8×10^{-7} mol L^{-1} (as estimated by least-squares optimization). Our estimate of K_a is similar to the binding site affinity reported for Cd with fish gills (2×10^{-7} to $8 \times 10^{-7} \ mol \ L^{-1}$; Playle *et al.* 1993). Overall, this result suggests that *C. punctipennis* could be used to monitor Cd exposure in lakes ranging in pH from approximately 4.5 to 7.5.

To further expand (and simplify) the use of *Chaoborus* as a Cd biomonitor, we combined our data for *C. punctipennis* with those for three other *Chaoborus* species and re-estimated the values for the model constants (Figure 3, lower panel). The model predicted Cd concentrations in the biomonitor well ($r^2 = 0.70$, p < .001; $F_{Cd-H} = 9500 \pm 880 \ \mu g \ g^{-1}$, $K_a = 8 \times 10^{-7} \ mol \ L^{-1}$) when the four *Chaoborus* species were considered together, which suggests that this model would be reliable even if *Chaoborus* species were pooled for metal analyses.

The aforementioned data augur well for using *Chaoborus* to monitor Cd exposure in lakes located along a spatial gradient in Cd concentrations. Because contaminant inputs to lakes near Canadian smelters have declined over the last several decades (Gunn 1995; Croteau *et al.* 2002b), we also tested whether *Chaoborus* larvae would be



Figure 4. Changes in lakewater pH (upper panel), free Cd ion concentrations (middle panel), and Cd concentrations in larvae of *C. punctipennis* (lower panel) collected at two times approximately a decade apart. Lakes are ordered according to their initial pH. Stars represent model predictions using Eq. (2) (see text).

effective as biomonitors of temporal changes in Cd by revisiting, after approximately a decade, lakes located near metal smelters in Rouyn-Noranda (QC) and Sudbury (ON). As shown in Figure 4, pH had increased in most lakes (uppermost panel), whereas Cd²⁺ concentrations had declined in all lakes (middle panel), with the greatest changes being measured in lakes that were formerly most highly acidic. Although these Cd²⁺ decreases were undoubtedly a result of reduced inputs from the nearby smelters, they were also likely related to the increase in lakewater pH; with increasing pH, Cd sorbs more strongly onto particles that subsequently settle out from the water column and more-readily forms complexes with dissolved ligands (Sigg 1987).

When we measured temporal changes in Cd concentrations in *C. punctipennis* (Figure 4, bottom panel), we found that while they had either declined or shown

negligible change in seven of the nine lakes, they had actually *increased* over time in 2 of the most highly acidic lakes (pH initially <5), despite substantial *decreases* in $[Cd^{2+}]$ (Figure 4, middle panel). We used Equation (2) to predict the effect of these concomitant changes in pH and Cd²⁺ on Cd concentrations in the biomonitor (as indicated by the stars in the lower panel of Figure 4). Overall, there was reasonable agreement between our measured and modeled values ($r^2 = 0.56$, p < .001). For example, in the four lakes in which [Cd] *Chaoborus* declined markedly (initial pHs of 5.8, 6.5, 6.7, 7.2), the model predicts these changes, as it does for the direction of change for the 2 lakes in which [Cd] *Chaoborus* increased over time (initial pHs of 4.5 and 4.8). However, the magnitude of modeled and measured values differs for the lake having an initial pH of 4.8 as well as for the 3 lakes in which there was little change over time (initial pHs of 4.7, 5.9, 6.9); that is, the model predicts larger increases in [Cd] *Chaoborus*.

Differences between measured and predicted values (Figure 4, lower panel) are likely related to the fact that *Chaoborus* larvae take up their Cd from prey rather than from lakewater (Munger et al. 1997, 1999) and thus the relationships described by Equations (1) and (2) are indirect. As a result, Cd and H ions likely compete for Cd-uptake sites not on Chaoborus but on organisms at lower trophic levels and the effect of reduced Cd uptake by phytoplankton and zooplankton is transferred up the food chain to Chaoborus. We tested this hypothesis in the laboratory using copepods, a common prey of Chaoborus (Fedorenko 1975; Hare and Carter 1987). We discovered that copepods take up Cd from water ($\approx 60\%$) and that their Cd uptake is correspondingly suppressed at low pH (Orvoine et al. 2006). Yan et al. (1990) have also reported that Cd concentrations are low in the zooplankton of highly acidic lakes. We then determined that the transfer of Cd from copepods to *Chaoborus* is efficient; indeed, $\approx 50\%$ of a copepod's Cd is assimilated by this predator (Orvoine et al. 2006). These results suggest that suppression of Cd uptake in the food chain leading to Chaoborus can explain the low Cd concentrations measured in this predator in highly acidic lakes. Because prey Cd concentrations determine those in Chaoborus, temporal changes in prey species composition and abundance will likely influence [Cd] Chaoborus. Such changes in plankton communities do occur in lakes recovering from acidification and metal contamination (Keller and Yan 1991; Nicholls et al. 1992; Gunn 1995), and they are likely to reduce the predictive power of Equation (2).

Because model predictions are not perfect, we can ask the question: Are we satisfied in explaining the majority of the variation between Cd concentrations in our biomonitor and those in lakewater? In the context of exposure assessment for ERAs, the answer to this question is likely yes. To improve the model we would likely have to both improve our estimates of $[Cd^{2+}]$ as well as make the model more complex by taking into account differences in plankton communities among lakes. However, making the model more complex would likely deter the average user whose goal is simply to rank lakes according to a biologically meaningful scale of Cd contamination. In practice, considering differences in plankton communities would not be simple; attempts to relate Cd concentrations in *Chaoborus* to those in various size fractions of zooplankton have proven difficult and strong correlations are obtained only when Cd concentrations are measured in individual prey types that are known to be consumed by the predator (Croteau *et al.* 2003b). Sorting bulk zooplankton





Figure 5. Temporal changes in Cd concentrations in *Chaoborus punctipennis* (solid lines) and *Chaoborus americanus* (dashed lines) exposed to dietborne Cd at either 5°C or 22°C. Model curves were obtained using the parameters and Eq. (4) presented in Croteau et al. (2002c).

samples to perform prey Cd analyses would clearly be beyond the reach of most biomonitoring programs!

One advantage of using biomonitors is that they integrate changes in contaminant concentrations over time (Phillips and Rainbow 1993). For example, Cd concentrations in large freshwater bivalves integrate those in their surroundings over a period of a year or more (Couillard et al. 1995). This begs the question: How long does it take Cd concentrations in Chaoborus larvae to reach an apparent steady state? To answer this question, we used a dynamic bioaccumulation model (Croteau et al. 2002c; Luoma and Rainbow 2005) that includes terms for both Cd uptake (including Cd concentrations in prey, prey ingestion rates, and Cd assimilation efficiency) and Cd loss (physiological loss and dilution due to animal growth). The result of this modeling exercise suggests that Cd concentrations in Chaoborus would reach a steady state with those of its surroundings within a time frame of several weeks to months depending on the temperature and the species involved (Figure 5). It is interesting to note that larval Cd concentrations at steady state tend to be greater at higher temperatures, in part because prey ingestion rates and Cd assimilation efficiency increase with increasing temperature (Croteau et al. 2002c). Furthermore, a steady state in Cd concentrations tends to be reached sooner at higher temperatures for migratory species such as C. punctipennis (because its rate constants for growth and Cd loss are greater at higher temperatures, Croteau et al. 2002c); however, this is not the case for non-migratory species such as C. americanus (Figure 5).

Although model simplicity is a virtue, the result of the modeling exercise (Figure 5) shows that the complexity of biodynamic models (Luoma and Rainbow 2005, Goulet *et al.* 2007) is warranted if we need to answer mechanistic questions about the biomonitor to optimize its rational application. Such models have also proven useful for

explaining differences in Cd concentrations among *Chaoborus* species (Croteau *et al.* 2001) as well as for determining the route of entry of metals into *Chaoborus* larvae (Munger and Hare 1997; Munger *et al.* 1999).

CONCLUSION

Because Cd can be highly toxic (Borgmann *et al.* 2004) and because it is released into the environment by numerous human activities (Chapman *et al.* 2003), a means of ranking lakes according to their potential for Cd exposure and toxicity would be useful for the purposes of ERAs. Our data suggest that *Chaoborus* is a good biomonitor for Cd, but not for the essential metals Cu and Zn. We recommend that it be tested as a biomonitor for other trace elements such as Co, Hg, Ni, Se, and Tl. Although other organisms might also fit the bill as Cd biomonitors in lakes (*e.g.*, the amphipod *Hyalella azteca* in circum-neutral lakes; Stephenson and Mackie 1988), there are few for which the necessary work has been done to show that their metal concentrations are indeed correlated with those in their surroundings and even fewer that have harnessed the predictive power of mechanistic-type models that have the potential for predicting metal bioaccumulation in nature (Pace 2001; Luoma and Rainbow 2005). We suggest that the type of mechanistic models described in this article provide a promising means for developing biomonitors for metals in aquatic systems.

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