Calcium declines in northeastern Ontario lakes

W. Keller, S.S. Dixit, and J. Heneberry

Abstract: Thousands of lakes in northeastern Ontario, Canada, have been acidified by sulphur deposition associated with emissions from the Sudbury area metal smelters. However, water quality improvements including increased pH and reduced sulphate concentrations have followed large reductions in Sudbury emissions that were implemented, beginning in the 1970s. Substantial decreases in Ca concentrations accompanied these other changes in lakewater chemistry. Monitoring of 38 lakes 20–128 km from Sudbury showed declines in Ca concentrations, averaging 2.7 $\mu eq \cdot L^{-1} \cdot year^{-1}$, over the period 1981–1999. Declines were particularly apparent during the 1990s, averaging 3.8 $\mu eq \cdot L^{-1} \cdot year^{-1}$. Paleolimnological reconstructions of the long-term Ca patterns in six lakes suggest that general lakewater Ca declines occurred through much of the 20th century. Comparison of recent measured Ca concentrations in 16 lakes with diatom-inferred pre-industrial Ca concentrations indicates that overall decreases in Ca have been large, averaging 74.6 $\mu eq \cdot L^{-1}$ or 46%. Long-term Ca patterns may reflect a combination of factors including climatic changes, forest harvesting activities, and leaching by acid deposition, the effects of which we can not separate. Calcium declines have biological implications that will need to be considered in the development of appropriate targets as these lakes continue to recover from acidification.

Résumé : Des milliers de lacs du nord-est de l'Ontario, Canada, ont été acidifiés par les dépôts de soufre provenant des émissions des fonderies de la région de Sudbury. Cependant, les réductions importantes des émissions depuis les années 1970 ont entraîné une amélioration de la qualité de l'eau et, en particulier, un accroissement du pH et une diminution des concentrations de sulfates. Des réductions importantes des concentrations de Ca ont accompagné ces changements dans la chimie des eaux des lacs. Le suivi de 28 lacs situés à des distances de 20 à 128 km de Sudbury indique des déclins dans les concentrations de Ca d'en moyenne 2,7 $\mu eq \cdot L^{-1} \cdot année^{-1}$ de 1981 à 1999, particulièrement durant les années 1990 où les taux étaient en moyenne de 3,8 $\mu eq \cdot L^{-1} \cdot année^{-1}$. Des reconstitutions paléolimnologiques de l'évolution à long terme du Ca dans six des lacs laissent croire que le déclin général du Ca dans l'eau des lacs s'est poursuivi pendant presque tout le vingtième siècle. Une comparaison des concentrations récentes de Ca dans 16 lacs avec les concentrations estimées d'après les peuplements de diatomées avant l'ère industrielle montre que le déclin de Ca a été important, en moyenne de l'ordre de 74,6 $\mu eq \cdot L^{-1}$ ou de 46%. Cette évolution à long terme du Ca peut être le reflet d'une combinaison de facteurs, dont les effets ne peuvent être séparés, en particulier les changements climatiques, les activités de coupe des forêts et le lessivage dû aux précipitations acides. Les déclins du Ca ont des implications biologiques qu'il sera nécessaire de considérer dans la définition d'objectifs appropriés, à mesure que ces lacs se rétablissent de l'acidification.

[Traduit par la Rédaction]

Introduction

In response to decreases in atmospheric deposition of sulphur, lakes in some areas of the world are now beginning to show signs of chemical recovery from acidification, including decreased sulphate concentrations and decreased acidity (Skjelkvale et al. 1998; Stoddard et al. 1999). However, in many regions, a large part of the declines in lakewater sulphate that have resulted from reduced sulphur deposition has been balanced by decreased concentrations of base cations, with the result that there has been little change in pH or alkalinity (Driscoll et al. 1995; Stoddard et al. 1999). Reduced export from watersheds and declines in atmospheric deposition have been implicated in the observed decreases in base cations in lake waters (Hedin et al. 1987; Likens et al. 1996). Declining concentrations of base cations, particularly Ca, may have important implications for the biological as well as the chemical recovery of acidified lakes. If the chemical recovery of acidified lakes leads to Ca concentrations that are substantially lower than historical conditions, habitat quality for aquatic biota could be affected.

Metal mining and smelting activities began around Sudbury, in northeastern Ontario, Canada, in the late 1800s. Ultimately, thousands of lakes in a large area surrounding the metal smelters near Sudbury were acidified by sulphur deposition associated with the smelter emissions (Neary et al. 1990). However, with the substantial reductions in emissions (Fig. 1) at Sudbury area smelters (over 90% since peak years in the 1960s), that began in the 1970s, considerable chemical

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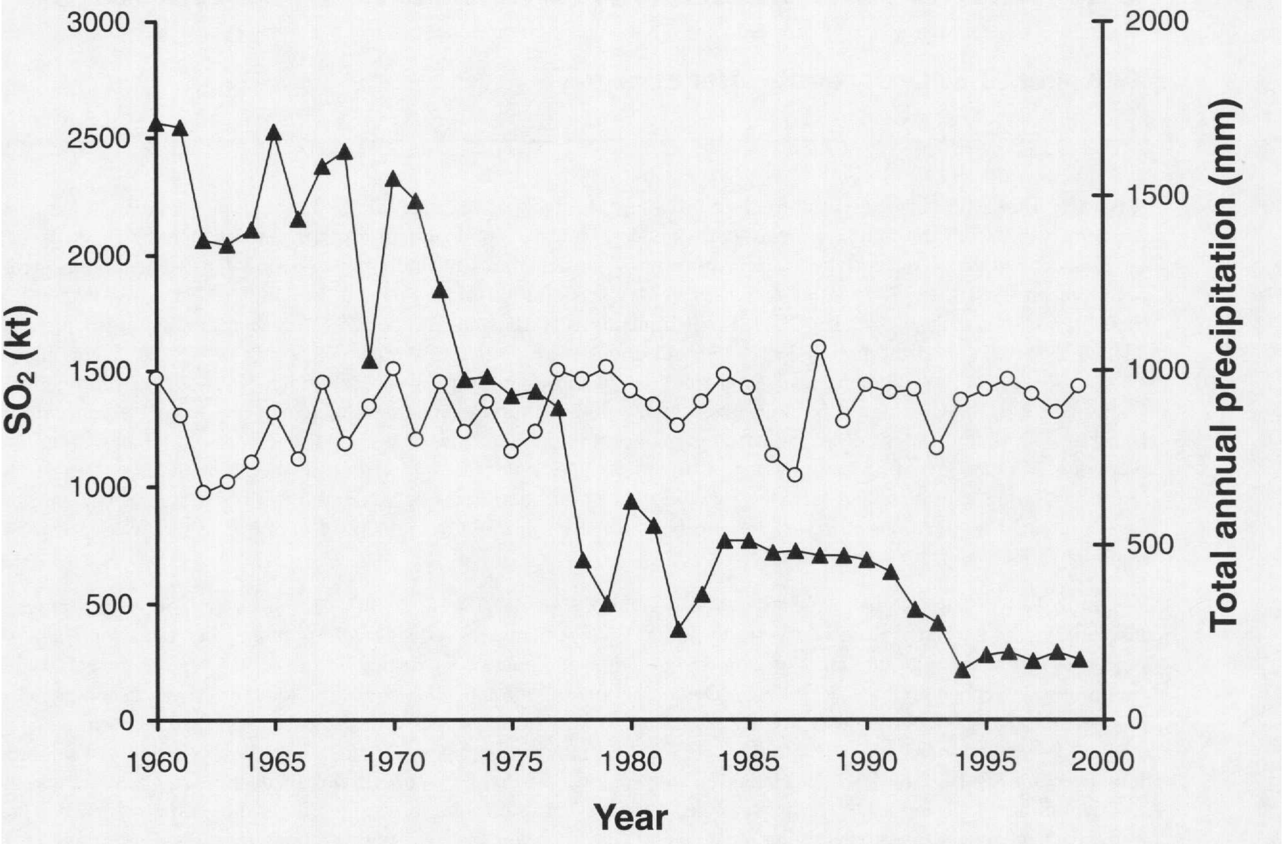
Fig. 1. Total annual precipitation (○) and sulphur dioxide emissions (▲) from the Sudbury area smelters.



and biological recovery has occurred in Sudbury area lakes (Keller 1992). At a time when evidence of chemical recovery is only beginning to emerge from lakes in other acidified regions, results from lake monitoring programs in the Sudbury area provide a unique opportunity to examine long-term patterns in lakewater Ca concentrations in acid-damaged lakes in which substantial recovery has occurred over several decades. We are rarely in a position to know what actual pre-acidification Ca concentrations were in acid-damaged areas, such as around Sudbury and elsewhere. However, paleolimnological techniques provide the opportunity to reconstruct the past in damaged lakes, and infer the magnitude of the changes in chemistry that have occurred (Smol 1995). A diatom-based Ca inference model is now available for the Sudbury region (Dixit et al. 2002). By coupling paleolimnological inferences of background Ca concentrations with measurements from ongoing monitoring studies we are able to estimate the extent of the changes in Ca that have occurred during the acidification and recovery of Sudbury area lakes.

The specific objectives of this paper are to (1) determine trends in measured Ca concentrations in 38 Sudbury area lakes over the last two decades; (2) reconstruct, using a diatom-based Ca inference model, the long-term temporal patterns in Ca in six Sudbury area lakes that are recovering from acidification; (3) estimate overall changes by comparing recent Ca concentrations to inferred pre-industrial conditions in 16 of our monitoring lakes for which paleolimnological analyses have been conducted; and (4) discuss the factors potentially responsible for Ca declines. Our overall goal is to evaluate the changes in Ca that have occurred in Sudbury area lakes and examine the implications of these changes for the lake recovery process and aquatic biota.

Methods

Chemical monitoring

The measured Ca data examined in this paper are from synoptic (single annual mid-summer samples) surveys of 38 lakes (Fig. 2) 20–128 km from Sudbury, which have been sampled since 1981. The lakes are in various stages of recovery from acidification. When monitoring began in 1981 the pH of these lakes ranged from 4.3 to 5.8. In 1999 lakewater pH ranged from 4.6 to 6.7. A summary of general chemical and physical characteristics of the lakes is provided in Table 1. These lakes are a subset of a slightly larger lake set ($n = 44$) that is regularly sampled (Keller et al. 1998). For this analysis, however, we excluded lakes that are located within 20 km of Sudbury in which urban influences might complicate the interpretation of Ca trends. Calcium data are available for most lakes for every year from 1981 to 1999, but some lakes are missing data for some years.

Sampling methods and general descriptions of the lakes are given in Keller and Pitblado (1986) and Keller et al. (1998). Briefly, mid-lake chemistry samples were collected at surface or as non-volume-weighted epilimnion–metalimnion composites, which are comparable in these lakes (Keller and Pitblado 1986). Water samples were analysed for Ca by atomic absorption spectrophotometry at the Ontario Ministry of the Environment laboratories in Toronto (Keller et al. 1998).

Fig. 2. The zone of lakes influenced by the Sudbury smelters, defined by the extent to which sulphate has replaced bicarbonate (sulphate/[sulphate + alkalinity] > 0.7) as the dominant anion in lake waters. This 17 000 km^2 zone contains over 7000 lakes estimated to have been acidified to pH < 6.0, the apparent threshold for significant biological damage (Neary et al. 1990). ●, locations of the 38 monitoring lakes; ○, locations of the six lakes with downcore profiles shown in Fig. 6 (AD, Acid; AWP, Aurora Whitepine; GE, George; LWP, Little Whitepine; LN, Lumsden; WPM, Whitepine McLeod). ■, locations of major current (Cc, Copper Cliff; Fa, Falconbridge) and historical (Co, Coniston) smelter sites.

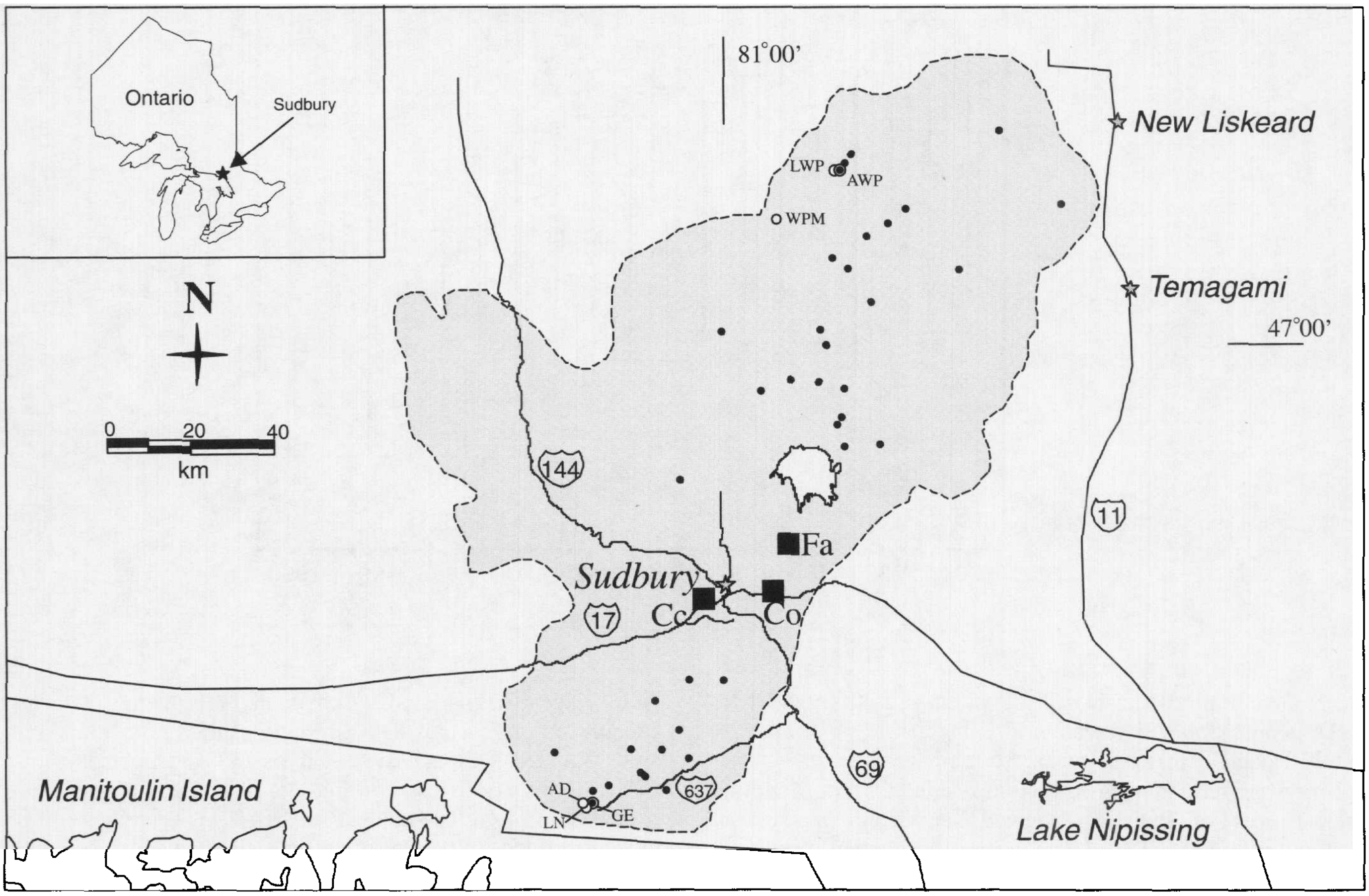


Table 1. General physicochemical characteristics of the 38 monitoring lakes.

Parameter	Mean	Median	Min.	Max.	*n*
Area (Ha)	295.3	192.5	14.5	1315.5	38
Mean depth (m)	9.8	8.0	4.1	24.1	34
Maximum depth (m)	33.5	32.9	11.0	90.3	35
pH	5.3	5.6	4.6	6.7	38
Conductivity ($\mu S \cdot cm^{-1}$)	26.9	27.1	20.2	34.3	38
Total phosphorus ($\mu g \cdot L^{-1}$)	3.9	4.0	2.0	16.0	38
Total nitrogen ($\mu g \cdot L^{-1}$)	150.0	150.0	40.0	360.0	38
Dissolved organic carbon ($mg \cdot L^{-1}$)	2.2	2.3	0.1	6.6	38

Note: Chemistry data are from 1999. Min., minimum; Max., maximum.

Paleolimnology

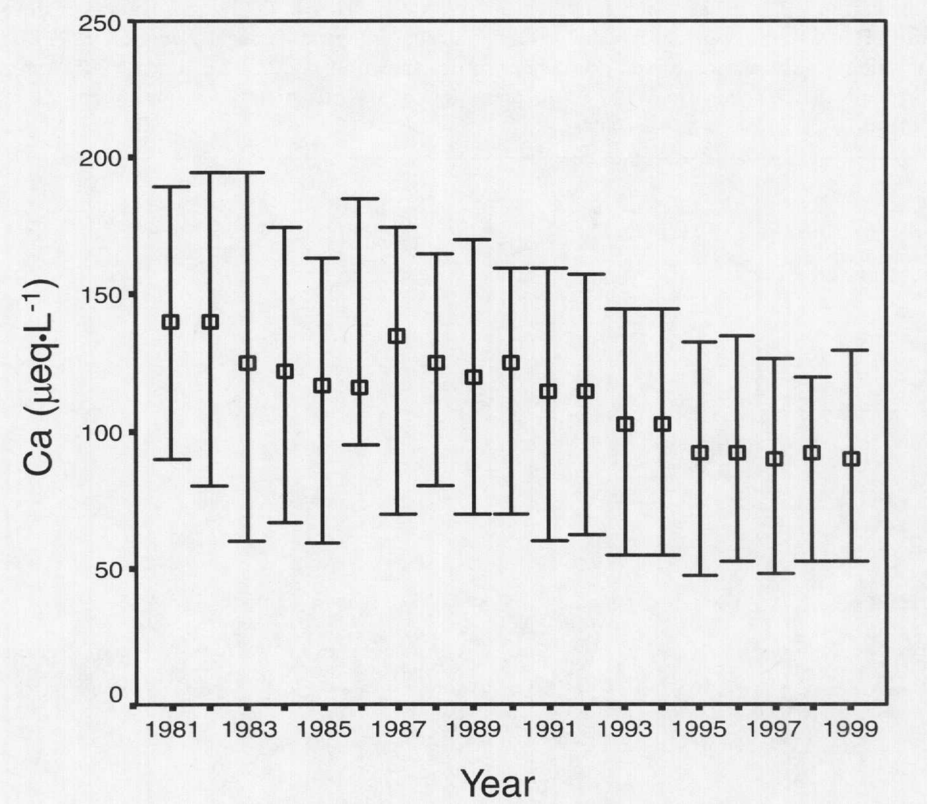
Details of paleolimnological methods, including sediment core collection, preparation of diatom slides, and analysis of diatoms are presented in Dixit et al. (1991, 2002). The WACALIB (version 3.3) program (Line et al. 1994) was used for developing a weighted-averaging (WA) regression and calibration model for Ca (for details see Dixit et al. 2002). Our model included the surface sediment diatom assemblages from 105 Sudbury area lakes. To reconstruct past Ca concentrations, we applied our Ca inference model to downcore samples from six Sudbury area lakes and the bottom sediment samples (representing pre-industrial conditions) from 16 lakes. The detailed diatom stratigraphy of the six lakes considered in this study and their pH reconstructions are presented in Dixit et al. (1992*a*, 1993, 1996). For the use of bottom sediments in assessing post-industrial water quality changes in Sudbury lakes see Dixit et al. (1992*b*).

Results

Trends in measured calcium, 1981–1999

Calcium concentrations in 23 of our 38 monitoring lakes that

Fig. 3. Annual median and range for Ca concentrations in 23 of the monitoring lakes with data from 1981 to 1999.



have data for all years (Fig. 3) ranged from 89.8 to 189.6 µeq·L^{-1} in 1981 (mean, 136.2; median, 139.7) and 52.4 to 129.7 µeq·L^{-1} in 1999 (mean, 86.1; median, 89.8).

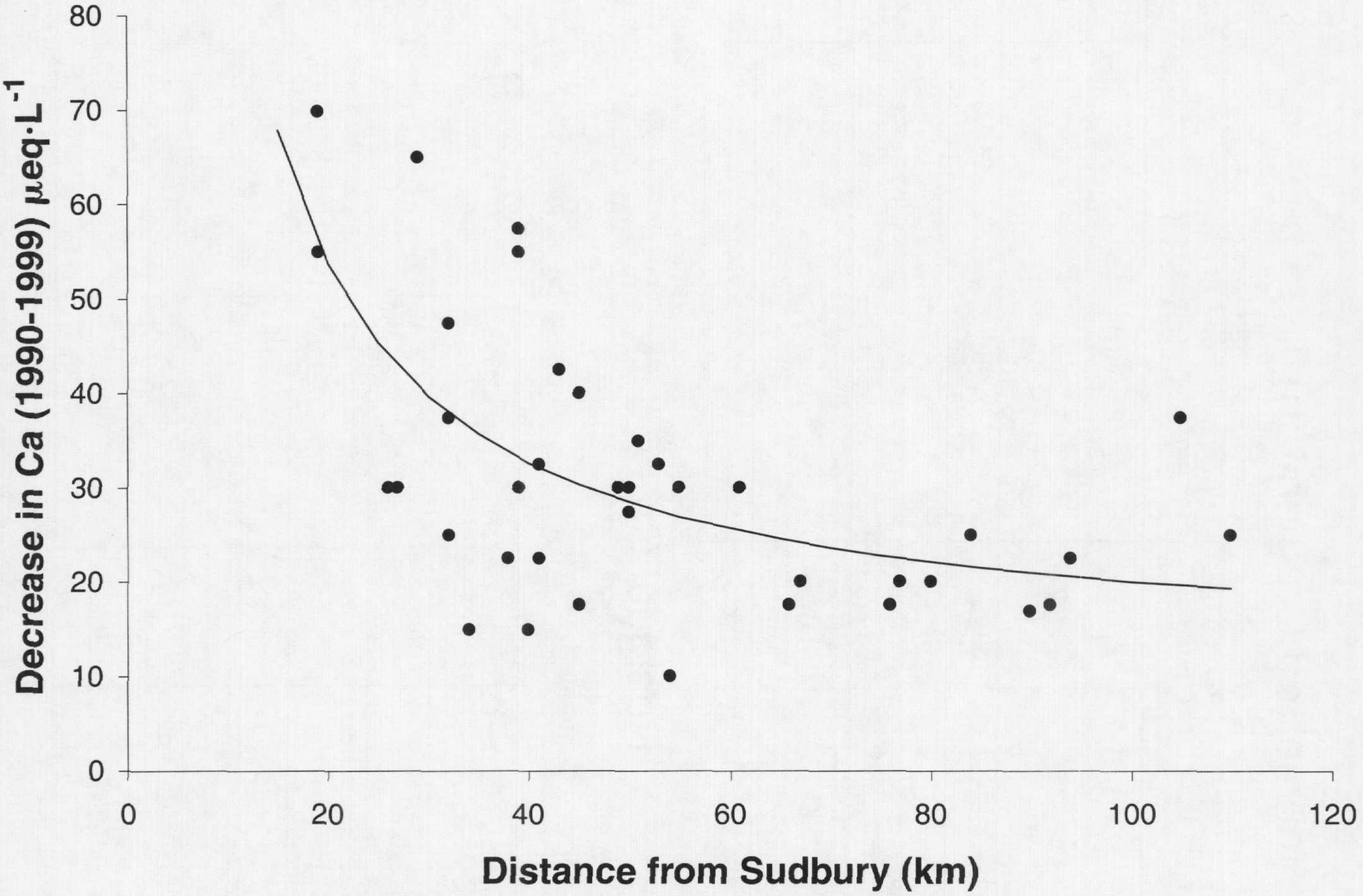
Linear regression analyses of measured Ca concentration against year of sampling showed significant ($p < 0.05$) declines in all 38 of the lakes during the overall continuous monitoring period of 1981–1999 (n = 17–19), and during 1990–1999 (n = 9–10). Average rates of decline were 2.7 µeq·L^{-1}·year^{-1} and 3.8 µeq·L^{-1}·year^{-1} during 1981–1999 and 1990–1999, respectively. Significant ($p < 0.05$) linear declines in Ca concentrations were found in only 15 (39%) of the study lakes during 1981–1989 (n = 7–9), although all but two of the lakes did in fact decrease in Ca over this period, and on average Ca declined by 1.9 µeq·L^{-1}·year^{-1}. Exploratory analyses examining nonlinear relationships (logarithmic, inverse, exponential) between Ca and sampling year for the above study periods did not improve our ability to explain temporal patterns. The magnitude of the Ca declines during the 1990s showed a strong relationship to distance from the Sudbury smelters (Fig. 4).

The calcium inference model

Statistical details considered in evaluating the significance of environmental variables in determining the distribution of diatom assemblages in surface sediments of the 105 Sudbury calibration lakes are presented in Dixit et al. (2002). Here we summarize details pertaining to Ca data. Canonical correspondence analysis (CCA) identified seven significant ($p < 0.01$) environmental variables (pH, Al, Ca, Secchi depth, Ni, Fe, and elevation) in the 105-lake calibration data set, explaining 77% of the total diatom species variance. Among these variables, Ca explained 11% of the total variance in diatom species data and only ranked after pH (31%) and Al (12%). Constrained and partial CCAs and Monte Carlo permutation tests further confirmed the significance ($p < 0.005$) of Ca in our data set. High λ_1/λ_2 values for Ca in constrained (0.65) and partial (0.39) CCAs provided strong evidence that Ca is one of the most important variables in explaining the distribution of diatoms in Sudbury lakes and that a robust diatom-based inference model can be developed for inferring lakewater Ca.

The WA regression and calibration approach (classical regression without tolerance downweighting) was used for developing the diatom-inferred Ca model. The WA approach is widely used in paleolimnological research for the quantitative reconstruction of past environmental conditions (Birks 1998). The relationship between measured and inferred Ca indicates that the simple WA model (Fig. 5*a*) has a high correlation ($r^2 = 0.72$) and low apparent root mean square error (RMSE) (0.32), and the residuals (plot of measured minus inferred Ca and measured Ca) do not show any pattern (Fig. 5*b*). In comparison to simple WA, the WA bootstrap model for Ca (Fig. 5*c*) has a lower correlation ($r^2 = 0.58$) and higher bootstrap RMSE (0.35). Because bootstrap models provide more realistic assessments of the strength of inference models (Birks 1998), this model was used for computing downcore Ca inferences in this study. Bootstrapping is a computer-intensive resampling procedure where a subset of calibration samples that is the same size as the original calibration set is selected at random, with replacement, and the remaining unselected samples form an independent test set. A trend in the residuals of the bootstrap

Fig. 4. Decrease in Ca in Sudbury area lakes between 1990 and 1999 as a function of distance from Sudbury ($y = 11.6010 + (843.534/x)$, $n = 38$, $F = 22.27$, $r^2 = 0.382$, $p < 0.001$).



model (Fig. 5*d*) suggests that our Ca model likely underestimates inferred Ca at higher concentrations. Although we recognize that the statistics of our Ca model are not as strong as the bootstrap pH model ($r^2 = 0.79$) for Sudbury lakes (Dixit et al. 2002), our Ca inferences are useful for assessing the past trends in lakewater Ca concentrations in Sudbury area lakes. There was a good correlation ($r^2 = 0.43$, $p < 0.05$, $n = 16$) between inferred downcore Ca and measured Ca, in the four of the lakes with detailed core profiles (Aurora Whitepine, George, Little Whitepine, Whitepine McLeod) for which there was some temporal overlap in measured and inferred values. Average Ca values for these downcore inferences and measurements (2.31 $\mathrm{mg \cdot L^{-1}}$ and 2.22 $\mathrm{mg \cdot L^{-1}}$, respectively) were not significantly different ($p > 0.05$, $n = 16$) based on a paired *t* test.

Long-term changes in calcium

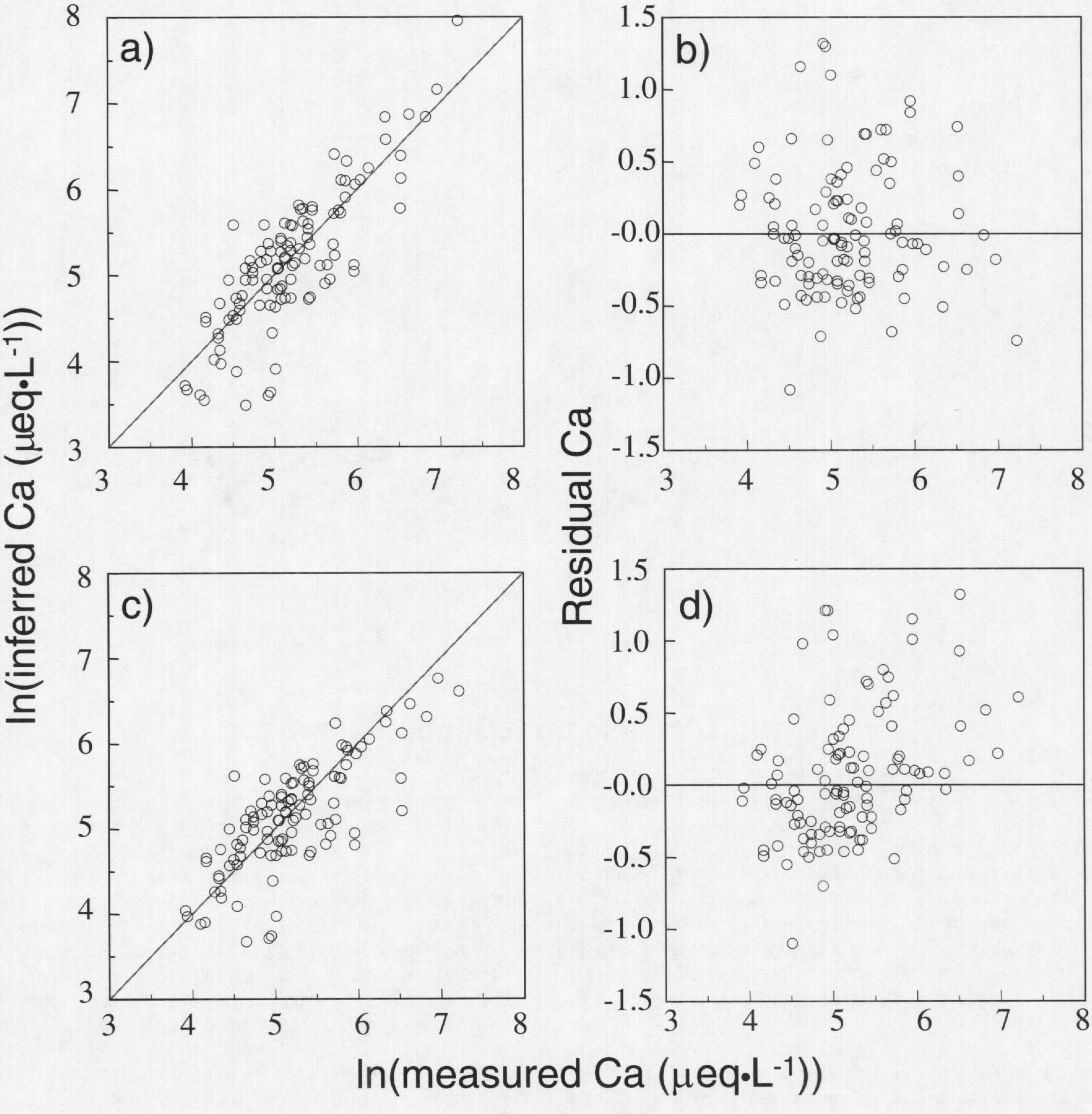
In the six lakes for which detailed profiles were examined, inferred temporal patterns showed substantial variation between lakes over the period covered by our sediment cores, from the mid-1800s to the late 1980s (Fig. 6). Lake-specific factors such as differences in catchment soils and forest cover may account for this variability. However, with the exception of Aurora Whitepine Lake, which showed little change in inferred Ca, the lakes showed substantial declines in Ca beginning in the early to mid-1900s (Fig. 6). While our inferences do describe the long-term Ca trends in these lakes, they do not appear to be sensitive enough to effectively capture shorter-term variations in Ca that likely occurred, such as the elevated concentrations reported in the early to mid-1970s in many Sudbury area lakes (Conroy et al. 1978) following the period of maximum smelter emissions.

Overall changes in Ca concentrations in Sudbury area lakes have been substantial. For the 16 of our 38 monitoring lakes for which we have pre-industrial Ca inferences, the estimated decreases ranged from 27.2 to 133.0 $\mathrm{\mu eq \cdot L^{-1}}$ (26.4–64.0%) and have averaged 74.6 $\mathrm{\mu eq \cdot L^{-1}}$ (46%) based on a comparison of pre-industrial inferences and recent (1999) measurements (Fig. 7).

Discussion

Water quality improvements, including increases in pH and decreases in sulphate concentrations, have followed the large reductions in Sudbury area sulphur emissions (Keller et al. 1992). These improvements have been accompanied by substantial decreases in Ca concentrations, averaging 2.7 $\mathrm{\mu eq \cdot L^{-1} \cdot year^{-1}}$ over the 1980s and 1990s. During our two-decade monitoring period, declining trends in Ca concentrations, averaging 3.8 $\mathrm{\mu eq \cdot L^{-1} \cdot year^{-1}}$, were universal during the 1990s. Assessment of trends in Ca during the 1980s is complicated by the effects of a two-

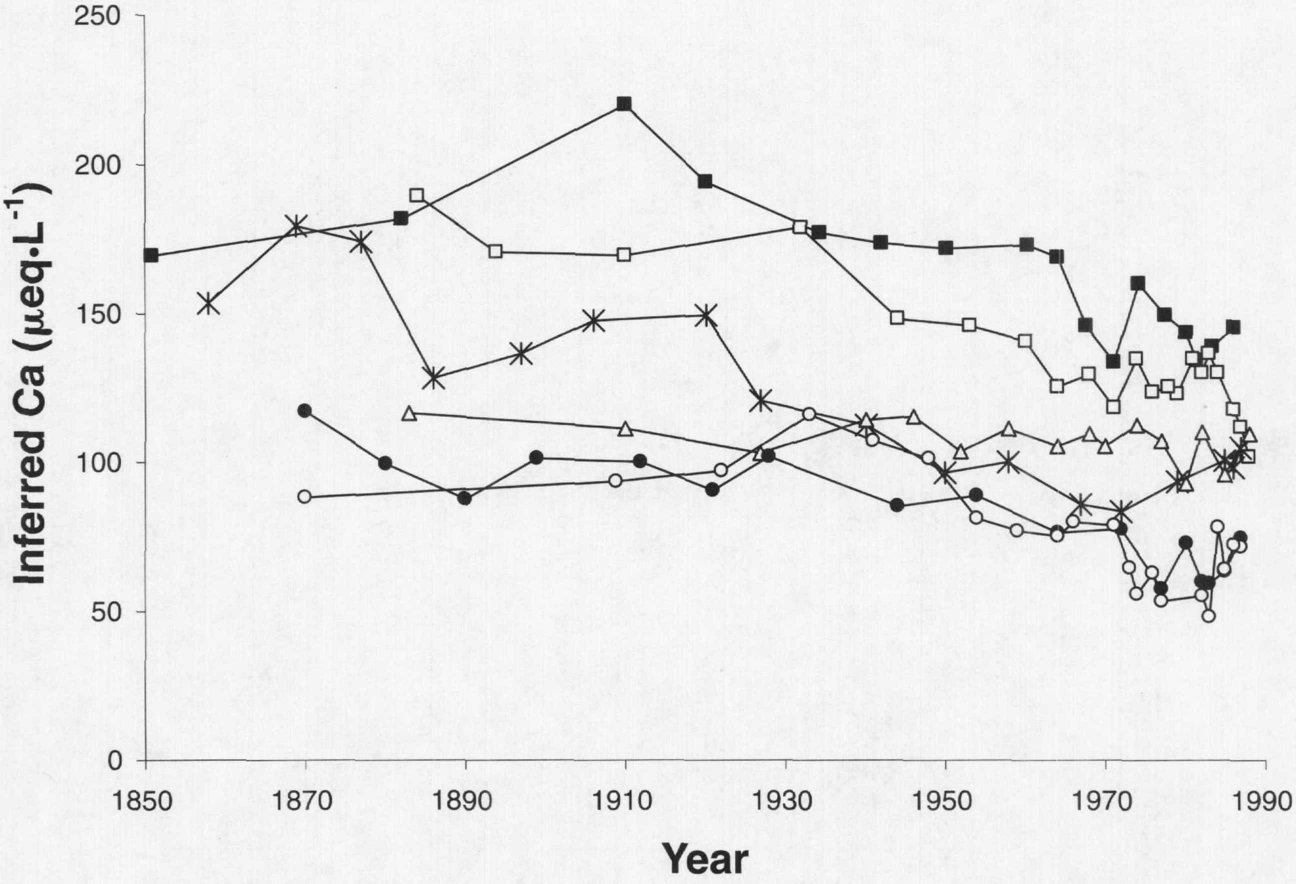
Fig. 5. Diatom-based inference models for lakewater Ca. The relationships between ln measured and diatom-inferred Ca and residuals for simple weighted averaging (*a* and *b*) and bootstrap weighted averaging (*c* and *d*) are shown. (*a*) $r^2 = 0.72$, RMSE = 0.32; (*b*) $r^2 = 0.00$; (*c*) $r^2 = 0.58$, $\text{RMSE}_{\text{boot}} = 0.35$; (*d*) $r^2 = 0.21$.



year (1986–1987) drought followed by abundant precipitation, which caused short-term Ca increases and other water quality changes in some Sudbury area lakes in the late 1980s (Keller et al. 1992; Yan et al. 1996). Nevertheless, almost all of our lakes showed overall Ca declines during the 1980s, although less than half (39%) showed significant trends. The average rate of decline of 1.9 $\mu eq \cdot L^{-1} \cdot year^{-1}$ in our study lakes during the 1980s is substantially higher than rates of 0.6–1.3 $\mu eq \cdot L^{-1} \cdot year^{-1}$ reported by Driscoll et al. (1995) for seven Adirondack lakes that showed significant declines in Ca during the 1980s.

The positive relationship between Ca declines in the 1990s and increasing proximity to Sudbury indicates a continuing "Sudbury" effect on lake chemistry, even though we have excluded the lakes closest (<20 km) to Sudbury from this analysis. However, this effect is only apparent in lakes relatively close to the smelters, within about 45 km, as has been previously observed for lakewater sulphate concentrations (Keller et al. 2001). Much of this effect may be historical, and not related to current smelter emissions. The additional sulphur emission controls that were implemented at the Sudbury smelters during the 1990s may be contributing to continuing lake recovery (Keller et al. 1999). How-

Fig. 6. Downcore diatom-inferred Ca trends for six study lakes. Acid (●), George (✳), and Lumsden (○) lakes are 60–62 km southwest of Sudbury; Aurora Whitepine (△), Little Whitepine (□), and Whitepine MacLeod (■) lakes are 88–102 km northeast of Sudbury (see Fig. 2).

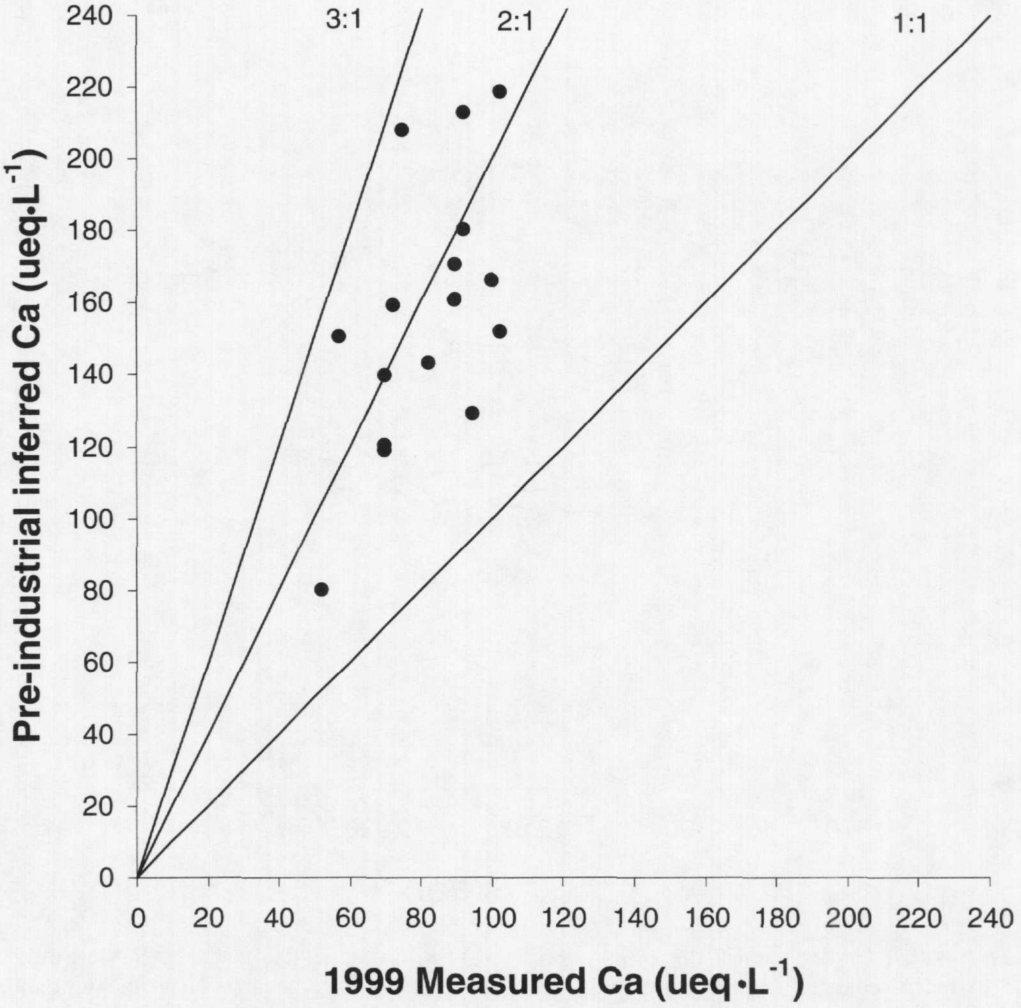


ever, evidence suggests that Ca declines in the 1990s were not primarily due to recent changes in acid deposition and associated Ca leaching attributable to the Sudbury smelters. Studies in 1978–1980 indicated that the Sudbury emissions were no longer a major contributor to sulphur deposition in the Sudbury area, constituting about 25% or less (Chan et al. 1984). The current Sudbury contribution to regional sulphur deposition is expected to be even lower, with the additional emission reductions that were implemented in the 1990s. Recent (1990s) decreases in Ca in lakes near Sudbury are correlated with declines in sulphate ($r^2 = 0.53$, $p < 0.01$), and may be a continuation of the long-term recovery of lakes and watersheds around Sudbury that began decades ago (Keller 1992) and may also still be reflecting recovery from the drought-induced re-acidification event in the 1980s (Keller et al. 1992; Yan et al. 1996).

Our observation that the 1990s Ca declines in lakes further than about 45 km from Sudbury were not related to distance suggests that since the Sudbury smelter emissions have been greatly reduced, base cation changes in Sudbury lakes more distant from the smelters may now be affected primarily by broad patterns of continental long-range transport and atmospheric deposition. Generally, similar patterns of a strong decline during the 1990s were also observed for base cations in the surface waters of other areas of North America, including south-central Ontario, and the Adirondack and Catskill mountains of the U.S.A. (Stoddard et al. 1999). While the large local sources of sulphur emissions clearly dominated the acidification process in Sudbury area lakes (Keller 1992), it appears that the recovery process in many of these lakes will now be more linked to the effects of long-range atmospheric transport.

Comparison of recent lakewater Ca concentrations in Sudbury area lakes and paleolimnological inferences of pre-industrial conditions indicates that substantial overall declines in Ca concentrations, averaging 46%, have occurred. The general patterns of decline in Ca observed over the latter half of the 20th century in our lakes are consistent with the hypotheses that (1) base cations in lake catchments were gradually depleted as a result of acid deposition, and (2) that leaching rates of easily exchangeable Ca have then declined as acid deposition decreased owing to sulphur emission controls in the Sudbury area and elsewhere. However, other factors including climate variations, forest harvesting, and reduced Ca deposition from the atmosphere may also have substantially influenced the Ca concentrations in these lakes over the long term. The same general pattern of Ca decline has been observed for waters in other regions, notably streams in the Hubbard Brook Experimental Forest in New Hampshire, and has been attributed to a combination of leaching by acid deposition, decreased Ca inputs from the atmosphere, and changing net Ca storage in biomass (Likens

Fig. 7. Plot of pre-industrial inferences vs. recent (1999) measured Ca for 16 monitoring lakes. Lines representing 1:1, 2:1, and 3:1 relationships are shown.



et al. 1998). Changes in climate can also affect temporal patterns of Ca in lakes (Schindler et al. 1990; Sommaruga-Wograth et al. 1997).

While we cannot currently evaluate the relative roles of the different factors potentially affecting Ca concentrations in our lakes, the net effect has been a substantial decline in lakewater Ca concentrations. This may have important biological implications for these lakes as they continue to recover from acidification. Calcium is known to ameliorate the toxicity of acid and metals to fish, thus concern has been expressed that in some cases, declines in Ca during lake recovery may offset some of the biological benefits of modest acidity decreases (Skeffington and Brown 1992). It has recently been demonstrated that the sensitivity of *Daphnia* to UV radiation increases at low Ca concentrations (Hessen and Alstad Rukke 2000). Calcium may also have other, direct effects on biota since Ca is an essential element for aquatic species with a calcified exoskeleton, including some crustacean zooplankton (Alstad et al. 1999). Calcium availability may influence competitive interactions between some zooplankton species and influence species distributions (Hessen et al. 1995; Alstad et al. 1999).

Tessier and Horowitz (1990) demonstrated that substantial changes in zooplankton community size structure, largely attributable to losses of large-bodied *Daphnia* at lower Ca levels, occurred along a gradient of Ca concentrations. Thresholds for changes in zooplankton communities appeared to occur between 200 μeq·L^{-1} and 300 μeq·L^{-1} and at about 50 μeq·L^{-1}. There is also evidence for increased sensitivity of fish to H^+ and Al at Ca levels below about 50 μeq·L^{-1} (Brown 1983). Based on our sample, most acidified lakes in our study area likely never had Ca concentrations over 200 μeq·L^{-1} before industrialization. While they are not as Ca poor as some acidified lakes in other affected regions such as Norway (Skjelkvale et al. 1998) or the Adirondack Mountains of New York (Driscoll and Van Dreason 1993), some of our study lakes are nonetheless approaching 50 μeq·L^{-1}. For crustacean zooplankton and other invertebrates that have relatively high Ca requirements, Ca limitation may become an important influence if decreases continue. Calcium limitations on invertebrates could also have nutritional effects on other components of food webs. The potential effects on aquatic birds of reduced availability of Ca from prey in acidic lakes are already of concern (McNicol 1999). Calcium concentrations in Sudbury area lakes, and in lakes of other acid-affected regions will need to be closely monitored. Ca declines may be an important factor to consider in the development of realistic biological targets for lakes recovering from acidification.

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