1993

Cadmium accumulation in the bottom sediments and fish of seepage lakes in north-central Wisconsin: relation to lake chemistry

David Emerson Powell

Iowa State University

Follow this and additional works at: https://lib.dr.iastate.edu/rtd

Part of the Biogeochemistry Commons, Environmental Sciences Commons, and the Fresh Water Studies Commons

Recommended Citation


https://lib.dr.iastate.edu/rtd/10261

This Dissertation is brought to you for free and open access by the Iowa State University Capstones, Theses and Dissertations at Iowa State University Digital Repository. It has been accepted for inclusion in Retrospective Theses and Dissertations by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.
INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

UMI

University Microfilms International
A Bell & Howell Information Company
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
313/761-4700  800/521-0600
Cadmium accumulation in the bottom sediments and fish of seepage lakes in north-central Wisconsin: Relation to lake chemistry

Powell, David Emerson, Ph.D.
Iowa State University, 1993
Cadmium accumulation in the bottom sediments and fish of seepage lakes in north-central Wisconsin: relation to lake chemistry

by

David Emerson Powell

A Dissertation Submitted to the Graduate Faculty in Partial Fulfillment of the Requirements for the Degree of DOCTOR OF PHILOSOPHY

Department: Animal Ecology
Interdepartmental Major: Toxicology
Co-major: Fisheries Biology

Approved:

Signature was redacted for privacy.

In Charge of Major Work
Signature was redacted for privacy.

For the Major Department
Signature was redacted for privacy.

For the Interdepartmental Major
Signature was redacted for privacy.

For the Graduate College

Iowa State University
Ames, Iowa

1993
DEDICATION

This dissertation is dedicated to the memories of Rev. Ella Elvina Powell, Daisy May Frantz, and Roy Leslie Valentine. Each in their own way gave up something very important along the path to its completion.
# TABLE OF CONTENTS

**GENERAL INTRODUCTION**

Explanation of Dissertation Format

**PAPER 1. WHOLE-LAKE BURDENS AND SPATIAL DISTRIBUTIONS OF CADMIUM IN SURFICIAL SEDIMENTS IN WISCONSIN SEEPAGE LAKES**

**ABSTRACT**

**INTRODUCTION**

**MATERIALS AND METHODS**

Study Area

Sampling Design and Field Methods

Laboratory Methods

Quality Assurance

Data Analysis

**RESULTS**

**DISCUSSION**

**REFERENCES**
PAPER 2. EFFECTS OF EXPERIMENTAL ACIDIFICATION ON THE ACCUMULATION OF CADMIUM IN YELLOW PERCH (*PERCA FLAVESCENS*) IN LITTLE ROCK LAKE, WISCONSIN

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>63</td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>65</td>
</tr>
<tr>
<td>MATERIALS AND METHODS</td>
<td>67</td>
</tr>
<tr>
<td>Study Area</td>
<td>67</td>
</tr>
<tr>
<td>Study Organism</td>
<td>70</td>
</tr>
<tr>
<td>Experimental Design</td>
<td>71</td>
</tr>
<tr>
<td>Sampling and Analysis of Fish</td>
<td>71</td>
</tr>
<tr>
<td>Quality Assurance</td>
<td>76</td>
</tr>
<tr>
<td>Data Analyses</td>
<td>78</td>
</tr>
<tr>
<td>RESULTS</td>
<td>80</td>
</tr>
<tr>
<td>DISCUSSION</td>
<td>95</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>102</td>
</tr>
<tr>
<td>GENERAL SUMMARY</td>
<td>109</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>114</td>
</tr>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>118</td>
</tr>
</tbody>
</table>
Cadmium, which is obtained primarily as a by-product of the zinc-smelting industry, is used extensively in a wide array of applications and products. Cadmium is important in the electroplating industry; is found in coal and certain alloys, fungicides, and plastics; is used extensively in the manufacture of chemicals, paint, and ink; and is a primary component in solar cells and rechargeable batteries (nickel-cadmium composition). In the United States, more than 30% of the total cadmium consumption goes to the production of rechargeable batteries, which in 1987 accounted for more than 50% of the estimated 1,775 tons of cadmium in the municipal waste stream (Erickson 1991).

Use of cadmium and cadmium-containing products has resulted in substantial anthropogenic emissions of the metal to the environment. For example, temporal accumulation of anthropogenic cadmium in bottom sediments of Lake Pepin, a natural riverine lake on the Upper Mississippi River, has increased more than 100-fold since 1900, closely paralleling the human population growth within the Twin Cities (Minneapolis-St. Paul) metropolitan area of Minnesota (J. G. Wiener, U.S. Fish and Wildlife Service, La Crosse, WI; personal communication). Because of its usage in consumable products, substantial amounts of cadmium are released to the atmosphere via combustion, resulting in long-range transport of the metal. Sediment-core profiles suggest that the influx of cadmium to remote and semi-remote lakes in Canada and the
United States has increased in recent years (Galloway and Likens 1979; Heit et al. 1981; Evans et al. 1983; Brezonik et al. 1990; Norton et al. 1990), presumably from increased atmospheric deposition of cadmium aerosols that can account for a substantial fraction of the cadmium influx to semi-remote and remote lakes (Johnson 1987; Cole et al. 1990; Verta et al. 1990).

Because of the toxicity and anthropogenic mobility of cadmium, contamination of aquatic environments with the metal has become an environmental issue of international concern, notably in the United States, Canada, and Scandinavia. Consequently, much research has been devoted to the biogeochemistry of cadmium in lakes and streams (reviewed by Nelson and Campbell 1991; Spry and Wiener 1991). However, many questions remain regarding the mobility of cadmium between sediments and the water column, the uptake and accumulation of cadmium by aquatic biota, the trophic transfer of cadmium, the physicochemical speciation (i.e., complexation) of cadmium, and the effects of acidification and alkalization on cadmium cycling in aquatic ecosystems.

Unlike mercury, cadmium does not biomagnify in aquatic food webs and does not accumulate appreciably in the axial muscle of fish (Wren et al. 1983; Campbell et al. 1985; Kay 1985; Harrison and Klaverkamp 1989). Thus, cadmium accumulation by fish should not pose a significant threat to human consumers. Because of its toxicity (reviewed by Spry and Wiener 1991), however, cadmium contamination does present a potential threat to the viability of fishery resources that generate millions of dollars annually to the sports and recreation industries of states such as Minnesota, Wisconsin,
and Michigan. These three states have thousands of low-alkalinity lakes that are precipitation dominated (reviewed by Wiener and Eilers 1987). Consequently, these lakes are susceptible to acidification from atmospheric deposition and to contamination by metal aerosols, such as cadmium.

To provide insight into the within-lake processes regulating the biogeochemical cycling of cadmium in whole-lake ecosystems, this study focused on two main goals: (1) to examine the relationship between lake chemistry and cadmium accumulation in lake sediments, and (2) to evaluate the effect of lake acidification on cadmium accumulation in fish. The specific objectives of the study were as follows:

1. To estimate the whole-lake burdens and spatial distributions of cadmium in sediments of six seepage lakes.
2. To evaluate sediments from selected lakes as potential sources of biologically available cadmium.
3. To assess the effects of acidification on relative rates of cadmium accumulation by fish in the treatment and reference basins of Little Rock Lake, the site of an experimental whole-lake acidification project.
4. To estimate the inventory of cadmium in fish populations in the two basins of Little Rock Lake.

Explanation of Dissertation Format

The two main sections of this dissertation represent two manuscripts to be submitted for publication in the *Canadian Journal of Fisheries and Aquatic Sciences*. The accumulation and spatial distribution of cadmium in bottom sediments of the six
study lakes is described in Paper 1. Bioaccumulation of cadmium by yellow perch (*Perca flavescens*) in the acidified and reference basins of Little Rock Lake is described in Paper 2. In addition to the two manuscripts, there is a general introduction and general summary with accompanying references specific to those sections. The two manuscripts of the dissertation were formatted according to the *Canadian Journal of Fisheries and Aquatic Sciences* to facilitate their publication in that journal.
PAPER I. WHOLE-LAKE BURDENS AND SPATIAL DISTRIBUTIONS OF CADMIUM IN SURFICIAL SEDIMENTS IN WISCONSIN SEEPAGE LAKES
Whole-lake burdens and spatial distributions of cadmium in surficial sediments in Wisconsin seepage lakes

David Emerson Powell

From the Department of Animal Ecology,
Iowa State University, Ames, Iowa 50011.
ABSTRACT

I quantified cadmium concentrations in the surficial sediments of six seepage lakes (lacking surface inlets or outlets) in north-central Wisconsin. The lakes ranged from 8 to 70 ha in surface area, from 6 to 20 m in maximum depth, from 5.2 to 7.0 in annual mean epilimnetic pH, and from 1.7 to 6.8 mg · L⁻¹ in dissolved organic carbon (DOC). A random sampling design, stratified by water depth, was used to select 50 sampling sites in each lake, where surficial sediment (uppermost 5 cm) was collected with diver-operated corers. Whole-lake burdens of cadmium in the surficial sediment ranged from 625 to 5785 g · lake⁻¹ and were strongly correlated (rₓ > 0.99; Spearman rank order correlation) with lake surface area, suggesting that cadmium influxes to the lakes are due largely to atmospheric deposition. When normalized for lake area, whole-lake burdens of cadmium varied about 1.5 fold (from 62 to 92 g · ha⁻¹) and were strongly correlated with DOC (rₓ = 0.94), but not with pH, indicating that cadmium transport to the sediments may be related to organic matter. Mean mole-ratios of mercury to cadmium in the sediments were strongly correlated with epilimnetic pH (rₓ < -0.99) and lake surface area (rₓ = -0.83) indicating that the net flux of mercury to sediments in the lakes decreased, relative to cadmium, with increasing pH and the area exposed to the atmosphere.

Dry-weight concentrations of cadmium in the sediments ranged from 0.02 to 7.17 µg · g⁻¹ and were strongly correlated with volatile matter content (rₓ ranged from 0.53 to 0.93 for the individual lakes). When expressed as dry-weight concentrations, cadmium content of
the sediments was significantly \((p < 0.05)\) correlated with water depth in all six study lakes \((r, \text{ ranged from 0.68 to 0.87})\). When concentrations were expressed on a volumetric basis (i.e., mass per volume of wet sediment), however, cadmium content and water depth were correlated in only two of the lakes. Moreover, the dry-weight concentrations did not accurately reflect the spatial distribution of cadmium in the surficial sediments of the study lakes. Therefore, it is recommended that the cadmium content of sediments be expressed on a volumetric basis when assessing the spatial distribution of cadmium in surficial sediment.
INTRODUCTION

The concentration of cadmium in the water column of a lake is influenced by the net flux of cadmium across the sediment-water interface. Aqueous concentrations of cadmium in dilute, clear-water lakes are often negatively correlated with lake pH in semi-remote lakes (Borg 1983; Schmidt 1985; Borg 1987; Stephenson and Mackie 1988), possibly due to greater cadmium efflux from the sediments at low pH (Trefry and Metz 1984; Borg et al. 1989; Mach and Brezonik 1989). Hence, the sediments represent a potential source of cadmium for aquatic biota in low-pH waters. However, the classification and significance of sediments as sources or sinks of cadmium is likely dependent on the type of sediment (i.e., compacted oxic shallow-water sediments compared to flocculent anoxic deep-water sediments) and on the mass of cadmium associated with the sediment.

When expressed on a dry weight basis, the concentrations of trace metals and organic matter in sediments increase with water depth, reflecting the focusing of fine-grained particulate material (e.g., silts, clays, biogenic matter) into the deeper zones of a lake (Brezonik et al. 1990; Rada et al. 1993). Consequently, the potential of shallow-water sediments as sources of biologically available trace metals such as cadmium may be underestimated or ignored. However, a companion study (Rada et al. 1993) on total mercury in bottom sediments of low-alkalinity seepage lakes indicated that 23-48% of the whole-lake mercury burdens, representing 27-141 g of mercury, were
located in epilimnetic sediments of the lakes that underwent stratification. The results of Rada et al. (1993) clearly demonstrate that epilimnetic sediments can represent significant reservoirs of mercury and, possibly, other sediment-associated contaminants.

I examined the spatial distribution and burdens of cadmium in surficial sediments of six seepage lakes in north-central Wisconsin. The two specific objectives for the study were as follows:

1. To estimate the whole-lake burdens and spatial distributions of cadmium in sediments of the six lakes.
2. To evaluate sediments of the lakes as potential reservoirs of biologically available cadmium.

In this chapter I will (1) describe the spatial distribution of cadmium in surficial sediments of the lakes, (2) present estimates of the whole-lake burdens of cadmium in the surficial sediments, (3) examine the relation of the areal burdens of cadmium to selected physicochemical characteristics of the lakes, and (4) contrast the findings of this study of cadmium to those of a companion study of mercury (Rada et al. 1993).

The term "whole-lake burden," is defined as the total mass of cadmium in the uppermost 5 cm of sediment in an entire lake. The term "areal burden" is the mass of cadmium in the uppermost 5 cm of sediment per unit of lake area (i.e., the whole-lake burden to lake area ratio).
MATERIALS AND METHODS

Study Area

The study area is in Vilas County in north-central Wisconsin (Fig. 1) within the Northern Highland Lake District, an area containing thousands of lakes formed during Pleistocene glaciation. About 17% of the surface area of Vilas County is open water (Magnuson et al. 1984). About 40% of the lakes in the area have low acid-neutralizing capacity (ANC<50 μeq·L⁻¹) and about 3% are acidic (ANC≤0; Eilers et al. 1988). The six study lakes (Table 1) are small seepage lakes (no surface inlets or outlets) that span gradients in pH (5.2-7.0), ANC (-5-127 μeq·L⁻¹), and dissolved organic carbon (DOC, 1.7-6.8 mg·L⁻¹). Lake area ranges from 8 to 70 ha, and maximum depth ranges from 6 to 20 m.

The low-ANC seepage lakes in this study have long hydrologic residence times and receive nearly all (>95%) of their hydrologic inflow from precipitation directly onto the lakes. For example, the hydrologic residence time of Vandercook Lake is about 4 to 5 yr (Schnoor et al. 1986), and only Pallette and Russett lakes received measurable (less than 8 x 10⁴ m³·yr⁻¹) groundwater input during 1987-1990 (Krabbenhoft and Babiarz 1992). The lakes are located in rural, mostly forested watersheds in close proximity to one another, and have limited or no public access. The use of motorized boats on all the lakes, except Vandercook, is restricted. There are no identifiable, on-site industrial sources of cadmium and no cadmium-enriched ores in the watersheds. However,
Figure 1. Location of the six study lakes in Vilas County, Wisconsin.
Table 1. Characteristics of the study lakes in north-central Wisconsin, listed in order of increasing mean pH. Water chemistry data are mean epilimnetic values for 1990 (from Watras et al. 1991) for all lakes except Max Lake\textsuperscript{a}. ANC is acid neutralizing capacity, DOC is dissolved organic carbon, and $K_s$ is specific conductance.

<table>
<thead>
<tr>
<th>Lake</th>
<th>Coordinates</th>
<th>pH</th>
<th>ANC ($\mu$eq L$^{-1}$)</th>
<th>DOC (mg L$^{-1}$)</th>
<th>$K_s$ ($\mu$S cm$^{-1}$)</th>
<th>Surface area (ha)</th>
<th>Depth (m)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Max</td>
<td>46°01'N, 89°42'W</td>
<td>5.16</td>
<td>-5</td>
<td>2.1</td>
<td>16.0</td>
<td>9.2</td>
<td>6.1</td>
<td>2.9</td>
</tr>
<tr>
<td>Russett</td>
<td>46°12'N, 89°36'W</td>
<td>5.77</td>
<td>27</td>
<td>6.8</td>
<td>15.1</td>
<td>19.2</td>
<td>11.0</td>
<td>2.9</td>
</tr>
<tr>
<td>Little Rock\textsuperscript{b}</td>
<td>46°00'N, 89°42'W</td>
<td>6.12</td>
<td>25</td>
<td>3.0</td>
<td>13.5</td>
<td>8.1</td>
<td>6.5</td>
<td>3.1</td>
</tr>
<tr>
<td>Crystal</td>
<td>46°00'N, 89°37'W</td>
<td>6.34</td>
<td>25</td>
<td>1.7</td>
<td>13.6</td>
<td>36.0</td>
<td>20.4</td>
<td>10.4</td>
</tr>
<tr>
<td>Vandercook</td>
<td>45°59'N, 89°40'W</td>
<td>6.37</td>
<td>42</td>
<td>4.1</td>
<td>16.2</td>
<td>43.6</td>
<td>7.2</td>
<td>4.7</td>
</tr>
<tr>
<td>Pallette</td>
<td>46°04'N, 89°36'W</td>
<td>7.03</td>
<td>127</td>
<td>5.3</td>
<td>22.8</td>
<td>70.0</td>
<td>18.2</td>
<td>9.6</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The chemistry of Max Lake was experimentally altered by pumping groundwater into the basin, beginning in April 1990. Chemical data shown for Max Lake are from 1988-1989, before manipulation of the lake's chemistry (P.J. Garrison, Wisconsin Department of Natural Resources, Madison, WI, personal communication).

\textsuperscript{b} Reference basin only.
analyses of cadmium concentrations in sediment cores from two of the study lakes, Crystal and Vandercook, indicate that surficial sediments in these lakes are cadmium-enriched, relative to deeper, precolonial sediments (R. G. Rada, Univ. Wisconsin-La Crosse, La Crosse, WI, unpublished data). The widespread enrichment of cadmium in surface sediments of other remote and semi-remote lakes in Canada and the United States (Galloway and Likens 1979; Heit et al. 1981; Evans et al. 1983; Brezonik et al. 1990) has been interpreted as evidence of increased atmospheric deposition of anthropogenic cadmium (Johnson 1987; Verta et al. 1989; Cole et al. 1990; Norton et al. 1990; Verta et al. 1990). Further description of the area and study lakes has been given elsewhere (Eilers et al. 1983; Wiener and Eilers 1987; Watras et al. 1991; Rada et al. 1993).

Little Rock Lake, the site of an experimental acidification study, was separated in September 1984 with a plastic sea curtain into two experimental units, a treatment basin (area 9.8 ha; mean depth 3.9 m) and a reference basin (area 8.1 ha; mean depth 3.1 m). Experimental acidification of the treatment basin with sulfuric acid began in spring 1985 and continued for 6 yr (Watras and Frost 1989). In this paper, only data for the non-acidified reference basin are presented.

Sampling Design and Field Methods

A stratified random sampling design (Gilbert 1987) was used to spatially allocate sampling effort within each lake \( N_{i} = 50 \) samples per lake. Sample allocation within a
depth interval was determined as a function of the surface area occupied by the depth
interval on a morphometric map of each lake, with areas of greater depth weighted more
heavily. The following equation (adapted from Gilbert 1987) was used to allocate the
sampling effort spatially in each lake:

\begin{equation}
N_i = N_t \cdot \frac{W_i}{\Sigma W_i}
\end{equation}

where \( N_i \) = the number of sediment samples to be collected from the \( i \)th
stratum within a lake (a stratum is defined as the area of
lake-bottom between two defined depth contours on a
morphometric map);

\[ N_t \] = the total number of sediment samples to be collected from a
lake (defined \textit{a priori} as \( N_t = 50 \));

\[ W_i \] = the weight of the \( i \)th stratum, which was used to allocate
sampling effort among strata, defined as:

\begin{equation}
W_i = A_i \cdot D_i^{0.5}
\end{equation}

where \( A_i \) = the area of water overlying the \( i \)th stratum and;

\( D_i \) = the approximate mean water depth (m) of the \( i \)th stratum.

The factor \( D_i^{0.5} \) in equation 2 allocates more samples to sediment underlying deeper
waters within each lake. The decision to allocate greater sampling effort to deeper
sediments was based on earlier data showing that dry-weight concentrations of volatile
matter, mercury (Wiener \textit{et al.} 1990), and cadmium (D. E. Powell, Iowa State Univ.,
unpublished data) in surficial sediments from Little Rock Lake increased concomitantly
with increasing water depth.
Methods for collection of sediments have been described elsewhere (Rada et al. 1993). Briefly, divers collected surface sediments with PVC core samplers (20-cm inner diameter) designed to collect the top 5 cm of sediment with minimal disturbance and compaction (modified from Rada et al. 1989). Sediment samples were collected from Little Rock (reference basin), Crystal, and Vandercook lakes during August 1988 and from Max, Pallette, and Russett lakes during June 1989. After collection, samples were sealed in acid-washed plastic bags (for determinations of cadmium and volatile matter) or tared plastic bottles (for determinations of water content), held on ice in the dark in the field, and placed in a domestic freezer (-20°C) at the nearby University of Wisconsin, Trout Lake Station, within 5 h after collection. At the conclusion of a sampling trip, sediments were transported in frozen condition to the University of Wisconsin-La Crosse, and stored at -30°C until further processed (within 2 to 4 wk).

Laboratory Methods

Sediment water content was determined by weight loss of sample after drying at 103°C (American Public Health Association et al. 1989). Frozen sediment samples to be analyzed for cadmium and volatile matter were thawed and dried at room temperature, ground with a porcelain mortar and pestle, passed through a 2-mm sieve, and homogenized. Total volatile matter (an estimate of organic matter) was determined by weight loss on sample ignition at 550±50°C for 1 h (American Public Health Association et al. 1989).
Total acid-extractable cadmium was determined for subsamples of homogenized dry sediment (0.5 to 5.0 g, depending on the amount of volatile matter) that were digested with 10 mL of 16M HNO₃, 5 mL of 12M HCl, and 5 mL of H₂O in ignition tubes that were heated at 120°C for 12 h in aluminum blocks. After cooling, digested samples were filtered through 0.45-μm Nucleopore® polycarbonate filters, diluted to 100 mL with deionized water, and stored at 4°C in high-density linear polyethylene (HDLP) bottles. Total cadmium concentrations in the diluted samples were quantified with an Instrumentation Laboratory model 551 atomic absorption spectrophotometer equipped with a 655 furnace atomizer and a 254 FASTAC® auto-sampler. Deuterium background correction was used during all cadmium determinations. Both flame and electrothermal atomization were used for the analyses, depending on cadmium concentrations.

Quality Assurance

Rigid quality assurance protocols were strictly followed during collection, storage, and processing of all samples to reduce contamination and assure validity of data. Core samplers, sample containers, and laboratory glassware were acid-washed and rinsed with deionized water. Reagents used in digestions and analyses were suitable for use in low-level cadmium analyses. Deionized water had a nominal resistance ≥10 MΩ·cm⁻¹.

Accuracy of the cadmium determinations was evaluated by digesting and analyzing the following quality assurance samples with each analytical batch of samples: U.S.
National Institute of Standards and Technology (NIST, formerly the National Bureau of Standards) standard reference materials (river sediment, Buffalo River sediment, and estuarine sediment), surrogate standards (samples spiked with cadmium before digestion), internal standards (samples spiked with cadmium just before analysis), replicate samples, procedural blanks, and calibration standards. The mean measured concentration and 99% confidence interval (CI) for each NIST reference material were within the certified ranges, with 84 of the 91 individual measurements within the certified ranges. All analyses of NIST river sediment and estuarine sediment yielded concentrations within the certified ranges. For Buffalo River sediment, 7 of 32 analyses yielded concentrations less than, but within 7% of, the certified range. The recovery of cadmium from analyses of 124 surrogate standards averaged 101±2% (99% CI) and ranged from 76% to 126%. The recovery of cadmium from analyses of 20 internal standards averaged 100±4% (99% CI) and ranged from 85% to 120%. Method precision (relative standard deviation), estimated from analyses of 50 sets of triplicate subsamples of sediment from the study lakes, averaged 4% and ranged from <1% to 23%. Cadmium concentrations exceeded our calculated method detection limit (American Public Health Association et al. 1989) of 10 ng·g⁻¹ (dry weight) in all of the 300 sediment samples analyzed and exceeded our calculated limit of quantitation (34 ng·g⁻¹) in 98%. Cadmium concentrations in all procedural blanks were less than or equal to the calculated lower limit of detection of 8.5 ng·L⁻¹.
Calculations of mean volatile matter and cadmium concentrations of surficial sediments in each lake were weighted for the proportion of the lake surface area (A, in equation 2) within each defined depth stratum (Gilbert 1987) used in the stratified sampling design. The bulk density of sediment was calculated from the measured water content and volatile matter concentration in the sample (described by Håkanson and Jansson 1983). The volumetric concentration (mass per unit of volume of wet sediment) of volatile matter and cadmium were calculated from the corresponding dry-weight concentrations and the calculated bulk density of the sediment sample. The whole-lake burden of cadmium in the uppermost 5 cm of sediment in each lake was calculated with the contaminant inventory procedure described by Gilbert (1987). The mole-ratio of mercury to cadmium in the sediments (Hg:Cd) was calculated as the quotient of moles of mercury and moles of cadmium in each sediment sample. Results for mercury content of the sediments are presented elsewhere (Rada et al. 1993).

Statistical analyses were performed with the StatPac Gold® Statistical Analysis Package (Walonick Associates 1988) and the Statistical Analysis System (SAS Institute, Inc. 1985). Spearman rank correlation coefficients \( r_s \) were used to evaluate relations between the following pairs of variables for each lake: volatile matter and cadmium concentration, water depth and volatile matter concentration, and water depth and cadmium concentration. Correlations involving the cadmium or volatile matter concentrations of sediments were calculated for both dry-weight and volumetric
concentrations. Spearman rank correlation coefficients ($r_s$) were also used to examine relations between the dependent variables whole-lake cadmium burden, areal cadmium burden, and whole-lake Hg:Cd ratio and the independent variables whole-lake volatile matter burden, areal volatile matter burden, and selected lacustrine characteristics (surface area, epilimnetic pH, DOC, conductance, and chlorophyll $a$; from Watras et al. 1991). A Type I error ($\alpha$) of 0.05 was used to judge the significance of all statistical tests.
RESULTS

Sediment samples from each study lake were operationally classified into three types, based upon their bulk density and the relative water depth from which the sediments were taken (Fig. 2). Relative water depth (Zrel) was defined as the ratio of sample collection depth (Zsample) to the mean depth (Zmean) of a lake. Sediments collected from water depths less than Zmean (i.e., Zrel ≤ 1) typically had bulk densities greater than 1.25 g · cm⁻³ and were classified as shallow-water sediments (Fig. 2). Sediments collected from water depths greater than Zmean (i.e., Zrel > 1) usually had bulk densities less than 1.25 g · cm⁻³ and were classified as deep-water sediments. Sediments that did not fall into either of these two operational classifications were considered to be transitional (Fig. 2); these sediments probably were taken from shallow-water depositional zones (Zrel ≤ 1; density < 1.25 g · cm⁻³) or from deep-water erosional zones (Zrel > 1; density > 1.25 g · cm⁻³).

Results for bulk density, water content, and volatile matter concentration of the sediments have been presented elsewhere (Rada et al. 1993). Generally, bulk density ranged from about 1.0 to 2.0 g · cm⁻³ (Table 2) and was inversely related to water content (Fig. 3), which varied from 18% to 98% (Table 2). Within each lake, the bulk density of sediments from shallow water greatly exceeded that of sediments from deeper water (Figs. 2 and 4). Mean volatile matter concentrations ranged from 19 to 43% (dry weight) and from 17 to 40 mg · cm⁻³ (Table 2).
Figure 2. Bulk density of surficial sediment (uppermost 5 cm) in the six study lakes in north-central Wisconsin, in relation to relative water depth ($Z_{\text{sample}}/Z_{\text{mean}}$).
Sediment type
- Shallow–water
- Deep–water
- Shallow depositional
- Deep erosional

Density (g/cm³)

Relative water depth
Table 2. Characteristics of the uppermost 5 cm of sediments in each study lake. The weighted mean, range (in parentheses), and standard deviation of the mean (below the ranges) are given for each variable. Lakes are listed in order of increasing mean pH.

<table>
<thead>
<tr>
<th>Lake</th>
<th>Water (%)</th>
<th>Bulk density (g·cm⁻³)</th>
<th>Volatile matter</th>
<th>Cadmium</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>% dry wt</td>
<td>mg·cm⁻³</td>
</tr>
<tr>
<td>Max</td>
<td>70</td>
<td>1.28</td>
<td>28</td>
<td>32</td>
</tr>
<tr>
<td>(21 - 98)</td>
<td></td>
<td>(1.01 - 1.93)</td>
<td>(1 - 67)</td>
<td>(8 - 100)</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>0.03</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Russett</td>
<td>84</td>
<td>1.11</td>
<td>43</td>
<td>40</td>
</tr>
<tr>
<td>(34 - 98)</td>
<td></td>
<td>(1.00 - 1.78)</td>
<td>(2 - 69)</td>
<td>(17 - 86)</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>0.05</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>Little Rock*</td>
<td>80</td>
<td>1.16</td>
<td>31</td>
<td>36</td>
</tr>
<tr>
<td>(21 - 95)</td>
<td></td>
<td>(1.01 - 1.92)</td>
<td>(1 - 61)</td>
<td>(14 - 196)</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>0.05</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Crystal</td>
<td>60</td>
<td>1.41</td>
<td>19</td>
<td>17</td>
</tr>
<tr>
<td>(21 - 97)</td>
<td></td>
<td>(1.01 - 1.93)</td>
<td>(1 - 50)</td>
<td>(4 - 62)</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>0.02</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Vandercook</td>
<td>65</td>
<td>1.34</td>
<td>19</td>
<td>19</td>
</tr>
<tr>
<td>(22 - 96)</td>
<td></td>
<td>(1.02 - 1.90)</td>
<td>(1 - 45)</td>
<td>(1 - 60)</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>0.03</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Pallette</td>
<td>60</td>
<td>1.43</td>
<td>25</td>
<td>17</td>
</tr>
<tr>
<td>(18 - 97)</td>
<td></td>
<td>(1.01 - 2.00)</td>
<td>(1 - 73)</td>
<td>(7 - 61)</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td>0.01</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

* Reference basin.
Figure 2. Bulk density of surficial sediment (uppermost 5 cm) in the six study lakes in north-central Wisconsin, in relation to relative water depth ($Z_{\text{sample}}/Z_{\text{mean}}$).
Sediment type
- Shallow-water
- Deep-water
- Shallow depositional
- Deep erosional

Water content (%) vs. Density (g/cm³)
Figure 4. Bulk density of surficial sediment (uppermost 5 cm) in relation to water depth of each study lake in north-central Wisconsin.
Cadmium concentrations in the surficial sediments varied widely within each study lake; however, concentration ranges were similar among the lakes (Table 2). On a dry-weight basis, cadmium concentrations in sediments from the six study lakes ranged from 0.02 to 7.17 \( \mu g \cdot g^{-1} \). The means and 95\% confidence intervals for cadmium concentrations in the operationally defined sediment types were 2.54±0.14 \( \mu g \cdot g^{-1} \) for deep-water sediments (range 1.00 to 7.17 \( \mu g \cdot g^{-1} \)), 0.15±0.03 \( \mu g \cdot g^{-1} \) for shallow-water sediments (range 0.02 to 0.60 \( \mu g \cdot g^{-1} \)), 1.06±0.19 \( \mu g \cdot g^{-1} \) for sediments taken from shallow-water depositional areas (range 0.08-2.21 \( \mu g \cdot g^{-1} \)), and 0.24±0.09 \( \mu g \cdot g^{-1} \) for sediments taken from deep-water erosional areas (range 0.06-0.79 \( \mu g \cdot g^{-1} \)). Mean whole-lake concentrations of cadmium (Table 2) ranged from 1.2 \( \mu g \cdot g^{-1} \) dry weight in Max and Vandercook lakes to 1.9 \( \mu g \cdot g^{-1} \) in Russett Lake. When expressed on a volumetric basis, cadmium concentrations in the sediments ranged from 0.004 to 0.67 \( \mu g \cdot cm^{-3} \) (Table 2). Mean whole-lake concentrations ranged from 0.13 \( \mu g \cdot cm^{-3} \) in Crystal Lake to 0.18 \( \mu g \cdot cm^{-3} \) in Russett and Vandercook lakes.

Cadmium concentrations in sediments of all six lakes were strongly correlated with volatile matter (Table 3) when expressed as dry-weight concentrations (\( r_s \), range of 0.53 to 0.93). However, when volumetric concentrations were used, the correlations between cadmium and volatile matter were weaker (\( r_v = -0.12 \) to 0.61) and nonsignificant for sediments in Pallette Lake.

Both cadmium and volatile matter were strongly and positively correlated with water depth in all six study lakes when concentrations were expressed on a dry-weight
Table 3. Spearman correlation coefficients ($r_s$) between characteristics of surficial sediments, as follows: volatile matter (VM), cadmium (Cd), total mercury (Hg), and depth of water (Z) overlying the sediment. Subscripts denote concentrations based on dry weight (dw) or volume (vol).

<table>
<thead>
<tr>
<th>Lake</th>
<th>VM$<em>{dw}$:Cd$</em>{dw}$</th>
<th>VM$<em>{vol}$:Cd$</em>{vol}$</th>
<th>Z:VM$_{dw}$</th>
<th>Z:Cd$_{dw}$</th>
<th>Z:VM$_{vol}$</th>
<th>Z:Cd$_{vol}$</th>
<th>Cd$<em>{dw}$:Hg$</em>{dw}$</th>
<th>Cd$<em>{vol}$:Hg$</em>{vol}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max</td>
<td>0.89</td>
<td>0.39</td>
<td>0.81</td>
<td>0.87</td>
<td>-0.04</td>
<td>0.26</td>
<td>0.78</td>
<td>0.56</td>
</tr>
<tr>
<td>Russett</td>
<td>0.70</td>
<td>0.61</td>
<td>0.42</td>
<td>0.70</td>
<td>-0.19</td>
<td>0.24</td>
<td>0.84</td>
<td>0.81</td>
</tr>
<tr>
<td>Little Rock$^b$</td>
<td>0.93</td>
<td>0.57</td>
<td>0.77</td>
<td>0.82</td>
<td>-0.09</td>
<td>0.28</td>
<td>0.92</td>
<td>0.66</td>
</tr>
<tr>
<td>Crystal</td>
<td>0.80</td>
<td>0.59</td>
<td>0.73</td>
<td>0.68</td>
<td>0.58</td>
<td>0.45</td>
<td>0.79</td>
<td>0.56</td>
</tr>
<tr>
<td>Vandercook</td>
<td>0.89</td>
<td>0.52</td>
<td>0.81</td>
<td>0.74</td>
<td>0.55</td>
<td>0.06</td>
<td>0.90</td>
<td>0.61</td>
</tr>
<tr>
<td>Pallette</td>
<td>0.53</td>
<td>-0.12</td>
<td>0.64</td>
<td>0.86</td>
<td>0.22</td>
<td>-0.29</td>
<td>0.86</td>
<td>0.11</td>
</tr>
</tbody>
</table>

$^a$ $r_s > 0.28$ or $r_s < -0.28$ indicates significance at $p \leq 0.050$ for $n=50$.

$^b$ Reference basin.
basis (Table 3). However, when expressed as volumetric concentrations, volatile matter was positively correlated with water depth only in Crystal and Vandercook lakes. Volumetric concentrations of cadmium were correlated with water depth only in Crystal and Pallette lakes, but the correlation with water depth was negative in Pallette. Furthermore, water depth was less well correlated with volumetric concentrations than with dry-weight concentrations of volatile matter and cadmium in all study lakes. Concentrations of cadmium and total mercury in the sediments of each lake were strongly correlated, whether expressed on a dry weight or volumetric basis, except for volumetric concentrations in Pallette (Table 3).

The perceptible relation between water depth and cadmium distribution in surficial sediments of the six study lakes differed markedly, depending on whether cadmium concentrations were expressed on the basis of dry-weight (Fig. 5) or volume (Fig. 6). The mean dry-weight concentrations of cadmium typically increased with water depth, whereas mean volumetric concentrations of cadmium did not exhibit a consistent pattern with water depth.

Estimated whole-lake burdens of volatile matter in the uppermost 5 cm of sediment ranged from 145 t in Max Lake to 596 t in Pallette Lake (Table 4) and were strongly correlated with ANC ($r_s=0.98$, $p<0.001$), lake surface area ($r_s=0.89$, $p=0.02$), and epilimnetic pH ($r_s=0.83$, $p=0.04$). Whole-lake burdens of cadmium in the surficial sediments ranged from 625 g in the reference basin of Little Rock Lake to 5785 g in Pallette Lake (Table 4), a 9.2-fold variation, and were strongly correlated with
Figure 5. Depth distribution of cadmium (mean values expressed on a dry-weight basis) in surficial sediment (uppermost 5 cm) in the six study lakes in north-central Wisconsin.
Depth distribution of cadmium (mean values expressed on a volumetric basis) in surficial sediment (uppermost 5 cm) in the six study lakes in north-central Wisconsin.
Cadmium concn (μg/cm³)

Depth strata (m)
Table 4. Whole-lake burdens of volatile matter, cadmium, and total mercury in the uppermost 5 cm of sediments.

<table>
<thead>
<tr>
<th>Lake</th>
<th>pH</th>
<th>Whole-lake burden</th>
<th>Areal burden</th>
<th>Cadmium burden</th>
<th>Areal burden</th>
<th>Total mercury burden</th>
<th>Areal burden</th>
<th>Hg:Cd ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Whole-lake(^a)</td>
<td>Areal (^a)</td>
<td>Whole-lake(^a)</td>
<td>Areal (^a)</td>
<td>Whole-lake(^a)</td>
<td>Areal (^a)</td>
<td></td>
</tr>
<tr>
<td>Max</td>
<td>5.16</td>
<td>145 (11.9)</td>
<td>15.8</td>
<td>703 (68)</td>
<td>76</td>
<td>53 (4.0)</td>
<td>5.8</td>
<td>0.049</td>
</tr>
<tr>
<td>Russett</td>
<td>5.77</td>
<td>379 (18.5)</td>
<td>20.0</td>
<td>1750 (88)</td>
<td>92</td>
<td>149 (7.0)</td>
<td>7.8</td>
<td>0.048</td>
</tr>
<tr>
<td>Little Rock(^c)</td>
<td>6.12</td>
<td>147 (17.9)</td>
<td>18.2</td>
<td>625 (61)</td>
<td>77</td>
<td>45 (2.5)</td>
<td>5.6</td>
<td>0.045</td>
</tr>
<tr>
<td>Crystal</td>
<td>6.34</td>
<td>258 (21.0)</td>
<td>8.4</td>
<td>1927 (166)</td>
<td>62</td>
<td>80 (6.7)</td>
<td>2.6</td>
<td>0.028</td>
</tr>
<tr>
<td>Vandercook</td>
<td>6.37</td>
<td>384 (20.5)</td>
<td>9.6</td>
<td>3616 (369)</td>
<td>90</td>
<td>141 (7.5)</td>
<td>3.5</td>
<td>0.025</td>
</tr>
<tr>
<td>Pallette</td>
<td>7.03</td>
<td>596 (30.2)</td>
<td>8.5</td>
<td>5785 (642)</td>
<td>83</td>
<td>115 (6.8)</td>
<td>1.6</td>
<td>0.015</td>
</tr>
</tbody>
</table>

\(^a\) Standard deviation of the estimated whole-lake burden in parentheses.

\(^b\) Mercury data from Rada \textit{et al.} (1993).

\(^c\) Reference basin.
Lake surface area ($r_s > 0.99$, $p < 0.001$), the whole-lake burden of volatile matter ($r_s = 0.89$, $p = 0.02$), and epilimnetic pH ($r_s = 0.83$, $p = 0.04$). When normalized for lake area, the areal burdens of cadmium in sediment varied only 1.5 fold among lakes, ranging from 62 g·ha$^{-1}$ in Crystal Lake to 92 g·ha$^{-1}$ in Russett Lake (Table 4). The areal burden of cadmium was strongly correlated with epilimnetic DOC ($r_s = 0.94$, $p = 0.005$), but was not significantly correlated with epilimnetic pH ($r_s = 0.14$), conductance ($r_s = 0.37$), or chlorophyll $a$ ($r_s = 0.77$).

The areal burdens of cadmium (Fig. 7) varied considerably among lakes and had similar depth-distribution patterns to those observed for volumetric concentrations of cadmium (Fig. 6). Areal burdens of cadmium in the sediments did not appear to increase with increasing water depth, except in Crystal and Russett Lakes (Fig. 7).
Figure 7. Areal burdens of cadmium in surficial sediment (uppermost 5 cm) in the six study lakes in north-central Wisconsin, in relation to water depth (solid bars are g·ha⁻¹; open bars are percent of the whole-lake burden present in individual depth strata).
Burden: ■ g/ha; □ %

Depth strata (m)

Cadmium burden (g/ha)

Max

Russett

Vandercook

Crystal

Little Rock

Pallette

Percent of total burden

Depth strata (m)
DISCUSSION

The estimated whole-lake burdens of cadmium in the uppermost 5 cm of sediment in the study lakes ranged from 625 g to 5785 g (Table 4). The small standard deviations associated with these estimates (range 5-11%, relative standard deviation), clearly indicate that uncertainties associated with estimates of whole-lake cadmium burdens in bottom sediments can be small, if analytical results are of high quality and if sampling is appropriately allocated. I concur with the conclusions of a companion study on mercury (Rada et al. 1993) that a stratified sampling design with a sample size (N, in equation 1) of 50 sediment samples per lake is sufficient for estimating sedimentary burdens of cadmium in small (≤ 70 ha) lakes and that allocation of sampling effort be based on volumetric rather than dry-weight concentrations of metals. Moreover, a sampling design allocating equal sampling effort per unit area among depth-strata would have been more appropriate than allocating more samples to sediments of deep water, because areal burdens of cadmium did not consistently increase with water depth (as assumed a priori based on dry-weight concentrations of cadmium and mercury). Even so, the estimates of whole-lake burdens were acceptably precise for all lakes studied, presumably due to the large sample size (N).

Dry-weight concentrations for cadmium in the deep-water surface sediments of the study lakes (range 1.00 to 7.17 μg·g⁻¹) were similar to concentrations reported for surface sediments collected from areas of maximum water depth in other semi-remote
lakes in Wisconsin (Iskandar and Keeney 1974), Adirondack State Park (Heit et al. 1981), New Jersey (Sprenger and McIntosh 1989), Ontario (Evans et al. 1983; Johnson 1987), Manitoba (Harrison and Klaverkamp 1990), Finland (Verta et al. 1990; Iivonen et al. 1992), and Sweden (Andersson and Borg 1988; Johansson 1989). Dry-weight concentrations for cadmium in shallow-water surface sediments (range 0.023 to 0.600 μg·g⁻¹) were comparable to concentrations reported for sediments collected from shallow waters in Wisconsin rivers (Dong et al. 1984) and semi-remote lakes in Ontario and Quebec (Stephenson and Mackie 1988; Tessier et al. 1993), but were substantially less (by about 2-20 fold) than concentrations reported for sediments from metal-contaminated lakes in Quebec and Ontario (Tessier et al. 1993). The low concentrations observed in some of the shallow-water sediments of this study, particularly those from Crystal, Vandercook, and Pallette lakes, are attributed to the composition of the substrate. These samples consisted mostly of fine gravel, course sand, or packed clay—material presumably from the original lake bottom. Collection of these types of samples required much physical exertion by the divers and created turbulence at the sediment-water interface, resulting in the thin flocculent layer overlying the compacted sediment being lost during sample collection.

The strong positive correlations observed between water depth and the dry-weight concentrations of cadmium and volatile matter (Table 3) have also been reported for mercury (Evans 1986; Rada et al. 1986; Wiener et al. 1990; Rada et al. 1993), and reflect focusing of fine-grained particulate matter (and associated metals such as cadmium
and mercury) into the deeper reaches of a lake (Håkanson and Jansson 1983; Hilton 1985; Brezonik et al. 1990; Petticrew and Kalff 1991). Expression of cadmium concentration on a volumetric basis does not show the same trend of increasing concentration with increasing water depth (Table 3, Fig. 6). This apparent anomaly in spatial distributions of cadmium, depending on whether concentrations are expressed on a dry-weight or volumetric basis, is due to the sediment types involved. If the cadmium content of the sediment is considered relative to water content and bulk density, it becomes apparent that differences between dry-weight and volumetric concentrations reflect a mass-dilution effect. Expressed as volumetric concentrations, the mass of cadmium in a sample of sediment is diluted by the volume of solids plus interstitial water. On a dry weight basis, however, the mass of cadmium is diluted only by solids because the water is lost to evaporation during sample processing. Shallow-water sediments from the study lakes typically consisted of dense (＞1.25 g·cm⁻³) consolidated sands with water content ranging from about 18 to 60% (Fig. 3), whereas deep-water sediments consisted mainly of water and fine-grained solids (density ≤1.25 g·cm⁻³; water content 79-98%). As a result, expression of cadmium on a dry-weight basis increasingly overestimates cadmium concentrations as water content of the sediments increases, i.e., as the water depth increases in these lakes. Thus, expression of concentrations on a dry weight basis does not accurately reflect the spatial distribution of cadmium and presumably other metals, such as mercury (Rada et al. 1993), in the surface sediments in these lakes. This may promote the misconception that shallow-water sediments
(Z<Z_{water}) contain substantially less cadmium than sediments in deeper areas of a lake and result in an underestimation of the potential of shallow-water sediments as sources of biologically available cadmium. In contrast, volumetric concentrations more accurately reflect spatial distributions of cadmium in surficial bottom sediments (Fig. 6) and emphasize the potential reservoir of cadmium in shallow-water sediments (Fig. 7), which accounted for 28-57% of the whole-lake burdens of cadmium in the study lakes. This represents significant masses of cadmium, ranging from about 322 g (Max Lake and the reference basin of Little Rock Lake) to about 3276 g (Pallette Lake) and greatly exceeds the inventories of cadmium in other abiotic and biotic compartments of the lakes. In the reference basin of Little Rock Lake, for example, the estimated inventory of cadmium in the fish population was 24 mg (3.0 mg·ha⁻¹) in 1989 (Powell 1993). Efflux of cadmium from these shallow-water sediments could greatly increase the amount of cadmium available to biota in these lakes. A release of 1% of the cadmium from the shallow-water sediments alone would add an additional 3-33 g of cadmium to the water columns of the study lakes, increasing aqueous cadmium concentrations an estimated 2-15 ng·L⁻¹, depending on the lake. In comparison, total aqueous concentrations of cadmium in low-alkalinity lakes in northern Wisconsin and central Ontario appear to range from less than 10 ng·L⁻¹ to about 211 ng·L⁻¹ (reviewed by Spry and Wiener 1991).

Aqueous cadmium concentrations in dilute, clear-water lakes are often negatively correlated with lake pH in semi-remote lakes (Borg 1983; Schmidt 1985; Borg 1987; Stephenson and Mackie 1988), suggesting that depressed pH may increase cadmium
efflux from the sediments (Trefry and Metz 1984; Brezonik et al. 1986, 1990), decrease cadmium deposition to the sediments (Evans et al. 1983; Stephenson and Mackie 1988; Borg et al. 1989), or both. It is not likely that pH-induced releases of cadmium would occur from deep-water sediments which, typically, are anoxic and contain large amounts of organic matter. Studies have demonstrated that microbial reduction of strong acid anions (e.g., \( \text{SO}_4^{2-} \) and \( \text{NO}_3^- \)) can generate substantial amounts of alkalinity in anoxic lake sediments (Schiff and Anderson 1986; Schafram and Driscoll 1990), such that the pH of porewaters of anoxic sediments is often circumneutral even in acidified waters (Rudd et al. 1986). One study, however, demonstrated that porewaters in oxic, shallow-water sediments of an acidified lake were generally more acidic than the overlying water (Schafram and Driscoll 1990), suggesting that cadmium may potentially be released from these shallow water sediments—a trend that was observed for lead and aluminum (Schafram and Ika 1991). In a laboratory study on sediments collected from two low-alkalinity seepage lakes (mean annual pH=5.4 to 6.0) in north-central Wisconsin (Powell 1986; Powell and Rada 1987), cadmium was released to porewaters of shallow-water sediments at pH \( \leq 6.0 \) but not to porewaters of deep-water sediments until pH \( \leq 5.2 \) was established.

The whole-lake burdens of cadmium in the surficial sediments varied almost 10-fold among lakes (Table 4 and Fig. 8) and were strongly correlated with lake surface area \( (r_2 > 0.99, p < 0.001) \), which supports the hypothesis that atmosphere deposition is the primary anthropogenic source of cadmium to the lakes. Although the atmospheric
Figure 8. Relation between whole-lake cadmium burdens in surficial sediment (uppermost 5 cm) and lake surface area for the six study lakes in north-central Wisconsin. Error bars around each mean represent the standard deviation of the estimated burden of cadmium. The correlation coefficient ($r$) is the Pearson product-moment correlation coefficient of $x$ (lake area) and $y$ (Cd burden).
$y = 0.081x + 0.105$

$r = 0.97$

$r^2 = 0.95$
influx of cadmium to the study lakes could vary substantially from year to year, it is reasonable to assume that spatial variation in the depositional flux of cadmium (per unit area) within any time period would be similar among lakes due to their close proximity—an assumption supported by the strong relation that exists between cadmium burden and lake area (Fig. 8). Consequently, variation in the whole-lake burdens of cadmium in the surficial bottom sediments of the study lakes should reflect differences between the within-lake processes controlling cadmium sedimentation and not differential loading rates of cadmium.

Whole-lake burdens of cadmium were strongly correlated with volatile matter burdens ($r=0.89$, $p=0.02$). A strong correlation also existed between areal burdens of cadmium and epilimnetic concentrations of DOC ($r=0.94$, $p=0.005$). These data suggest that deposition of cadmium to sediments in the study lakes may be related to organic material. Studies of other atmospherically derived metals indicate that downward fluxes of mercury (Hurley et al. 1991; Hurley et al. 1993) and lead (Talbot and Andren 1984) through the water column to the sediment-water interface are strongly coupled to the settling of biogenic particles.

The stability of metal-organic complexes follows the Irving-Williams series, which indicates that mercury should be much more strongly complexed by organic matter than cadmium (Mantoura et al. 1978). Correlations based on volumetric concentrations were stronger between volatile matter and total mercury (Rada et al. 1993) than between volatile matter and cadmium (Table 3) for sediments in all six study lakes. Moreover,
the similarities observed between depth-distribution patterns for areal burdens of mercury and volatile matter (Rada et al. 1993), were greater than those observed between cadmium (Fig. 7) and volatile matter (Fig. 9), especially in the higher pH lakes, Vandercook and Pallette. However, the whole-lake mercury and volatile matter burdens (Table 4) were not significantly correlated in the study lakes ($r_s=0.71, p=0.11$), nor were areal mercury burdens correlated with DOC ($r_s=0.20, p=0.70$). These relations suggest that different within-lake processes regulate deposition of cadmium and mercury to sediments in the study lakes.

Because atmospheric deposition is likely the primary source of anthropogenic cadmium (this study) and mercury (Rada et al. 1983) to the study lakes, it is reasonable to assume that the gross influxes of cadmium and mercury to the lakes have been relatively uniform with respect to each other. In contrast to the trends observed for cadmium, however, Rada et al. (1993) reported that whole-lake mercury burdens in the study lakes were not correlated with lake surface areas, and that areal mercury burdens were strongly correlated with epilimnetic pH. Rada et al. (1993) speculated that the variation between areal burdens of mercury was in part due to differences among lakes in the pH-related efflux of gaseous mercury (Hg$^+$) from the water column to the atmosphere—a process that removed geochemically significant amounts ($>10\%$) of the annual atmospheric input of mercury entering the study lakes (Fitzgerald et al. 1991; Vandal et al. 1991).
Figure 9. Areal burdens of volatile matter in surficial sediment (uppermost 5 cm) in the six study lakes in north-central Wisconsin, in relation to water depth (solid bars are t·ha⁻¹; open bars are percent of the whole-lake burden present in individual depth strata).
Burden:  ■ metric tons/ha;  ■ %

Volatile matter burden (metric tons/ha)

Depth strata (m)

Max

Russet

Vandercook

Crystal

Little Rock

Pallette
The results presented here for cadmium support the hypothesis of Rada et al. (1993) that the pH-related formation of Hg°, leading to the efflux of mercury from the lakes to the atmosphere, may affect the quantity of mercury in low-alkalinity lakes. It is improbable that significant amounts of cadmium are lost through volatilization from the water column to the atmosphere because cadmium does not have a volatile species under conditions in the study lakes. Consequently, if there were no efflux of volatile Hg° from the lakes to the atmosphere, one would expect that the mole-ratio of total mercury to cadmium (previously defined as Hg:Cd ratio) in the sediments would be similar among the study lakes. However, mean Hg:Cd ratios in the lakes ranged from 0.015 in Pallette Lake to 0.049 in Max Lake (Table 4) and were strongly correlated with epilimnetic pH ($r_z < -0.99$, $p < 0.001$) and lake surface area ($r_z = -0.83$, $p = 0.04$). The negative correlation between pH and the mean Hg:Cd ratios suggests that as pH decreases (1) mercury transport to sediments increases, (2) cadmium transport to the sediments decreases, or (3) both. If decreased cadmium transport to the sediments were responsible for the observed variation in mean Hg:Cd ratios, then areal burdens of cadmium should be correlated with pH—a correlation that was not found ($r_z = 0.14$, $p = 0.79$). The correlation between pH and areal burdens of mercury ($r_z = -0.89$, $p = 0.02$), however, indicates that mercury transport to the sediments increases with decreasing pH. Moreover, the negative correlation between mean Hg:Cd ratios and lake surface areas indicates that the net flux of mercury to sediments in the lakes decreases with increasing
area exposed to the atmosphere—a trend that would only be observed for the efflux of a volatile compound such as Hg°.
REFERENCES


PAPER 2. EFFECTS OF EXPERIMENTAL ACIDIFICATION ON THE ACCUMULATION OF CADMIUM IN YELLOW PERCH (PERCA FLAVESCENS) IN LITTLE ROCK LAKE, WISCONSIN
Effects of experimental acidification on the accumulation of cadmium in yellow perch (*Perca flavescens*) in Little Rock Lake, Wisconsin

David Emerson Powell

From the Department of Animal Ecology,
Iowa State University, Ames, Iowa 50011.
ABSTRACT

The effect of whole-lake acidification on the bioaccumulation of cadmium by yellow perch (*Perca flavescens*) was studied in Little Rock Lake, the site of an experimental pH manipulation project. Little Rock Lake was separated with an impermeable curtain into a reference basin (mean pH 6.1) and treatment basin that was acidified with sulfuric acid for 2 years to pH 5.6, 2 years to pH 5.2, and 2 years to pH 4.9. I determined cadmium in age-1 yellow perch that were netted annually from each basin in April, after 1 year of residence in the lake, after each year of the pH-5.2 treatment (1988 and 1989) and after each year of the pH-4.9 treatment (1990 and 1991). A random sampling design, stratified by 1-cm total-length groups, was used to sample older yellow perch in April 1989, at the end of the pH-5.2 treatment, and again in April 1991, at the end of the pH-4.9 treatment. Mean whole-body concentrations and burdens (masses) of cadmium in age-1 yellow perch did not differ between basins during the pH-5.2 treatment, but were greater in reference-basin fish than in treatment-basin fish after each year of the pH-4.9 treatment. In 1989 and 1991, mean whole-body concentrations and burdens of cadmium were greater in the reference basin than in the treatment basin for fish age-2 and older and for fish from total-length groups larger than 130 mm. The observed decrease in the bioaccumulation of cadmium by yellow perch in the acidified treatment basin may reflect increased competition between cadmium and hydrogen ions for binding sites on cell membranes of the gill surface. Bioaccumulation
of cadmium by yellow perch paralleled age and growth of fish sampled from both basins in 1989 but not in fish sampled in 1991, with the relationship being strongest for reference-basin fish. The estimated inventory of cadmium in the yellow perch populations in Little Rock Lake, based on analyses of samples collected in 1989, was 24 mg in the 8-hectare reference basin and 19 mg in the 10-hectare treatment basin.
INTRODUCTION

Cadmium is a toxic, nonessential element (reviewed by Spry and Wiener 1991), and contamination of aquatic environments with the metal poses a potential threat to freshwater biota. Fish in low-alkalinity seepage lakes may be susceptible to cadmium contamination because these waters are typically very dilute and contain low concentrations of calcium. Cadmium accumulation by fish has been widely attributed to the direct uptake of Cd\(^{2+}\) across the gills (Williams and Giesy 1978; Pärt and Svanberg 1981; Kay 1985; Pärtn et al. 1985) and appears to be directly related to the activity of the Cd\(^{2+}\) ion (Pärt and Svanberg 1981; Pärt and Wikmark 1984; Pärtn et al. 1985). Consequently, it is assumed that cadmium is not as toxic or readily available to fish in hard or alkaline waters as in soft waters because of decreased Cd\(^{2+}\) activity (Pärtn et al. 1985) and the ameliorating effects of aqueous Ca\(^{2+}\) on cadmium uptake at the gill surface (Pascoe et al. 1986; Wicklund and Runn 1988; Pärtn et al. 1985). Conversely, in soft waters, such as those found in low-alkalinity seepage lakes, cadmium exists primarily as free Cd\(^{2+}\) (Campbell and Stokes 1985; Campbell and Tessier 1987) and should presumably be more available for uptake by fish (Spry and Wiener 1991).

Cadmium concentrations in fish in low-alkalinity waters are often elevated, even at locations far from industrial sources of the metal. However, studies of the relation between lake pH and cadmium accumulation in fish have produced inconsistent results. Some field surveys have found higher cadmium concentrations in fish from low-pH lakes
than in fish from circumneutral-pH lakes (Wiener 1983, 1987; Hamilton and Haines 1989; Stripp et al. 1990), whereas other studies found no correlation between cadmium concentration in fish and lake pH (Bendell-Young et al. 1986; Haines et al. 1987; Suns et al. 1987). Such inconsistencies suggest that the accumulation of cadmium by fish varies in response to within-lake processes that influence the bioavailability of cadmium.

Cadmium does not seem to biomagnify in aquatic food webs (Campbell et al. 1985; Kay 1985; Spry and Wiener 1991), yet one study has shown that the uptake of dietary cadmium can be substantial and can exceed the direct uptake of cadmium across the gill (Harrison and Klaverkamp 1989). Consequently, the bioaccumulation of cadmium by fish in low-alkalinity lakes is presumably influenced by (1) the mass loading of cadmium to the lake, (2) the within-lake processes affecting the bioavailability of aqueous cadmium, and (3) the within-lake processes affecting the trophic transfer of cadmium.

I examined the influence of lake acidification on the bioaccumulation of cadmium in yellow perch (Perca flavescens) populations in Little Rock Lake (Wisconsin, USA), the site of an experimental lake acidification project (Watras and Frost 1989). The effects of experimental acidification to pH 5.2 and pH 4.9 on cadmium bioaccumulation in the lake were examined. Specific objectives were (1) to assess the influence of acidification on the relative rates of cadmium accumulation in age-1 yellow perch and (2) to estimate the inventories of cadmium in perch populations in the acidified and reference basins of Little Rock Lake.
MATERIALS AND METHODS

Study Area

Little Rock Lake (46° 00'N, 89° 37'W) is in north-central Wisconsin (Fig. 1), in the Northern Highland Lake District, an area with hundreds of low-alkalinity lakes and many acidic lakes (Magnuson et al. 1984; Linthurst et al. 1986; Eilers et al. 1988). It is a small, clear-water seepage lake (no surface inlets of outlets) that receives nearly all (>95%) of its hydrologic inflow from precipitation falling directly onto its surface (Watras and Frost 1989). The lake's watershed is state-owned, uninhabited, and covered with forest. In September 1984, the lake was separated (Fig. 1) with an impermeable curtain of dacron fiber reinforced with polyvinyl into two experimental units, a treatment basin (area 9.8 ha; mean depth 3.9 m) and a reference basin (area 8.1 ha; mean depth 3.1 m). The deeper treatment basin (maximum depth 10.3 m) thermally stratifies during the summer months into a well mixed epilimnion and a small (about 8% of the basin volume) anoxic hypolimnion (Brezonik et al. 1986) whereas the shallower reference basin (maximum depth 6.3 m) does not. Experimental acidification of the treatment basin with technical-grade sulfuric acid began after ice melt in spring 1985 and continued for 6 years (Watras and Frost 1989). Each year, addition of acid to the treatment basin began after ice melt and continued as necessary throughout the ice-free season. The untreated reference basin had a mean annual pH of about 6.1 during the study. The pH of the treatment basin was incrementally decreased in 2-year treatment intervals while chemical
Figure 1. Location of Little Rock Lake in Vilas County, Wisconsin. The morphometric map of the lake shows the location of the curtain separating the treatment and reference basins. Depth contours are shown as 2-m intervals.
and biological responses to acidification were studied (Brezonik et al. 1986, 1990; Swenson et al. 1989; Watras and Frost 1989; Wiener et al. 1990; Webster et al. 1992). Two years of acidification of the treatment basin to pH 5.6 ended in April 1987, 2 years of acidification to pH 5.2 ended in April 1989, and 2 years of acidification to pH 4.9 ended in April 1991. The chemical composition (mean pH 6.1, alkalinity 26 µeq·L⁻¹, specific conductance 12 µS·cm⁻¹, calcium 0.9 mg·L⁻¹) and biota of the two basins were very similar before experimental acidification began (Brezonik et al. 1986; Watras and Frost 1986).

Study Organism

Yellow perch (*Perca flavescens*) were selected as the study organism for examining the effect of acidification on cadmium bioaccumulation. Yellow perch are the most abundant fish in Little Rock Lake (Swenson et al. 1989), contributing more than 80% of the fish-community biomass. It is one of the more widespread and acid-tolerant fish in low-alkalinity lakes of the study area (Wiener and Eilers 1987), and the treatment-basin population persisted throughout the experimental acidification project. Furthermore, small yellow perch are the preferred prey of certain piscivorous fish, such as walleye (*Stizostedion vitreum*; Colby et al. 1979), and maybe important in the trophic transfer of cadmium to piscivorous fishes.
Experimental Design

To assess relative rates of cadmium accumulation by fish in the treatment and reference basins of Little Rock Lake, the cadmium content of whole, age-1 yellow perch was quantified after a 1-year, in situ exposure period. A random sample of at least 30 calendar age-1 perch (i.e., fish that had hatched the previous spring and resided in the lake for about 1 year) was annually obtained in April from each basin during a 4-yr period (1988-1991). Yellow perch spawn soon after ice-melt, usually during mid to late April or early May in northern Wisconsin lakes. Consequently, the period of exposure of age-1 yellow perch to conditions in the treatment basin coincided closely with either the first or second year of a given pH treatment.

Temporal trends in cadmium accumulation and estimates of the inventories (masses) of cadmium in yellow perch populations were assessed for both basins of the lake. A random sampling design, stratified by 1-cm total-length group, was used to allocate analytical effort among fish. Yellow perch of all total-length groups were sampled from both basins in April 1989, after the second year of the pH-5.2 treatment, and in April 1991, after the second year of the pH-4.9 treatment. In each basin, an attempt was made to obtain 10 or more fish from each 1-cm total-length group.

Sampling and Analysis of Fish

Yellow perch were obtained with modified (i.e., non-metallic) Indiana-style trap nets with 0.95-cm square mesh (Memphis Net and Twine Company, Memphis,
Tennessee) fished overnight in littoral habitat a few days after ice-out, when yellow perch were actively spawning. After removal from a net, fish were briefly held in polyethylene buckets containing lake water. On the day of capture, live fish were taken to the nearby University of Wisconsin's Trout Lake Station, where each was assigned an identification number, euthanized by a blow to the head, measured (total length) to the nearest millimeter, and weighed to the nearest 0.1 g. Scales for age estimation were taken from each fish near the area of insertion of the left pectoral fin. Each fish was then placed into a labeled and sealed Ziploc® bag that was stored in a domestic freezer (-20°C) at the Station. At the conclusion of a sampling trip, fish were transported in frozen condition to the University of Wisconsin-La Crosse, and stored at -35°C until further processed.

The calendar age of yellow perch was estimated by examining three or more scales from each fish. Age estimation of 20 percent of the fish analyzed was performed in duplicate by a second person. Age estimation of fish sampled in 1990 were not consistent with the length-frequency distribution, and scales from these fish are being re-analyzed. Consequently, I assigned a calendar age of 1 to all yellow perch sampled in 1990 that had fresh weight less than 11 g and total length less than 115 mm. These values were based on the length-frequency distributions of the two populations, and yielded samples that were similar in size to samples of age-1 fish during the other years of study.

A total of 537 fish from Little Rock Lake, with total lengths ranging from 80 to 210 mm, were analyzed for cadmium (Table 1). Of these, 240 were age-1 fish. The
Table 1. Total lengths (mm) of yellow perch (*Perca flavescens*) collected in April 1989 and April 1991 from the reference and treatment basins of Little Rock Lake, Wisconsin, grouped by estimated calendar age. The mean total length, range (in parentheses), and number of fish analyzed for cadmium (below the ranges) are given for each group.

<table>
<thead>
<tr>
<th>Calendar age (yr)</th>
<th>Reference basin</th>
<th>Treatment basin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Age-1</td>
<td>98</td>
<td>99</td>
</tr>
<tr>
<td></td>
<td>(91-104)</td>
<td>(81-112)</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Age-2</td>
<td>132</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>(121-151)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>17</td>
<td>16</td>
</tr>
<tr>
<td>Age-3</td>
<td>144</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>(127-167)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>24</td>
</tr>
<tr>
<td>Age-4</td>
<td>171</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>(158-189)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>8</td>
</tr>
<tr>
<td>Age-5</td>
<td>176</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>(164-189)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>Age-6</td>
<td>197</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>(182-210)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td></td>
</tr>
</tbody>
</table>
remaining 297 fish analyzed were age-2 and older (Table 1), representing all 1-cm
total-length groups exceeding 119 mm (Table 2). Calendar ages were not estimated for
all older fish.

Most of the fish sampled and analyzed for cadmium were males. All fish
collected in 1988 and 1990, 88% of those in 1989, and 71% of those in 1991 were
males. Spent females represented 9% of the fish in 1989, and 1% of those in 1991.
Four of the 218 fish in 1989 and 34 of the 199 fish in 1991 that were analyzed for
cadmium were gravid females. Fish of unknown sex comprised 3% of the sample in

For each basin, 30 age-1 fish to be analyzed for cadmium were randomly selected
from all age-1 fish collected during each year of study. Age-2 and older fish analyzed
for cadmium were randomly selected from each 1-cm total-length group. Except for
gravid females, frozen whole yellow perch were lyophilized to a constant dry weight in
their respective Ziploc® bags for 72-144 h at -60°C, weighed to the nearest milligram,
and homogenized to a fine powder with a stainless steel Waring blender at 20,000 RPM.

Many of the gravid females that were collected had released some or most of their
eggs during handling and processing in the field. Therefore, to reduce the mass dilution
of cadmium by variable masses of eggs, ovaries were removed from partially thawed
gravid females, before lyophilization, with a stainless steel scalpel that was rinsed
thoroughly with deionized water between dissections; ovaries were weighed to the nearest
milligram (wet weight). The mean mass of ovaries removed from the gravid females was
Table 2. Estimated abundance of each total-length group, and number of yellow perch (*Perca flavescens*) analyzed for cadmium, from the reference and treatment basins of Little Rock Lake, Wisconsin, in April 1989 and 1991. Abundance estimates were based on mark-recapture studies (William A. Swenson, University of Wisconsin-Superior, Superior, Wisconsin, unpublished data). Abundance estimates for the 1991 yellow perch populations were not available.

<table>
<thead>
<tr>
<th>Total-length group (mm)</th>
<th>Reference basin</th>
<th>Treatment basin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>estimated abundance</td>
<td>number analyzed</td>
</tr>
<tr>
<td>Fish collected April 1989</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&lt;120</td>
<td>10,234</td>
<td>30</td>
</tr>
<tr>
<td>120 - 129</td>
<td>3,368</td>
<td>14</td>
</tr>
<tr>
<td>130 - 139</td>
<td>13,477</td>
<td>11</td>
</tr>
<tr>
<td>140 - 149</td>
<td>7,168</td>
<td>12</td>
</tr>
<tr>
<td>150 - 159</td>
<td>2,374</td>
<td>8</td>
</tr>
<tr>
<td>160 - 169</td>
<td>399</td>
<td>11</td>
</tr>
<tr>
<td>170 - 179</td>
<td>452</td>
<td>12</td>
</tr>
<tr>
<td>≥180</td>
<td>521</td>
<td>16</td>
</tr>
<tr>
<td>Total</td>
<td>37,993</td>
<td>114</td>
</tr>
<tr>
<td>Fish collected April 1991</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&lt;120</td>
<td>--</td>
<td>35</td>
</tr>
<tr>
<td>120 - 129</td>
<td>--</td>
<td>8</td>
</tr>
<tr>
<td>130 - 139</td>
<td>--</td>
<td>10</td>
</tr>
<tr>
<td>140 - 149</td>
<td>--</td>
<td>8</td>
</tr>
<tr>
<td>150 - 159</td>
<td>--</td>
<td>9</td>
</tr>
<tr>
<td>160 - 169</td>
<td>--</td>
<td>7</td>
</tr>
<tr>
<td>170 - 179</td>
<td>--</td>
<td>7</td>
</tr>
<tr>
<td>≥180</td>
<td>--</td>
<td>9</td>
</tr>
<tr>
<td>Total</td>
<td>--</td>
<td>93</td>
</tr>
</tbody>
</table>
19.2% (SD 9.0%) of total body weight and ranged from 1.2% to 32.0%. Ovaries removed from gravid females were not analyzed.

Fish were digested and analyzed for cadmium at the University of Wisconsin-La Crosse, River Studies Center. A 500-mg subsample of each lyophilized whole-fish homogenate was digested in a 50-mL ignition tube with 10 mL of 16M HNO₃. Each ignition tube was gently vortexed, covered with a reflux funnel (constructed by fusing a 5 cm x 1 cm Pyrex® rod to the end of a 22-mm Pyrex® stemless funnel), placed into an aluminum heating block, allowed to stand for 1 h at room temperature, heated for 1 h at 50°C, heated for 48 h at 120°C, and then allowed to cool to room temperature for about 1 h. Each digested sample was diluted to 100 mL and stored in a high-density polyethylene bottle at 4°C until analyzed. Cadmium concentrations in diluted digestates were quantified with an Instrumentation Laboratory 551 atomic absorption spectrophotometer equipped with a 655 graphite furnace and a 254 FASTAC® auto-sampler.

Quality Assurance

Quality-assurance protocols were followed during the collection, storage, and preparation of all samples to reduce contamination and assure validity of data. Laboratory glassware and plasticware were acid-washed and rinsed with deionized water before use. All acids used in digestions and analyses were suitable for use in low-level cadmium analyses (Instra Analyzed®, J.T. Baker Chemical Co., Phillipsburg, NJ).
Deionized water had a nominal resistance $\geq 10 \text{ M}\Omega \cdot \text{cm}^{-1}$. Atomic absorption standards were prepared from 1000-mg·L$^{-1}$ certified standard solutions (Fisher Scientific).

Quality-assurance samples were included and analyzed with each analytical batch of samples. Specifically, the bias and precision of cadmium determinations for each batch of samples were quantified by analyses of the following: (1) standard reference materials from the U.S. National Institute of Standards and Technology (NIST; bovine liver) and the National Research Council of Canada (NRCC; dogfish muscle and dogfish liver), (2) surrogate standards (500-mg subsamples of homogenized whole yellow perch spiked with cadmium before digestion), (3) internal standards (500-mg subsamples of homogenized whole yellow perch spiked with cadmium just before analysis), (4) triplicate 500-mg subsamples of homogenized whole yellow perch, and (5) procedural blanks and calibration standards, taken through digestion and storage procedures to assess contamination from reagents and containers.

The means and associated 99% confidence intervals (CI) for measured concentrations of cadmium were within the certified concentration ranges for all three standard reference materials. The measured concentrations of cadmium in individual samples were within the certified concentration ranges in 35 of 39 analyses of NIST bovine liver, 34 of 39 analyses of NRCC dogfish liver, and 36 of 38 analyses of NRCC dogfish muscle. Eight of the 11 analyses yielding concentrations outside of the certified concentration ranges were less than, but within 5% of, the certified ranges and the other 3 exceeded, but were within 15% of, the certified ranges. The recovery of cadmium
from analyses of 149 surrogate standards averaged 100±2% (99% CI) and ranged from 72% to 140%. The recovery of cadmium from analyses of 27 internal standards averaged 104±7% (99% CI) and ranged from 86% to 138%. Method precision (relative standard deviation), estimated from analyses of 39 triplicate subsamples of homogenized whole yellow perch, averaged 7.1% and ranged from 1.3% to 19.9%. Cadmium concentrations in digested samples exceeded the calculated method limit of detection (American Public Health Association et al. 1989) of 4.8 ng or 9.6 ng·g⁻¹ (dry weight) in all of the yellow perch analyzed; cadmium concentrations exceeded the calculated limit of quantitation (16 ng or 32 ng·g⁻¹ dry weight) in 97% of the 537 fish analyzed. Cadmium concentrations in all procedural blanks were less than or equal to the calculated lower limit of detection of 8.5 ng·L⁻¹.

Data Analyses

The cadmium content of individual whole yellow perch was expressed as both a fresh-weight concentration and burden. Cadmium burden, defined as the total mass of cadmium accumulated in a whole fish, was calculated as the product of lyophilized (dry) body weight and the dry-weight concentration of cadmium in lyophilized whole-fish homogenate. Fresh-weight concentrations were calculated as the quotient of cadmium burden and fresh weight of the fish. Cadmium concentrations and burdens in gravid females were calculated with body weights obtained after removal of the ovaries. The inventories (masses) of cadmium in the yellow perch populations in both basins of Little
Rock Lake in 1989 were estimated from data on the mean whole-body cadmium burden and the abundance of fish in each total-length group (stratum), with formulae for stratified random sampling designs provided by Gilbert (1987). Mark-recapture estimates of the 1989 abundance (number of individuals) of yellow perch in Little Rock Lake (Table 2) used to calculate cadmium inventories were provided by William A. Swenson (University of Wisconsin-Superior, Superior, Wisconsin, unpublished data). Mark-recapture estimates of the 1991 abundance of yellow perch were not available.

Statistical analyses were performed with the StatPac Gold® Statistical Analysis Package (Walonick Associates 1988) and the Statistical Analysis System (SAS Institute, Inc. 1985). The effect of experimental acidification on the bioaccumulation of cadmium was based on within-year contrasts (t-tests) of mean cadmium concentrations and burdens in age-1 and age-2 yellow perch between the treatment and reference basins (Wiener et al. 1990). It was assumed that the atmospheric influx of cadmium to Little Rock Lake (per unit of lake area) did not differ between basins within a given year. The interpretation of temporal trends in cadmium accumulation between the two basins can be complicated by variation among years in several factors. The influx of cadmium to Little Rock Lake, for example, may have varied from year to year, possibly confounding interpretation of the influence of acidification of the treatment basin on the bioaccumulation of cadmium. A Type I error (α) of 0.05 was used to judge the significance of all statistical tests.
The growth of age-1 yellow perch did not differ between basins during the pH-5.2 treatment (both years) or during the second year of the pH-4.9 treatment (Table 3). The first-year growth of yellow perch during the first year of the pH-4.9 treatment was faster in the treatment basin than in the reference basin (Table 3). Growth of age-2 and older fish, sampled in 1989 and 1991, was generally greater in the treatment basin than the reference basin. Mean fresh weights of yellow perch sampled in 1989 were greater in the treatment basin than the reference basin for age-2 and age-3 fish (Fig. 2) and for fish from the 130-139 mm total-length group through the 170-179 mm group (Fig. 3). Similarly, mean fresh weights of fish sampled in 1991 were greater in treatment-basin fish than reference-basin fish of age-3 or older (Fig. 4) and for fish from the 150-159 mm and larger total-length groups (Fig. 5). In no case did the reference-basin fish grow faster than treatment-basin fish (Figs. 2-5).

Mean whole-body concentrations of cadmium in age-1 yellow perch ranged from 20 to 38 ng·g⁻¹ (fresh weight) in reference-basin fish and from 8 to 27 ng·g⁻¹ in treatment-basin fish. Mean cadmium concentrations in age-1 yellow perch did not differ between basins during the 2 years of acidification to pH 5.2 (Table 4). During the pH-4.9 treatment, mean concentrations in treatment-basin fish were about one-third those in reference-basin fish (Table 4). In 1991, after the second year of the pH-4.9 treatment, the ranges of cadmium concentrations in age-1 fish did not overlap between basins.
Table 3. Mean fresh weights and total lengths of calendar age-1 yellow perch (*Perca flavescens*) sampled from the treatment and reference basins of Little Rock Lake, Wisconsin, and analyzed for cadmium.

<table>
<thead>
<tr>
<th>Variable and date of sampling</th>
<th>Mean pH of treatment basin</th>
<th>Treatment basin</th>
<th>Reference basin</th>
<th>( p^a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean fresh weight (g)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>April 1988</td>
<td>5.2</td>
<td>7.4</td>
<td>7.6</td>
<td>NS</td>
</tr>
<tr>
<td></td>
<td>(0.19)</td>
<td>(0.14)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>April 1989</td>
<td>5.2</td>
<td>8.1</td>
<td>7.5</td>
<td>NS</td>
</tr>
<tr>
<td></td>
<td>(0.28)</td>
<td>(0.25)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>April 1990</td>
<td>4.9</td>
<td>6.0</td>
<td>4.3</td>
<td>**</td>
</tr>
<tr>
<td></td>
<td>(0.23)</td>
<td>(0.12)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>April 1991</td>
<td>4.9</td>
<td>7.0</td>
<td>6.8</td>
<td>NS</td>
</tr>
<tr>
<td></td>
<td>(0.25)</td>
<td>(0.25)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean total length (mm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>April 1988</td>
<td>5.2</td>
<td>98</td>
<td>98</td>
<td>NS</td>
</tr>
<tr>
<td></td>
<td>(0.8)</td>
<td>(0.6)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>April 1989</td>
<td>5.2</td>
<td>101</td>
<td>99</td>
<td>NS</td>
</tr>
<tr>
<td></td>
<td>(1.1)</td>
<td>(1.1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>April 1990</td>
<td>4.9</td>
<td>90</td>
<td>82</td>
<td>**</td>
</tr>
<tr>
<td></td>
<td>(1.1)</td>
<td>(0.9)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>April 1991</td>
<td>4.9</td>
<td>93</td>
<td>94</td>
<td>NS</td>
</tr>
<tr>
<td></td>
<td>(1.1)</td>
<td>(1.2)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Probability of equality of mean weights or mean total length between the two basins, based on a *t*-test; NS indicates no significant difference between means (\( p > 0.05 \)), and two asterisks (**) indicate that the means differed at \( p < 0.01 \); \( n=30 \) fish for each mean.
Figure 2. Mean cadmium concentration, weight, and cadmium burden of whole yellow perch (*Perca flavescens*) from the treatment and reference basins of Little Rock Lake, Wisconsin, in relation to fish age. Fish were sampled in April 1989 at the end of the second year of the pH-5.2 treatment. Error bars around each mean are 95% confidence intervals.
Reference ° pH-5.2 Treatment

- ng/g wet wt
- grams
- μg/fish

Calendar age (yr)
Figure 3. Mean cadmium concentration, weight, and cadmium burden of whole yellow perch (Perca flavescens) from the treatment and reference basins of Little Rock Lake, Wisconsin, in relation to total-length group. Fish were sampled in April 1989 at the end of the second year of the pH-5.2 treatment. Error bars around each mean are 95% confidence intervals.
Reference ° pH-5.2 Treatment

- Reference
- pH-5.2 Treatment

**Cd conc** (ng/g wet wt)

**Body burden** (μg/fish)

**Fresh weight** (grams)

**Total length group (mm)**:
- <120
- 120-129
- 130-139
- 140-149
- 150-159
- 160-169
- 170-179
- ≥180
Figure 4. Mean cadmium concentration, weight, and cadmium burden of whole yellow perch (*Perca flavescens*) from the treatment and reference basins of Little Rock Lake, Wisconsin, in relation to fish age. Fish were sampled in April 1991 at the end of the second year of the pH-4.9 treatment. Error bars around each mean are 95% confidence intervals.
Reference ° pH-4.9 Treatment

Cd conc

ng/g wet wt

grams

μg/fish

Calendar age (yr)
Figure 5. Mean cadmium concentration, weight, and cadmium burden of whole yellow perch (*Perca flavescens*) from the treatment and reference basins of Little Rock Lake, Wisconsin, in relation to total-length group. Fish were sampled in April 1991 at the end of the second year of the pH-4.9 treatment. Error bars around each mean are 95% confidence intervals.
There is a graph showing the distribution of cadmium concentration, body burden, and fresh weight in fish across different length groups. The graph compares two treatments: Reference and pH-4.9 Treatment.

**Cadmium Concentration (ng/g wet wt):**
- Reference: Continuous line with filled circles.
- pH-4.9 Treatment: Continuous line with open circles.

**Body Burden (μg/fish):**
- Reference: Continuous line with filled circles.
- pH-4.9 Treatment: Continuous line with open circles.

**Fresh Weight (grams):**
- Reference: Continuous line with filled circles.
- pH-4.9 Treatment: Continuous line with open circles.

The x-axis represents the total length group (mm) ranging from <120 to ≥180.
Table 4. Concentrations of cadmium in whole, age-1 yellow perch (*Perca flavescens*) from the treatment and reference basins of Little Rock Lake, Wisconsin, during experimental acidification of the treatment basin.

<table>
<thead>
<tr>
<th>Month and year of sampling</th>
<th>Mean pH of treatment basin</th>
<th>Mean Cd conc. (ng·g⁻¹ wet wt)</th>
<th>T:R ratio*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Treatment basin</td>
<td>Reference basin</td>
</tr>
<tr>
<td>April 1988</td>
<td>5.2</td>
<td>27.2 (1.5)</td>
<td>25.6 (1.0)</td>
</tr>
<tr>
<td>April 1989</td>
<td>5.2</td>
<td>20.4 (1.0)</td>
<td>19.8 (0.8)</td>
</tr>
<tr>
<td>April 1990</td>
<td>4.9</td>
<td>12.5 (0.4)</td>
<td>38.4 (2.2)</td>
</tr>
<tr>
<td>April 1991</td>
<td>4.9</td>
<td>8.0 (0.3)</td>
<td>25.3 (1.3)</td>
</tr>
</tbody>
</table>

* Mean pH of reference basin was about 6.1.

** Standard error is given in parentheses under each mean; n=30 fish for each mean.

* The T:R ratio is the ratio of the basin means (T/R) for cadmium; two asterisks (**) indicate that the means differed between basins at p<0.001; NS indicates no significant difference between means (p>0.05), based on a t-test.
Mean cadmium concentrations within a given basin were greater in age-1 fish sampled in 1990 (after the first year at pH 4.9) than in 1991, but the observed T:R ratios between treatment-basin and reference-basin fish were the same for both years (Table 4).

The mean whole-body burdens (mass) of cadmium accumulated in age-1 yellow perch did not differ between basins during the 2 years of acidification to pH 5.2, but were greater in the reference basin than in the treatment basin after the 2 years at pH 4.9 (Table 5). The mean burden of cadmium accumulated by age-1 treatment-basin fish during the first year of the pH-4.9 treatment was less than half that in reference-basin fish. After the second year of acidification to pH 4.9, the difference in whole-body burdens between basins was even more pronounced (Table 5).

In contrast to the age-1 fish sampled in 1989, mean whole-body concentrations of cadmium in age-2 and older yellow perch differed markedly between the treatment and reference basins (Fig. 2). The mean whole-body cadmium concentration in age-2 yellow perch from the reference basin (31 ng·g⁻¹; n=17) was significantly (t-test; p<0.001) greater than the mean whole-body cadmium concentration in age-2 yellow perch from the treatment basin (20 ng·g⁻¹; n=30). However, the mean whole-body burden in age-2 fish from the reference basin (504 ng Cd) did not differ from that in the treatment basin (461 ng Cd), owing to the greater fresh weights of the faster growing treatment-basin fish (Fig. 2). Similarly, mean concentrations of cadmium in the 130-139 mm total-length group sampled in 1989 (Fig. 3) were significantly (t-test; p=0.02) greater in the reference basin (36 ng·g⁻¹; n=11) than the treatment basin (23 ng·g⁻¹; n=11), yet
Table 5. Whole-body burdens of cadmium accumulated by calendar age-1 yellow perch (*Perca flavescens*) from the treatment and reference basins of Little Rock Lake, Wisconsin, during experimental acidification of the treatment basin.

<table>
<thead>
<tr>
<th>Month and year of sampling</th>
<th>Mean pH of treatment basin</th>
<th>Mean Cd burden (ng)</th>
<th>T:R ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Treatment basin</td>
<td>Reference basin</td>
</tr>
<tr>
<td>April 1988</td>
<td>5.2</td>
<td>200</td>
<td>194</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(10)</td>
<td>(7)</td>
</tr>
<tr>
<td>April 1989</td>
<td>5.2</td>
<td>159</td>
<td>144</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(7)</td>
<td>(6)</td>
</tr>
<tr>
<td>April 1990</td>
<td>4.9</td>
<td>74</td>
<td>162</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(3)</td>
<td>(8)</td>
</tr>
<tr>
<td>April 1991</td>
<td>4.9</td>
<td>56</td>
<td>171</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(3)</td>
<td>(10)</td>
</tr>
</tbody>
</table>

- Mean pH of reference basin was about 6.1.
- Standard error is given in parentheses under each mean; *n*=30 fish for each mean.
- The T:R ratio is the ratio of the basin means (T/R) for cadmium; two asterisks (**) indicate that the means differed between basins at *p*<0.001; NS indicates no significant difference between means (*p*>0.05), based on a *t*-test.
whole-body burdens in this length group did not differ between basins (t-test; p=0.12). Comparisons of mean whole-body cadmium concentrations and burdens in fish from the 120-129 mm total-length group were not feasible because only 2 treatment-basin fish from this size class were caught and analyzed (Table 2).

Mean concentrations and burdens of cadmium in the yellow perch populations differed substantially between basins in both 1989 and 1991. In 1989, mean concentrations in age-2 and older fish were greater in the reference basin than treatment basin, whether compared on the basis of age (Fig. 2) or total length (Fig. 3). In 1991, mean concentrations and burdens in reference-basin fish exceeded those in treatment-basin fish for all age and length groups (Figs. 4 and 5).

Mean cadmium concentrations in fish from the two basins in 1989 generally increased with increasing age (Fig. 2) and increasing total length (Fig. 3). Moreover, reference-basin fish bioaccumulated cadmium at faster rates than the treatment-basin fish, even though fish grew faster in the treatment basin. In contrast, mean concentrations of cadmium in fish in 1991 were weakly related to age (Fig. 4) and size (Fig. 5) of the fish.

Cadmium concentrations in yellow perch (all years and size classes) ranged from 12 to 138 ng·g⁻¹ fresh weight (mean 37 ng·g⁻¹; SD 3.4) in reference-basin fish and from 5 to 53 ng·g⁻¹ (mean 18 ng·g⁻¹; SD 1.5) in treatment-basin fish. Mean concentrations of cadmium in the yellow perch populations (all total-length groups) in Little Rock Lake, estimated from the stratified random sampling of fish in 1989, were 22 ng·g⁻¹ (SE 0.8 ng·g⁻¹) in the treatment basin and 33 ng·g⁻¹ (SE 1.4 ng·g⁻¹) in the reference
basin. The estimated inventories (masses) of cadmium in the yellow perch populations in 1989 were 24 mg (SD 1.1 mg) in the reference basin and 19 mg (SD 0.8 mg) in the treatment basin. Normalized to lake area, the cadmium inventories in the yellow perch populations were 3.0 mg·ha⁻¹ in the reference basin and 1.9 mg·ha⁻¹ in the treatment basin. Mark-recapture estimates of yellow perch abundance in the Lake (used to calculate mean concentrations and cadmium inventories) were not available for 1991.
95
DISCUSSION

My results from Little Rock Lake indicate that experimental lake acidification decreased the bioavailability of cadmium to fish. It is improbable that the difference in cadmium bioaccumulation between basins resulted from differences in cadmium loading rates. Little Rock Lake receives nearly all of its hydrologic inflow from precipitation falling directly onto the lake surface, and hydrologic inflows from the catchment (ground-water inflow plus overland flow) are small (Krabbenhoft and Babiarz 1992). Consequently, influxes of cadmium from the terrestrial catchment to the Lake are presumably, small relative to influxes from atmospheric deposition. In a companion study, Powell (1993) observed that whole-lake burdens of cadmium in the surficial sediments of six seepage lakes in the study area (including the reference basin of Little Rock Lake) were strongly correlated \( (r_{ij} > 0.99) \) with lake area, indicating that atmospheric deposition was the primary source of cadmium for the lakes. It is, improbable that the annual atmospheric influx of cadmium, on a per unit of lake area basis, differed between the treatment and reference basins during the present study. Consequently, the differences in bioaccumulation of cadmium by fish between the treatment and reference basins of Little Rock Lake probably resulted from differences in internal (within-basin) processes influencing the bioavailability and uptake of the metal.

The differences in cadmium bioaccumulation by age-1 yellow perch between the two basins cannot be logically attributed to differences in growth (i.e., to a
growth-dilution effect), because differences in body size were not evident after 1 year of
in situ exposure. Moreover, data on whole-body burdens (Table 5) show that age-1 fish
taken from the treatment basin in 1990 bioaccumulated significantly less cadmium than
the smaller reference-basin fish. Although concentrations and burdens of cadmium in
age-1 fish did not differ between basins in 1989, bioaccumulation of cadmium by larger
fish in 1989 was greater in the reference basin than the treatment basin. All age and
length groups sampled in 1991 bioaccumulated more cadmium in the reference basin than
in the treatment basin.

Cadmium accumulation by fish has been widely attributed to the direct uptake of
\( \text{Cd}^{2+} \) across the gills (Williams and Giesy 1978; Pärt and Svanberg 1981; Kay 1985; Pärt
et al. 1985). Consequently, the observed differences in the bioaccumulation of cadmium
in fish between the treatment and reference basins may have resulted from (1) changes in
the speciation of aqueous cadmium, (2) changes in the uptake rate of \( \text{Cd}^{2+} \) across the gill
lamellae, or (3) both.

It seems doubtful that the decrease in cadmium accumulation by yellow perch in
the acidified treatment basin, relative to the reference basin, occurred due to decreased
concentrations of biologically available cadmium (i.e., \( \text{Cd}^{2+} \)). In the absence of organic
ligands, cadmium is predicted to exist as free \( \text{Cd}^{2+} \) across the pH range of 4-7 (Campbell
and Stokes 1985; Campbell and Tessier 1987). Hence, acidification from pH 6.1 to the
treatment pHs of 5.2 and 4.9 should have had little influence on the speciation or
abundance of cadmium in the treatment basin. A significant fraction of the cadmium in
freshwater may exist in complexes with organic ligands (Hart 1981; Laxen and Harrison 1981; John et al. 1988). Complexed cadmium may be less available for biological uptake or may precipitate out of solution; however, the fraction of cadmium chelated by organic ligands seems to decrease with decreasing pH (Engel et al. 1981; Borg and Andersson 1984; John et al. 1988). Concentrations of dissolved manganese and iron increased in the treatment basin of Little Rock Lake in response to acidification (Mach and Brezonik 1989; Brezonik et al. 1990; King et al. 1992). However, cadmium and other trace metals were not removed from the water column by adsorption onto ferromanganese oxyhydroxides (Mach and Brezonik 1989). Consequently, available evidence suggests that the concentrations of Cd^{2+} available for uptake by fish and other biota were not diminished by acidification of the treatment basin.

Substantial evidence indicates that concentrations of aqueous cadmium in dilute, clear-water lakes are negatively correlated with lake pH (Borg 1983; Schmidt 1985; Borg 1987; Stephenson and Mackie 1988), possibly due to decreased cadmium deposition to the sediments (Evans et al. 1983; Stephenson and Mackie 1988; Borg et al. 1989). However, because atmospheric influx is the primary source of cadmium to Little Rock Lake (Powell 1993), it is doubtful that the concentration of aqueous cadmium in the treatment basin would increase substantially during the relatively short (6 yr) time span of the acidification project. King et al. (1992) reported that cadmium concentrations in filtered water samples from Little Rock Lake were greater in the treatment basin than the reference basin during the pH-5.2 and pH-4.9 treatments. However, the cadmium
concentrations reported by King et al. (1992) are higher than concentrations reported for unfiltered samples from other low-alkalinity lakes (reviewed by Spry and Wiener 1991).

The bioaccumulation of cadmium by fish in the treatment basin may have decreased partly in response to increased concentrations of aqueous Ca$^{2+}$ in the basin. Calcium in Little Rock Lake increased from a pre-acidification concentration of about 1 mg·L$^{-1}$ (25 μM) to about 1.6 mg·L$^{-1}$ (40 μM) during the pH-4.9 treatment (Mach 1992 as cited by Eaton et al. 1992; King et al. 1992). Laboratory studies have shown that the availability of cadmium to perfused fish gills is directly related to the activity of free Cd$^{2+}$ (Pärt and Svanberg 1981; Pärt and Wikmark 1984; Pärt et al. 1985), which is strongly influenced by ionic strength (Pärt et al. 1985). Consequently, cadmium in hard-water or alkaline systems is less toxic and less available to fish because of decreased Cd$^{2+}$ activity (a function of ionic strength) and because of the ameliorating effects of aqueous Ca$^{2+}$ on gill-membrane permeability and cadmium uptake (Pascoe et al. 1986; Wicklund and Runn 1988; Pärt et al. 1985). The results of the cited studies, however, may not readily apply to cadmium uptake by fish in dilute, low-alkalinity lakes because their studies were done with relatively hard waters (Ca$^{2+}$ concentrations 150-5400 μM) and with aqueous cadmium concentrations ranging from 10 ng·L$^{-1}$ to 1000 μg·L$^{-1}$ (Pascoe et al. 1986; Wicklund and Runn 1988; Pärt et al. 1985), concentrations much higher than those in many low-alkalinity lakes (reviewed by Spry and Wiener 1991), including Little Rock Lake (Mach and Brezonik 1989; Brezonik et al. 1990; King et al. 1992).
Competition between cadmium and hydrogen ions for binding sites on the gill surface (Pagenkopf 1983; Borgmann 1983; Cusimano et al. 1986; McDonald et al. 1989) may have greatly reduced the bioavailability of aqueous cadmium in the treatment basin. Laboratory studies show that a reduction in pH diminishes the direct uptake (and toxicity) of cadmium in fish and other aquatic organisms exposed to a fixed concentration of cadmium (Campbell and Stokes 1985; Peterson et al. 1985; Cusimano et al. 1986; McDonald et al. 1989). In contrast to the 0.6-fold increase in waterborne calcium, hydrogen ion concentrations in the treatment basin increased more than 10-fold, from about 1 μM (pH 6.0) before experimental acidification conditions to about 13 μM during the pH-4.9 treatment. Increases, if any, in aqueous cadmium concentrations in the treatment basin were, therefore, presumably small relative to the 10-fold increase in hydrogen ion concentration during acidification to pH 4.9.

The results for estimates of cadmium inventories of the yellow perch populations in Little Rock Lake clearly show that the uncertainty associated with such estimates can be small if analytical results are of high quality and if sampling and analytical effort are appropriately allocated. However, the passive gear (trap nets) used to sample the yellow perch populations in this study caught few females relative to the number of males caught. If this same sampling bias occurred during the mark-recapture sampling for estimation of abundance, the estimated population sizes and corresponding cadmium inventories in these yellow perch populations may be underestimated. Nonetheless, some
general statements can be made concerning the partitioning and potential bioavailability of cadmium in Little Rock Lake.

The estimated inventories of cadmium in the yellow perch populations in 1989 were 19 mg (1.9 mg ha\(^{-1}\)) in the treatment basin and 24 mg (3.0 mg ha\(^{-1}\)) in the reference basin. These amounts are minuscule relative to the estimated burdens of cadmium in the surficial (uppermost 5 cm) sediments, which were 625 g (77 g ha\(^{-1}\)) in the reference basin (Powell 1993) and 714 g (73 g ha\(^{-1}\)) in the treatment basin (D. E. Powell, Iowa State University, unpublished data). Clearly, release of cadmium from the bottom sediments could greatly increase the amount of cadmium available to biota in Little Rock Lake. For example, mobilization of only 1% of the cadmium in the shallow-water sediments (i.e., sediments at water depths less than the mean lake depth) of Little Rock Lake could add 3 g of cadmium to the water column of the reference basin and 4 g to the water column of the treatment basin. The basin volumes of Little Rock Lake are 3.8 x 10\(^5\) m\(^3\) for the treatment basin and 2.5 x 10\(^5\) m\(^3\) for the reference basin (Watras et al. 1991); consequently, release of 3 to 4 g of cadmium from the sediments to the water column would increase aqueous cadmium concentrations about 10 ng L\(^{-1}\). In comparison, total aqueous concentrations in low-alkalinity lakes in northern Wisconsin and central Ontario appear to range from less than 10 ng L\(^{-1}\) to about 200 ng L\(^{-1}\) (reviewed by Spry and Wiener 1991).

The data presented here indicate that acidification does not increase cadmium bioaccumulation in fish. Nonetheless, acidification may reduce the deposition of
cadmium to sediments, eventually increasing the concentrations of waterborne cadmium. From a biological perspective, it is inconsequential whether cadmium concentrations in the water column increase in response to decreased deposition to the sediments or increased efflux of cadmium from the sediments. Competition by hydrogen ions for binding sites on the gill surface may initially decrease the bioaccumulation of cadmium by fish during a rapid or episodic acidification event, such as that observed during acidification of the treatment basin in Little Rock Lake. However, the treatment basin was acidified over the relatively short time of 6 years, and it is doubtful that cadmium concentrations in the water column approached dynamic equilibrium. Therefore, it is not unreasonable to suspect that aqueous cadmium concentrations in the treatment basin may have been increasing in response to acidification, but at substantially slower rates than concentrations of hydrogen ion. Consequently, cadmium bioaccumulation by fish in the acidified treatment basin might be greater if the acidification occurred over a longer time period.
REFERENCES CITED


GENERAL SUMMARY

Cadmium and cadmium-containing products are used extensively in consumable goods that are often incinerated or carelessly discarded. As a result, substantial amounts of anthropogenic cadmium are released to the environment on an annual basis. Moreover, the practice of incinerating consumable wastes (notably rechargeable NiCd batteries) produces aerosols of cadmium that are released directly into the atmosphere. Enrichment of surficial sediments with cadmium seems to be a widespread pattern in many remote and semi-remote lakes, presumably due to increased atmospheric transport of the metal. Because of the toxicity and anthropogenic mobility of cadmium, contamination of aquatic ecosystems with the metal has, justifiably, become a concern of international significance.

The two papers in this dissertation summarize a study on the accumulation of cadmium in sediments and fish of six seepage lakes in north-central Wisconsin. The whole-lake burdens and spatial distributions of cadmium in the bottom sediments of the study lakes are described in Paper 1. Bioaccumulation of cadmium by yellow perch (Perca flavescens) in one of the lakes, Little Rock, which is the site of an experimental pH-manipulation project, is described in Paper 2. Results presented in the two papers clearly show that the biogeochemistry of cadmium in the lakes is strongly influenced by atmospheric fluxes of the metal and the process of lake acidification.
The results presented in Paper 1 show that the atmospheric flux of cadmium to the study lakes was substantial. Whole-lake burdens of cadmium in the surficial sediment (uppermost 5 cm) in the lakes ranged from 625 to 5785 g and were strongly correlated ($r_r > 0.99$) with lake surface area. Moreover, when normalized for lake area, the areal burdens of cadmium were similar (range 62-92 g·ha$^{-1}$), indicating that the flux of cadmium to the lakes was comparable and that deposition of cadmium to the sediments was similar among the lakes.

Dry weight concentrations of cadmium were substantially less in sediments from shallow water than in sediments from deeper water—a trend that was observed for all 6 lakes. However, volumetric concentrations of cadmium in the surficial sediments of the lakes did not appear to be related to depth in 4 of the lakes. Furthermore, 28-57% of the burden of cadmium in the lakes (representing cadmium masses of 322-3276 g) was found in shallow-water sediments (i.e., sediments at water depths less than the mean water depth of a lake). These results indicate that the mass of cadmium in shallow-water sediments may be underestimated in seepage lakes if concentrations of cadmium in the sediments are expressed on the basis of dry weight. Therefore, the significance of shallow-water sediments as reservoirs of potentially available cadmium is often ignored. But release of only 1% of the cadmium in the shallow-water sediments would add 32-328 g of cadmium to the water column of the study lakes and increase aqueous cadmium concentrations by about 2-15 ng·L$^{-1}$. 
The results presented in Paper 2 show that experimental lake acidification substantially decreased the bioaccumulation of cadmium by fish in Little Rock Lake, probably in response to increased competition between cadmium and hydrogen ions for binding sites on the gill lamellae. Mean whole-body concentrations and burdens (mass) of cadmium in age-1 yellow perch sampled after a 1-year *in situ* exposure period to conditions in the Lake, were greater in reference-basin fish than fish from the acidified treatment basin after each year of the pH-4.9 treatment (1990 and 1991). Bioaccumulation of cadmium by larger fish was also greater in the reference basin than the treatment basin. Mean whole-body concentrations and burdens of cadmium in age-2 and older fish were greater in the reference basin than the treatment basin after 2 years exposure to pH-5.2 conditions and after 2 years exposure to pH-4.9 conditions. These results suggest that bioaccumulation of cadmium by fish may decrease during the initial stages of acidification.

Concentrations of cadmium increased concomitantly with age and size of yellow perch in Little Rock Lake in April 1989, suggesting that diet may have been an important route of cadmium uptake. One study (Harrison and Klaverkamp 1989) has shown that dietary uptake of cadmium is more efficient than direct uptake of Cd$^{2+}$ across the gill, for fish exposed to low aqueous concentrations of cadmium in hard-water. However, the uptake of dietary cadmium by fish is widely considered to be small relative to the direct uptake of Cd$^{2+}$ across the gills (Kay 1985; Spry and Wiener 1991). Moreover, most studies indicate that cadmium does not biomagnify in aquatic food webs (Campbell *et al.*
Hence, cadmium concentrations in fish generally increase with increasing exposure concentrations of biologically available cadmium (i.e., Cd\(^{2+}\)).

It is not clear why concentrations of cadmium increased with the age and size of yellow perch in Little Rock Lake in April 1989 but not in April 1991. Weather, however, may have been a factor. The summer of 1988 was one of the hottest and driest summers on record. As a result, the water-level in Little Rock Lake dropped an estimated 1 m and littoral habitats previously utilized by aquatic biota no longer existed.

Lake survey studies indicate that whole-body cadmium concentrations in fish from low-pH waters are often elevated relative to concentrations in fish from waters having circumneutral pH (Wiener 1983, 1987; Hamilton and Haines 1989; Stripp et al. 1990). However, the results presented in Paper 2 show that competition by hydrogen ions for binding sites on the gill surface may initially decrease the bioaccumulation of cadmium by fish during a rapid or episodic acidification event. Consequently, the elevated concentrations of cadmium observed in fish inhabiting low-pH waters may reflect increased concentrations of waterborne cadmium rather than increased uptake rates.

Aqueous concentrations of cadmium in dilute, clear-water lakes, are often negatively correlated with lake pH in semi-remote areas (Borg 1983; Schmidt 1985; Borg 1987; Stephenson and Mackie 1988). Although rates of deposition of cadmium from the water column to the sediment-water interface were not measured in the study lakes, the data in Paper 1 indicate that decreased deposition of cadmium to the sediments could
account for the increased concentrations of cadmium reported for low pH waters, as has been suggested by others (Evans et al. 1983; Stephenson and Mackie 1988; Borg et al. 1989). The recent rate of sedimentation in Crystal Lake, one of the six lakes studied in Paper 1, was estimated at $1.4\pm0.2 \text{ mm} \cdot \text{yr}^{-1}$ (Talbot and Andren 1983), and is comparable to the mean rate of sedimentation of $4.3 \text{ mm} \cdot \text{yr}^{-1}$ reported for 10 lakes in south-central Ontario (Evans et al. 1986). Assuming that rates of sedimentation in the six study lakes are comparable to these estimates, then the net deposition of cadmium to sediments in the lakes is on the order of $2-8 \text{ g} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$. Clearly, the amount of cadmium available to biota in the water column of the study lakes could increase substantially over a sufficient period of time, if deposition of cadmium to the sediment-water interface decreased in response to decreasing pH. In Little Rock Lake, for example, the estimated inventory of cadmium in the yellow perch populations, based on analyses of samples taken in 1989, were $24 \text{ mg} (3.0 \text{ mg} \cdot \text{ha}^{-1})$ in the reference basin and $19 \text{ mg} (1.9 \text{ mg} \cdot \text{ha}^{-1})$ in the treatment basin.
REFERENCES


Financial support for this study was provided by the River Studies Center and Department of Biology and Microbiology at the University of Wisconsin-La Crosse; the U.S. Fish and Wildlife Service, National Fisheries Research Center, La Crosse, Wisconsin; and the Department of Animal Ecology at Iowa State University. Facilities and equipment were provided by the River Studies Center and the Department of Biology and Microbiology at the University of Wisconsin-La Crosse. Research stipends during my residence at Iowa State University were provided, in part, by the Toxicology and Animal Ecology Programs. I am grateful to my major advisors, Gary J. Atchison (Iowa State University) and Ronald G. Rada (University of Wisconsin-La Crosse) for their guidance, support, and scientific leadership. Thanks are also extended to my committee members, James G. Wiener (U.S. Fish and Wildlife Service, National Fisheries Research Center, La Crosse, WI), Joel R. Coats (Iowa State University), and Erwin E. Klaas (U.S. Fish and Wildlife Service, Cooperative Fish and Wildlife Research Unit, Ames, IA), for reviewing an earlier draft of the dissertation. I thank Carl Watras, Steven Claas, and the staff at the University of Wisconsin-Madison Trout Lake Station for the use of their equipment and laboratory facilities. William Van Atta of the University of Wisconsin-La Crosse provided scuba-diving equipment. Special thanks are extended to the following University of Wisconsin-La Crosse students for providing technical assistance: Bradley Frazier, Kristofer Rolfus, Joseph Anglehart, William Maurer, Wendy
(Crooks) Frazier, Beth Schmit, Pam Vetter, William Nelson, Suzanne Thorson, David Morrow, Christine Storlie, Christopher Weeks, Frederick Weeks, Suzanne Anglehart, and Steven Briggs. Finally, I am most grateful to my wife Christie, our children Jessica and Bryan, and my parents for their patience, understanding, and encouragement during my doctoral studies.