

Increases in Food Web Cadmium following Reductions in Atmospheric Inputs to Some Lakes

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We measured the toxic metal cadmium (Cd) over a 13-year interval in lakes located near two metal smelters to determine whether reductions in atmospheric Cd emissions have led to reductions in the Cd present in aquatic food webs. Although Cd in the lake water consistently declined over time, Cd in animals increased in some lakes. This apparent contradiction was explained when we considered the simultaneous reductions that have occurred in lake water acidity; under these conditions, animal Cd can increase if there are insufficient hydrogen ions to out-compete Cd ions at biological uptake sites. We conclude that the risk to organisms from metals has increased in some lakes recovering from smelter emissions.

Introduction

Awareness of the negative environmental impacts of atmospheric emissions from metal smelters has spurred costly increases in stack heights and changes in operations that have led to declines in the quantities of acid and metals reaching nearby lakes (1). Such declines have led to the partial recovery of animal communities in many impacted lakes (2–4). Recovery has likely been due to simultaneous declines in lake water acidity and the concentrations of toxic metals (4), although data on key metals such as Cd are lacking. To fill this void, we collected water from nine lakes located in the vicinity of two Canadian metal smelters to determine whether reductions in the acidity and the Cd content of atmospheric emissions were reflected in lake water. To determine if declines in lake water Cd have led to corresponding decreases in the exposure of aquatic organisms to this metal (5), we measured Cd in larvae of the phantom midge *Chaoborus punctipennis*. We chose this insect because it meets many of the criteria for an effective pollutant monitor (adequate size, easily identified, and widely distributed; 6) and because its Cd concentrations can be related to those in lake water using a theoretically based model (6–8).

Methods

Collection of Field Samples. Water samples and insect larvae were collected from a series of lakes in springtime (May–June) in the Sudbury and Rouyn-Noranda areas on several occasions between the years 1987 and 2000 (Table 1). Samples were collected from all lakes at the same time of year to minimize possible differences in the age and Cd-exposure history of larvae from the various lakes. Study lakes were

TABLE 1. Locations of the Lakes Sampled in the Present Study

lake	code	region	location
Bousquet	BO	Rouyn-Noranda, Québec	48°14'N, 78°43'W
Caron	CA	Rouyn-Noranda, Québec	47°56'N, 78°58'W
Clearwater	CL	Sudbury, Ontario	46°22'N, 81°03'W
Crooked	CK	Sudbury, Ontario	46°25'N, 81°02'W
Crowley	CW	Sudbury, Ontario	46°23'N, 80°59'W
Marlon	MA	Rouyn-Noranda, Québec	48°16'N, 79°04'W
Tilton	TI	Sudbury, Ontario	46°22'N, 81°04'W
Vaudray	VA	Rouyn-Noranda, Québec	48°07'N, 78°42'W
Wavy	WA	Sudbury, Ontario	46°17'N, 81°06'W

subject to relatively high atmospheric acid and metal deposition from nearby smelters (9–10).

Chaoborus punctipennis larvae were collected using either an Ekman grab sampler during the day or a 250- μ m plankton net at night. We maintained live insects at field temperatures during their transportation to the laboratory in plastic bags filled with lake water. In the laboratory, we identified *C. punctipennis* using the keys in Saether (11), and final (fourth) instar larvae were selected on the basis of head capsule lengths as given in Larow and Marzolf (12). For samples collected before 1998, larvae were held in filtered lake water for 24 h prior to metal analysis to allow them to defecate their gut contents. Where larval numbers permitted, 5–20 individuals were pooled (to minimize potential individual variations in Cd) and placed on a piece of preweighed acid-washed Teflon sheeting that was frozen until analysis. For samples collected after 1998, undepurated larvae of *C. punctipennis* were placed individually on pieces of preweighed acid-washed Teflon sheeting and frozen. For these samples, larvae were not given time to defecate their gut contents because Croteau et al. (13) showed that there was no significant difference in Cd concentrations between larvae that were allowed to eliminate their gut contents for 24 h and those that were not.

Water for chemical measurements was collected in the littoral water column using diffusion samplers (8) that were either suspended from the lake surface (1997–2000) or anchored in sediment (1987–1993). Samples for measurements of pH, organic and inorganic carbon, major ions, and trace metals were removed following the procedure and materials described in Croteau et al. (8) and in Hare and Tessier (6). Values for each lake are generally the means of measurements in 10–15 samples.

Analyses. To minimize inadvertent trace metal contamination, we soaked all labware and sampling materials in 15% nitric acid and rinsed them in ultrapure water prior to use.

We measured total dissolved Cd concentrations by flameless atomic-absorption spectrophotometry (AAS) (THGA graphite tube atomizer, 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 the measured trace metal concentrations were within the certified range. We measured major cations by flame AAS (Varian model Spectra AA-20), major anions by ion chromatography (Dionex Autolon, system DX300), dissolved inorganic carbon by gas chromatography (Hewlett-Packard GC 5890 Series 2), and dissolved organic carbon using a total organic carbon analyzer (Shimadzu, TOC-5000A) by the combustion–infrared method. Concentrations of the free Cd ion, [Cd²⁺], were estimated using the above measurements and the Windermere humic aqueous model (WHAM 1.0; 14) with the assumptions discussed in Croteau et al. (8).

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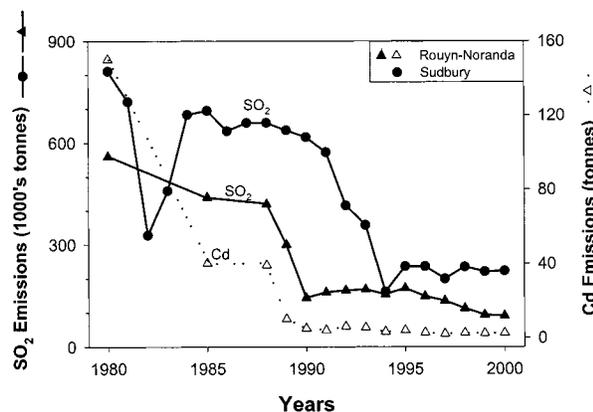


FIGURE 1. Temporal changes in annual atmospheric emissions of SO₂ (solid symbols) and Cd (open symbols) from 2 Canadian metal smelters between the years 1980 and 2000 (data courtesy of INCO (Sudbury) and Noranda Mines (Rouyn-Noranda)).

Chaoborus larvae were freeze-dried (FTS Systems), weighed on a micro-balance (Mettler ME30), and digested in concentrated nitric acid (100 $\mu\text{L mg}^{-1}$ d.w.; Aristar grade). For samples collected before 1998, we carried out digestions in thick-walled, screw-cap Teflon vials in an autoclave at 120 °C for 3 h. Cooled digested samples were diluted to volume with ultrapure water. For samples collected after 1998, we conducted digestions at room temperature in 4-mL HDPE vials for 7 d. Hydrogen peroxide (40 $\mu\text{L mg}^{-1}$ d.w.) was added 24 h prior to final dilution with ultrapure water (760 $\mu\text{L mg}^{-1}$ d.w.). We submitted samples of similar weight of a certified reference material (lobster hepatopancreas, TORT-1, NRCC) to the same digestion procedure during each run; values were comparable for the two digestion methods used. Cadmium concentrations in animals were analyzed by flameless AAS (Varian Spectra AA-30); Cd concentrations measured in the reference material were within the certified range, and the recovery of Cd in spiked samples was within 10% of the amounts added.

Results and Discussion

During the 1980s and 1990s sulfur emissions declined substantially from the Sudbury and Rouyn-Noranda metal smelters (Figure 1). We observed consequential increases in the pHs (Figure 2A, Table 2) of the 5 initially acidic lakes (pH < 6), which increased by up to 1.5 units during our study period (1987–2000). In a similar manner, reductions in the Cd content of smelter emissions (Figure 1) were paralleled by consistent declines in lake water Cd that were especially marked in acidic lakes (Figure 2B, Table 2). Concomitant with the reduction in anthropogenic inputs, declines in dissolved Cd also likely resulted from increased Cd sorption onto particles with increasing pH and loss of these particles from the water column by sedimentation (15). Because Cd is a highly toxic metal (16), declines in exposure could contribute to the recovery of metal-sensitive aquatic animals (2–3, 17–19).

In most of our study lakes, Cd concentrations in *C. punctipennis* declined or showed little change during the study period (Figure 2C, Table 2). However, in 2 highly acidic lakes (initial pH < 5, Clearwater and Crooked Lakes, Table 2), Cd concentrations increased in *C. punctipennis* (Figure 2C) despite substantial declines in concentrations of the free Cd ion (Cd²⁺, Figure 2B). We explain these counterintuitive increases in animal Cd using a modification of the free ion activity model. This model postulates that the concentration of metal taken up by an organism should be proportional to the concentration of the free ionic form of the metal to which it is exposed (20). In its modified version, this model takes

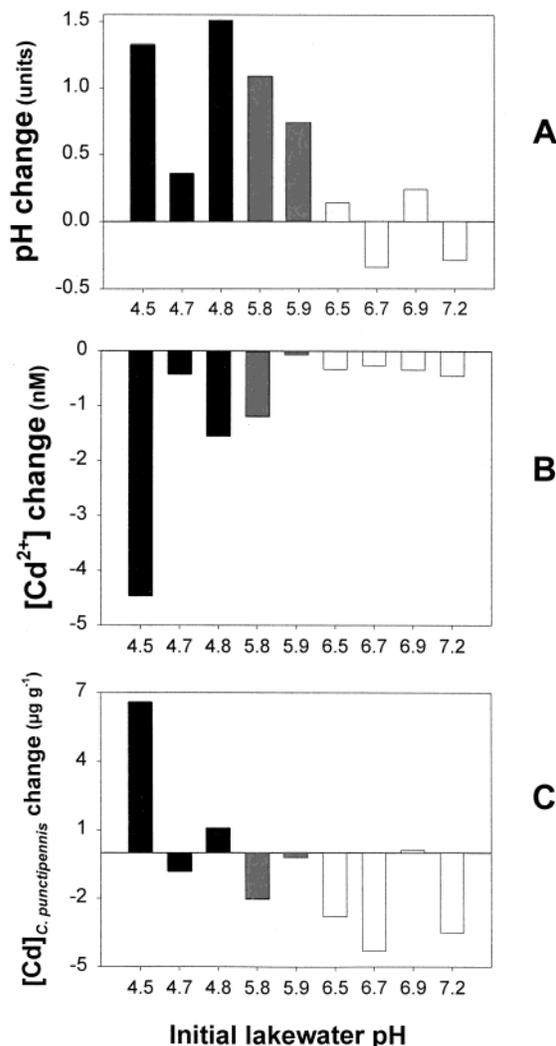


FIGURE 2. Changes in (A) lake water pH, (B) free Cd ion concentrations, and (C) Cd concentrations in larvae of *Chaoborus punctipennis*. Lakes are ranked in order of their initial pH: solid bars, pH < 5; gray bars, pH 5–6; open bars, pH > 6.

into account competition between hydrogen ions, H⁺, and free Cd ions for biological uptake sites (6–8), that is,

$$[\text{Cd}]_{C.punctipennis} = F \frac{[\text{Cd}^{2+}]}{[\text{H}^{+}] + K_a} \quad (1)$$

where F (20 500 $\mu\text{g g}^{-1}$) and K_a (1.9 $\times 10^{-6}$ mol L⁻¹) are constants (7).

Model predictions for Clearwater and Crooked Lakes (Figure 3) confirm that Cd concentrations in the biomonitor should have increased in these lakes despite declines in Cd²⁺ concentrations, that is, the influence of declines in H⁺ concentrations on insect Cd was greater than that of declines in Cd²⁺ over this time period. In Clearwater Lake (dotted curves in Figure 3), Cd concentrations in the biomonitor have likely reached a maximum judging from the proximity of the data point for recently collected animals (star) to the plateau in the model curve for the corresponding aqueous Cd concentration (1.13 nM Cd²⁺, Figure 3). In contrast, in Crooked Lake (broken curves in Figure 3), exposure to Cd will likely continue to increase with further declines in lake water [H⁺] judging from the substantial distance between the recent data point (star) and the plateau in the model curve (1.84 nM Cd²⁺, Figure 3). In our study lakes, declines

TABLE 2. Temporal Changes in the pH of Lakes near Two Metal Smelters, as Well as Cd Concentrations in Lake Water and in the Biomonitor *C. punctipennis*^a

region and lake	year	pH	Cd concentrations ± 95% CI			trends in [Cd] _{<i>C. punctipennis</i>} (observed, predicted)
			total dissolved (nM)	free (nM)	<i>C. punctipennis</i> (µg g ⁻¹)	
Sudbury, ON						
Crooked	1993	4.49	7.12 ± 0.11	6.29 ± 0.10	1.4 ± 0.2	↑,↑
	2000	5.82	3.86 ± 0.06	1.84 ± 0.03	8.0 ± 3	
Clearwater	1987	4.83	3.27 ± 0.22	2.67 ± 0.18	4.0 ± 0.4	↑,↑
	2000	6.34	1.45 ± 0.02	1.13 ± 0.02	5.1 ± 0.3	
Wavy	1988	4.71	2.59 ± 0.24	1.97 ± 0.18	2.5 ± 0.5	∅,↑
	2000	5.05	2.16 ± 0.18	1.54 ± 0.13	1.7 ± 0.3	
Crowley	1993	5.76	2.18 ± 0.05	1.82 ± 0.04	13 ± 0.9	↓,↓
	1997	6.85	1.23 ± 0.04	0.66 ± 0.02	11 ± 0.3	
Tilton	1987	5.87	1.91 ± 0.10	1.0 ± 0.05	7.8 ± 0.7	∅,↑
	1997	6.61	1.34 ± 0.07	0.94 ± 0.05	7.6 ± 0.8	
Rouyn-Noranda, QC						
Vaudray	1992	6.51	1.16 ± 0.06	0.51 ± 0.03	5.7 ± 0.4	↓,↓
	1997	6.65	0.57 ± 0.07	0.18 ± 0.02	2.9 ± 0.2	
Bousquet	1988	6.69	2.37 ± 0.29	0.49 ± 0.06	6.3 ± 0.7	↓,↓
	1997	6.35	0.85 ± 0.07	0.23 ± 0.02	2.0 ± 0.1	
Marlon	1992	6.93	1.43 ± 0.24	0.66 ± 0.11	4.8 ± 0.6	∅,↓
	1999	7.17	1.10 ± 0.03	0.32 ± 0.01	4.9 ± 1.8	
Caron	1988	7.20	3.10 ± 0.18	0.90 ± 0.05	8.9	↓,↓
	2000	6.91	1.09 ± 0.02	0.45 ± 0.01	5.4 ± 1.3	

^a Temporal trends in observed and predicted Cd concentrations in the biomonitor are represented by the following symbols: ↑ (increase), ↓ (decline), or ∅ (no change).

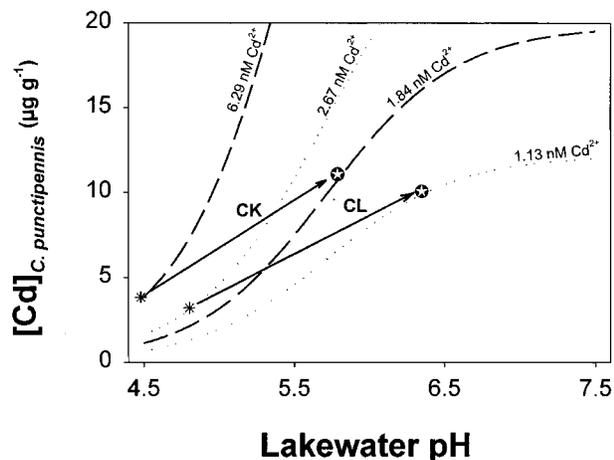


FIGURE 3. Model curves of predicted Cd concentrations in *C. punctipennis* at various pHs for the initial (*) and recent (☆) free Cd ion concentrations measured in Clearwater Lake (CL, dotted curves) and Crooked Lake (CK, dashed curves).

in hydrogen ions above a pH of about 7 would have little influence on Cd concentrations in *C. punctipennis*.

These historical increases in Cd exposure are likely not limited to *C. punctipennis* because this predator takes up most of its Cd from planktonic animals (13, 21–22) such as cladocerans, copepods, and rotifers (23). Furthermore, because some of these prey take up their Cd from algae (22), Cd increases have likely occurred throughout the planktonic food webs of these lakes. Although these counterintuitive increases in organism Cd were observed in a minority of our study lakes, they have probably occurred in large numbers of lakes recovering from acidification. For example, near the Sudbury smelters 25% of lakes that historically contained lake trout (*Salvelinus namaycush*) saw their pH increase from below 5.5 to above 6.0 between 1980 and 1996 (24). Similar increases in pH have also occurred in large numbers of northern European lakes (25–26).

For our data set as a whole, Cd concentrations in *C. punctipennis* predicted using eq 1 were directly and strongly related to those that we measured in this insect (Figure 4; r

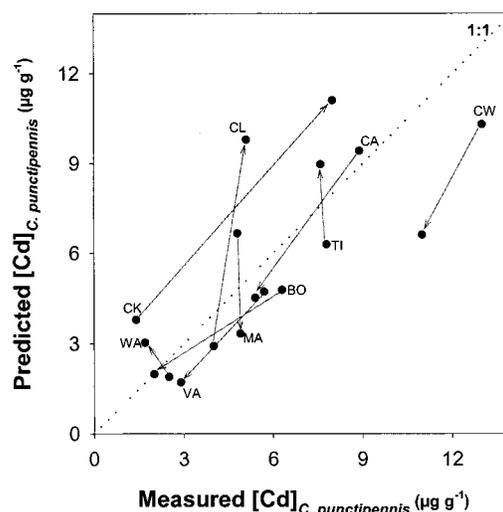


FIGURE 4. Relationship between predicted and measured Cd concentrations in *Chaoborus punctipennis* larvae. Paired letters refer to the lake codes given in Table 1. Arrows show the direction of temporal change for each lake.

$= 0.75, p < 0.001$). The majority of the unexplained variation between our predicted and measured Cd values is likely due to several factors including the following: differences in prey types among lakes and over time; the episodic nature of our pH and dissolved Cd measurements; and the fact that we estimated [Cd²⁺] using a chemical speciation model (WHAM, 14) whose database has been validated by a limited number of measurements (27) and whose application involves several assumptions about the nature and concentrations of dissolved organic matter (8).

We conclude from our study that although the water quality of lakes near metal smelters has generally improved, the recovery of communities in some highly acidified metal-contaminated lakes could be hampered by increases in the metal concentrations of organisms. Yan et al. (28) noted that although the pH of two acidic lakes near the Sudbury metal smelters had increased, the recovery of the zooplankton community in one of these lakes lagged behind that of the

other. They suggested that trace metals in this lake might explain the slow pace of recovery. Our results provide a mechanism by which metals could exert toxicity and inhibit recovery despite a decline in dissolved metal concentrations and increases in lake water pH. Our study also points to the danger of inferring reductions in the exposure of animals to metals from declines in aqueous metal alone. In this regard, use of a biomonitor along with a conceptual model provided an effective means of monitoring bioavailable Cd concentrations in lakes.

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