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Trace metal profiles in the varved sediment of an Arctic lake

P. M. OUTRIDGE,[1,2,*] G. A. STERN,[2] P. B. HAMILTON,[3] J. B. PERCIVAL,[1] R. MCNEELY,[1] and W. L. LOCKHART[2]
[1]Geological Survey of Canada, 601 Booth Street, Ottawa K1A 0E8, Canada
[2]Fisheries and Oceans Canada, 501 University Crescent, Winnipeg R3T 2N6, Canada
[3]Canadian Museum of Nature, P.O. Box 3443 Station D, Ottawa K1A 6P4, Canada

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Abstract—Varved (annually-laminated) sediments offer a rare and physically undisturbed archive of past trace metal deposition and limnological conditions. Here, a high-resolution 1,300 year record of metal accumulation is presented from a varved lake sediment on Devon Island in the Canadian High Arctic. Down-core concentration profiles of Cd, Cu and Zn were positively correlated ($P < 0.01$) with organic C (Cd, Zn) or with leachable Fe (Cu), while distinct sub-surface peaks of these metals coincided with those of Fe, S and other redox-sensitive elements such as Co, Cr and U. The fluxes of these metals since 1854 were correlated with elements such as Ca, Al and La ($P < 0.001$) which are predominantly of local geological origin. Furthermore, the Cd, Cu and Zn patterns did not match concurrent records in Greenland Summit ice over the last century, nor global industrial emission histories. These facts suggest that inputs from local geological sources, coupled with some degree of post-depositional mobility or association with organic matter inputs, explain the metals' sedimentary profiles, which were apparently not affected by long-range atmospheric metal pollution. Mercury concentrations were strongly correlated with total diatom abundance over the last 400 yrs, especially during the 20th Century when a two-fold increase in Hg concentrations and a four order-of-magnitude increase in diatoms occurred in tandem. Since 1854, 81% of the variation in Hg flux was associated with diatom and Ca fluxes. A similar correspondence between Hg and diatoms was found in a second lake nearby, confirming that the relationship was not unique to the main study lake. Recent Hg increases in Arctic and sub-Arctic lakes have been attributed to global anthropogenic Hg emissions. We propose an alternative hypothesis for High Arctic lakes: the recent Hg increases may be partly or entirely the product of elevated rates of Hg scavenging from the water column caused by markedly greater algal productivity, which in turn was driven by accelerating climate warming during the 20th Century. Given the important environmental assessment and policy implications if the alternative hypothesis is true, the possible effects of climate warming on sedimentary Hg fluxes in this region deserve further study. *Copyright © 2005 Elsevier Ltd*

1. INTRODUCTION

The reliability of lake sediments in recording and preserving the history of atmospheric metal concentrations and deposition is a continuing scientific issue with widespread environmental policy implications. Because lake sediments are widely used to reconstruct temporal changes in metal pollution, the data derived from them has had considerable influence in shaping environmental assessments and regulatory actions, especially in Arctic regions where instrumental records of atmospheric metal deposition are sparse (see AMAP 1998, 2002; INAC 2003). However, the interpretation of sedimentary metal profiles in most lakes as an unambiguous record of atmospheric metal deposition has been contested, due to the possibility of post-burial remobilization of metals resulting from diagenesis: physical mixing by wind and wave action, compaction, bioturbation and irrigation and, in extremely low sedimentation environments, diffusive migration of dissolved metals as a result of redox-related concentration gradients (Boudreau 1999; Boyle 2001). Elements which have been demonstrated to undergo redox-mediated migration in lake sediments include As, Co, Cr and V, although it is unclear whether other environmentally-important elements such as Hg, Cd, Cu, Pb and Zn are affected (Boyle 2001).

For temperate North America, confidence in the reliability of sediments as metal archives has been enhanced by various forms of corroborative evidence, including findings that sedimentary profiles of Hg agree well with known fluvial Hg input histories (Frazier et al. 2000; Lockhart et al. 2000), by modelling studies which suggest that significant metal remobilization is limited to lakes with very low sediment accumulation rates (Boyle 2001), by Hg trends in a glacier ice core in the western U.S.A. that match continent-wide trends in lake sediment cores (Schuster et al. 2002), and by good agreement between sediment-derived atmospheric Hg flux data and actual measurements (Swain et al. 1992). However, at Arctic latitudes, similar corroborative studies are lacking. Furthermore, Arctic lakes often have lower sediment accumulation rates and organic matter contents than many temperate lakes (Gajewski et al. 1995; Engstrom and Swain 1997), conditions which may favour metal remobilization. Extremely low sedimentation rates were the probable underlying cause behind diagenetic redistribution of Hg in Arctic marine sediments (Gobeil et al. 1999).

Another potential problem with respect to sediments as chemical archives is the largely-untested assumption that the transport processes of metals from atmosphere to sediments via the catchment and water column have not changed in recent

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[*] Author to whom correspondence should be addressed (outridge@nrcan.gc.ca).

history. This assumption is necessary for sedimentary metal concentrations or fluxes to be interpreted as simply and directly reflecting trends in the atmospheric deposition of metals. Findings that global warming has caused significant increases in the rate of spring thaw (Magnuson et al. 2000) and diatom productivity (Douglas et al. 1994; Wolfe 2000) in northern lakes, and the discovery of atmospheric Hg "depletion events" during polar spring (Schroeder et al. 1998), challenge this assumption, particularly for high-latitude lakes. The impact of climate warming on diatom communities over about the last 150 years through the lengthening of the ice-free growing season is especially noticeable in the Canadian High Arctic (above 65°N) whereas smaller changes occurred at lower latitudes, such as in northern Quebec and Labrador, which have experienced little or no recent warming (Smol et al. 2005). All of these phenomena either could produce new mechanisms of metal transport or are themselves (in the case of depletion events) possibly new mechanisms which may alter fluxes between various environmental compartments in northern lakes. If processes and fluxes changed significantly and the changes were not recognized and corrected for, conclusions about atmospheric metal history based on sediment profiles may be erroneous. For example, if Hg depletion events are a relatively recent process or have recently become more pronounced, the modern increases of Hg flux recorded in coastal lake sediments may reflect the depletion phenomenon rather than increased atmospheric Hg concentrations.

Varved (i.e. annually-laminated) lake sediments which, by definition, have not been affected by physical disturbance, offer a rare archive of metal accumulation. The in situ preservation of sediment layers as they were deposited eliminates one of the diagenetic mechanisms potentially affecting metal profiles. However, only a few examples of varved sediments have been discovered in the North American Arctic (see Gajewski et al. 1997; Overpeck et al. 1997; Hughen et al. 2000). This study examines elemental profiles within the varved sediment of Lake DV-09 on Devon Island in the Canadian High Arctic, and evaluates the alternative hypotheses that profiles of Hg, Cd, Cu, and Zn are either: (1) the products of diagenetic alteration or other processes which may obscure the original deposition pattern; or (2) accurate representations of trends in atmospheric metal concentrations or fluxes. To assist in interpretation of the metal profiles, the sediments were subjected to geochemical, radiometric and mineralogical characterization more extensive and detailed than most other studies of sedimentary metal deposition reported in the literature. Trends in diatom concentrations were also analysed to improve understanding of historical changes in lake productivity. Lake DV-09 is situated in the eastern Canadian High Arctic (i.e. above the Arctic Circle), a region from which only two other lake sediment Hg profiles have previously been published (Amituk Lake and Lake Hazen, Lockhart et al. 1995, 1998; but see also Muir et al. 2003). This study also subjected recent sediment collections from Amituk Lake to Hg and diatom analysis for comparison with Lake DV-09.

2. MATERIALS AND METHODS

The main study lake (Lake DV-09; 75°34.4′ N, 89°18.5′ W) is a small (3 ha), shallow (13.5 m maximum depth) lake situated 35 m above sea level and 1.3 km inland from the northern coast of Devon Island. It was originally described by Gajewski et al. (1997), who identified the sediment as varved on the basis of concordant radiometric ages and lamination counts in the upper 12 cm. The lake, which is underlain by Middle Ordovician Bay Fiord Formation dolomite, gypsum, shale, limestone and siltstone, is surrounded by till veneer and steep-sided cliffs on three sides and abuts an alluvial terrace on its ocean side. A small, shallow stream flows into the sea during the ice-free season; ephemeral streams entering the lake are believed to flow only during spring. Amituk Lake (75°02.9′ N, 93°45.8′ W) on Cornwallis Island is situated approximately 140 km west of DV-09 and has been described by Diamond et al. (2003). Like DV-09, it is a coastal lake and is underlain by similar geology, but is larger (37.8 ha) and deeper (43 m maximum depth).

Lake DV-09 was sampled for this study in May 1999 while completely ice-covered. A bathymetric map (Gajewski et al. 1997) was used to locate the lake's deepest depositional zone, which was then sampled with a 10 cm diameter Perspex® KB corer. Four cores, all exhibiting undisturbed sediment/water interfaces, were collected through the ice approximately 4 m apart and from a water depth of about 13 m. Two cores (1 and 2) were extruded in the field into 0.5 cm increments for the top 0–10 cm, 1.0 cm increments for 10–30 cm, and 2.0 cm increments from 30 cm to the bottom of the core (60–70 cm). Individual varves could not be reliably separated in the field and would have yielded far too little material for analysis, thus slicing the core at known increments was our preferred strategy. Core slices were immediately placed into plastic Whirlpak® bags, weighed, sealed and stored in the dark at ambient temperature (<5°C) until return to base, from which point they were kept refrigerated at 4°C. The other two cores (3 and 4) were frozen intact in their core tubes for return to the laboratory. Core 4 was archived frozen and not used further in this study. Amituk Lake sediment cores were collected in May 2003, using identical sampling and core extrusion procedures to those in DV-09, from the deepest part of the basin identified during the Lockhart et al. (1995) study (P. Wilkinson, pers. comm.).

For Lake DV-09, slices from cores 1 and 2 were freeze-dried in their sample bags and kept refrigerated in the dark until analysis. This material provided sub-samples for all analyses except diatoms and textural and mineralogical parameters, which were determined on core 3. Mercury analyses were performed on all slices of cores 1 and 2, whereas other parameters were determined on all slices of core 1 to a depth of 20 cm and at regular intervals thereafter. Radiometric dating, Hg, porosity and forms of carbon were determined at laboratories of Fisheries and Oceans Canada (DFO), and all other analytical work was performed at the Geological Survey of Canada. Dating, diatom counts and Hg analysis of Amituk Lake core AML-1 were performed using the same techniques and laboratories as were used for the DV-09 samples.

Slices from DV-09 cores 1 and 2, and AML-1, were radiometrically dated by measuring ^{210}Pb and ^{137}Cs activity as a function of depth (see Oldfield and Appleby, 1984 and Lockhart et al., 1995 for a description). Upper-core sedimentation rates and chronologies were calculated using the ^{210}Pb data and the constant rate of supply (CRS) model, which assumes a constant ^{210}Pb input and changing sedimentation rate over time, while the "linear" model which assumes a constant sedimentation rate was used to estimate dates throughout the entire cores (Oldfield and Appleby, 1984). In the text and figures, the estimated median date for each slice is used. Because the CRS model requires excess ^{210}Pb to assign dates to each sediment slice, sedimentation rates could only be calculated down to the point where excess ^{210}Pb was present (in DV-09, 9.5 cm or 1854; see below). ^{137}Cs, which was produced by the atmospheric testing of nuclear weapons that began in 1954 and peaked in 1963, and by the Chernobyl nuclear accident of 1986, was measured to check the ^{210}Pb-derived dates. For the purposes of this paper, in Amituk Lake only the ^{210}Pb-based linear model estimates of slice dates will be shown because these cover the whole core.

Trace and major element concentrations in Lake DV-09, except for Hg, were determined on dilute acid-leachable and residual fractions of sediment as described by Outridge et al. (2002) modified from Graney et al. (1995). All leaching treatments provide operationally-defined information on elemental speciation which, although not necessarily identifiable as specific chemical forms, provide a consistent measure of down-core changes of elemental binding. In this case, the dilute acid-leach treatment was chosen because it was shown to remove from sediments all forms of Pb up to aqua regia digestion (Graney et al.

1995). Total metal concentrations reported in the text are the sum of concentrations in the leachable and residual fractions. For the acid-leachable fraction, a 0.2–0.5 g DW sample was leached with 10 mL of 5% HNO_3 + 10% HCl for 7 d at room temperature with constant shaking. The supernatant was decanted and made up to 25 mL with distilled-deionized water. Residual material was completely digested with nitric, perchloric and hydrofluoric acids over heat, allowed to go to dryness and subsequently made up to 25 mL with 5% ultrapure HNO_3. Analyses were by ICP-OES for major elements, and by ICP-MS with internal standardization using Ru and Re at 5 μg/L final concentration for trace elements. Procedural blanks and standard reference material sediments (LKSD-3 and STSD-3, Canadian Centre for Materials and Energy Technology, Ottawa) were also carried through the procedures; results for SRMs indicated that precision was generally better than 10% relative standard deviation (RSD) and accuracy to within 10% of information or certified values for the elements discussed in this paper. Total S and Cl were determined by pyrolysis and ion chromotography (see Hall et al. 1986). Total Hg in DV-09 and Amituk sediment was analysed in DFO laboratories using cold vapour AAS (see Lockhart et al. 1995). Analyses of SRMs (MESS-2 and PACS-2, National Research Council of Canada) showed accuracy and precision to be better than 3% and 5% RSD, respectively. Organic carbon was determined by combustion of dried sediment in an oxygen-helium atmosphere at 950–975°C and quantization of CO_2 with a CEC 240-XA Elemental Analyser (Control Equipment Corporation Inc.).

For diatom enumeration, and physical and mineralogical studies, DV-09 core 3 was sliced length-wise to remove a 2 cm wide slab from the centre. X-ray investigation of this core showed that freezing had resulted in ice penetration and varve deformation only in the outer 3 cm of the core, and that the centre 3–4 cm was unaffected. Varves in this central slab were still clearly visible in X-ray images and were undeformed. From the slab, 0.4 cm diameter cores were removed with a hand-held auger at measured distances from the sediment surface, corresponding to the increments extruded in the field. For diatom enumeration of Amituk Lake sediment, freeze-dried sediment was taken directly from the sample bags. Diatom concentrations were determined at the Canadian Museum of Nature using methods described by Gajewski et al. (1997). The diatom slides enumerated in this study and associated notes are deposited in the National Diatom Collection in Ottawa (CANA 77719-77764). The results for DV-09 reported here were similar to those reported by Gajewski et al. (1997) from their 1994 sample, but were at higher temporal resolution because of finer incremental slicing of the core. Physical and mineralogical studies were performed on larger slices removed from the slab with a band saw at measured distances from the top of the core. Particle size was analysed using a Galai Particle Size Analyser on samples which were wet-sieved to recover the <90 μm fraction (Lindsay et al. 1998). Mineralogical composition was determined by X-ray powder diffraction analysis (XRD). Forty mg suspensions (in distilled water) of the samples were pipetted onto glass slides and air-dried overnight. X-ray patterns were recorded on a Philips PW1710 automated powder diffractometer equipped with a graphite monochromator, Co Kα radiation at 40 kV and 30 mA. The samples were also X-rayed following saturation with ethylene glycol and heat treatment (550°C). Digital data were captured and then processed using JADE™ (v3.1; Materials Data, Inc.), a PC-based program that enables manipulation of the X-ray pattern for optimization (e.g., correction for background, instrument error) in identification of mineral species. Semi-quantitative analyses were based on comparison with a set of mineralogical standards using a pre-determined reference intensity ratio (Percival et al. 2001).

Polished thin sections of selected samples were examined with a Leica Cambridge Stereoscan S360 scanning electron microscope (SEM) equipped with an Oxford/Link eXL-II energy-dispersion X-ray analyzer, Oxford/Link Pentafet Be window/light element detector, and an Oxford/Link Tetra backscattered electron detector. In order to take high resolution images, the SEM was operated at an accelerating voltage of 20 kV, a beam current of 100 pA and a working distance of 14 or 25 mm. SEM images were digitally captured at 768 × 576 pixels at 256 levels of greyscale and stored for further processing.

Mercury flux for each sediment slice in Lake DV-09 was calculated as the product of Hg concentration and incremental sedimentation rate; because sedimentation rate could only be calculated for the upper 9.5 cm, Hg flux calculations are similarly limited to this part of the core. Element and diatom concentrations and fluxes were $\log_e$ transformed to address statistical assumptions of normality and homoscedasticity (Sokal and Rohlf 1981), and were subjected to linear regression and forward stepwise regression analysis using SigmaStat ver. 2.03 statistical software (SPSS Inc.).

3. RESULTS

3.1. Lake DV-09

In cores 1 and 2, ^{210}Pb radioactivity exhibited similar exponential declines with depth in a pattern typical of an undisturbed sediment chronology (Fig. 1). A regression line fitted to the plot of ^{210}Pb versus accumulated dry weight gave r^2 values of 0.94 in core 1 and 0.92 in core 2. Sedimentation rates calculated with the CRS model averaged 273 and 293 g/m^2/yr, while the ^{210}Pb fluxes were 65 and 58 Bq/m^2/yr in cores 1 and 2, respectively. These average sedimentation values are 2–5% higher than reported by Stern et al. (2005) for the same cores, because the present model estimates have been adjusted for the "old age correction" (P. Wilkinson, pers. comm.); this difference does not affect the findings or conclusions of either paper. The linear fit dating model gave average sedimentation estimates of 300 and 290 g/m^2/yr, respectively. Using the data from the 1994 core of Gajewski et al. (1997), a sedimentation rate of 364 g/m^2/yr and ^{210}Pb flux of 70 Bq/m^2/yr were calculated using the CRS model, and a sedimentation rate of 295 g/m^2/yr with the linear model. Excess ^{210}Pb dissipated at 9.5 cm, corresponding to 1854 AD. When plotting data profiles for the entire cores, extrapolated dates using the linear model were employed, which in this instance will result in more recent ages compared to the CRS model. For example, at 9.5 cm, the linear model gave a median age of 1872 compared to 1854 from the CRS model. Based on the linear model, the approximately 65 cm length cores represent about the last 1,300 yrs of sediment formation but may be longer than that given the bias of the model. There was insufficient organic matter in the sediment to use accelerator mass spectrometry dating. ^{137}Cs activity showed a maximum value at a ^{210}Pb date of 1963 or 1964, coinciding with the period of greatest atmospheric nuclear bomb testing, thereby confirming the ^{210}Pb dating. There was also evidence of an additional ^{137}Cs input at about 1987 which coincided with the Chernobyl incident.

Physical properties and organic content of the core are presented in Figure 2. Porosity declined down-core, indicating some degree of compaction in the upper 20 cm (Fig. 2a). In terms of particle size, the sediments were silt-rich with relatively low sand and clay contents (Fig. 2b). Clay content decreased with a concomitant increase in silt above 18–20 cm depth, corresponding to the mid-1700's. Water content was in the range of 40–80% of total weight, declining down-core. Organic carbon content was mostly <2 % and declined from the surface to a constant 0.5–1.0% below 10 cm depth (Fig. 2d). Sedimentation rates in cores 1 and 2, calculated from the CRS model, increased from 1854 to the late 19th Century, but were thereafter of similar magnitude to the tops of the cores, except for two brief periods (median dates of slices: 1904 and 1971) when sedimentation rates spiked. These episodes corresponded to marked, temporary declines in porosity, water content and organic C content in the upper 10 cm of cores (indicated by

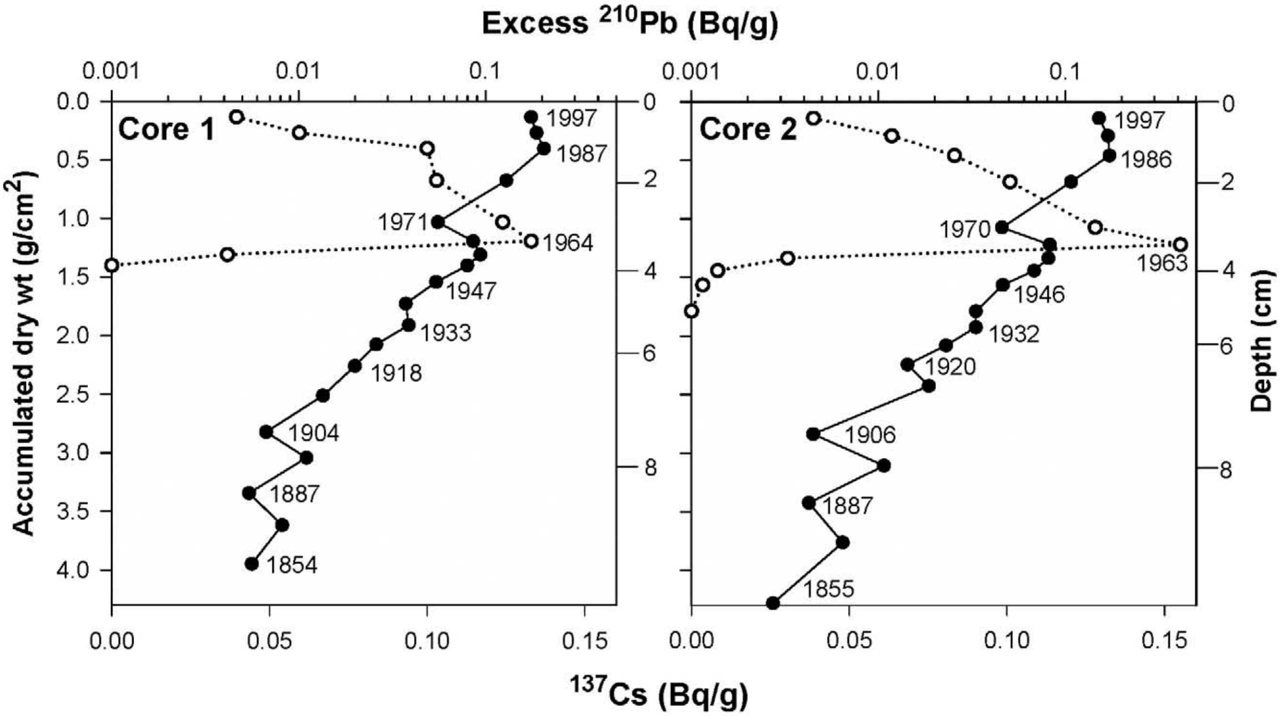

Fig. 1. Results of radiometric dating of sediment slices from cores 1 and 2 in Lake DV-09 (^{210}Pb data plotted with solid circles; ^{137}Cs data with open circles. Dates shown are the median dates estimated for each slice; each circle represents a separate 0.5 cm slice).

arrows in Figs. 2a, c and d) but not in relative particle size distributions (Fig. 2b).

Mineralogically, the sediment was dominated by carbonates (dolomite + calcite), K-feldspar and quartz (Fig. 3). Clay minerals (illite + chlorite) occurred in minor to trace amounts and consistently decreased above 12 cm whereas carbonates showed an increasing trend above 20 cm with major peaks at the surface and about 7 cm depth; the latter corresponded to increased sedimentation at about 1904. The 1971 sedimentation event did not apparently affect mineralogical composition. Hematite was detected by XRD only in trace amounts in a few samples above 12 cm. No discrete iron oxide grains were observed under the SEM.

Each varve consisted of a couplet of layers. A coarser, light-coloured layer contained subangular to asymmetrically-rounded carbonates and silicates which graded upwards into a finer-grained, reddish layer containing clay-sized minerals lightly coated with amorphous iron oxides. The boundary between each couplet was relatively sharp. Thickness of the light-coloured layers was variable and generally much thicker than the reddish layers. Evidence for incipient diagenesis included the compaction of clay minerals in the fine-grained layers and the presence of isolated patches of authigenic, framboidal pyrite (e.g., at 30–32 cm depth, Fig. 4).

Total and dilute acid-leachable concentrations of La (Fig. 5a) and total Cl (Fig. 5b), which are taken as indicators of possible changes of inputs of sediment material from the catchment and from sea spray, respectively, showed considerable variation throughout the core but no consistent trends. Total and leachable Fe (Fig. 5c) exhibited a clear peak at 4.0–4.5 cm depth, and leachable Fe was consistently >83% of total Fe. Virtually all Mn occurred in the leachable fraction, and Mn concentrations declined from 6.0–6.5 cm to the surface with a minimum value coinciding with the Fe peak (Fig. 5d). Other elements which displayed declining patterns similar to Mn included Sc, Th and Zr (data not shown). Elements known to be redox-sensitive, including Co (Fig. 5e), leachable U (Fig. 5f), total S (Fig. 5g) and Cr (data not shown), exhibited peak concentrations either coinciding with or 0.5 cm above the Fe maximum, although V, another supposedly redox-sensitive element, did not show a distinct peak (Fig. 5h). Among the elements not normally associated with redox gradients, measurable concentrations of Cd (Fig. 5i) and Cu (Fig. 5j) occurred only in the leachable fraction, with peak concentrations also coinciding with Fe. Elements which displayed maximum concentrations just above the Fe peak included Zn (Fig. 5k) as well as Cs, Na, Ni, P, Sr, Ti and Tl (data not shown).

Throughout the core, organic carbon was positively correlated ($P < 0.01$) with concentrations of Cd, Zn (leachable and total), total Hg, U (leachable and total), total S and V, accounting for >30% of explained variance in these elements (Table 1). Organic carbon concentrations were also strongly associated with total diatom abundance ($F=31.8$, $r^2=0.71$, $P < 0.001$). Leachable Fe was positively correlated ($P < 0.01$) with Cu, Co, total S and leachable V, accounting for >39% of explained variance. Other elements were correlated with these two parameters at $P < 0.05$ (see Table 1). However, owing to the large number of concentration-based comparisons tested statistically, the cumulative probability of Type I error at $P < 0.05$ was relatively large and so these results are not discussed further.

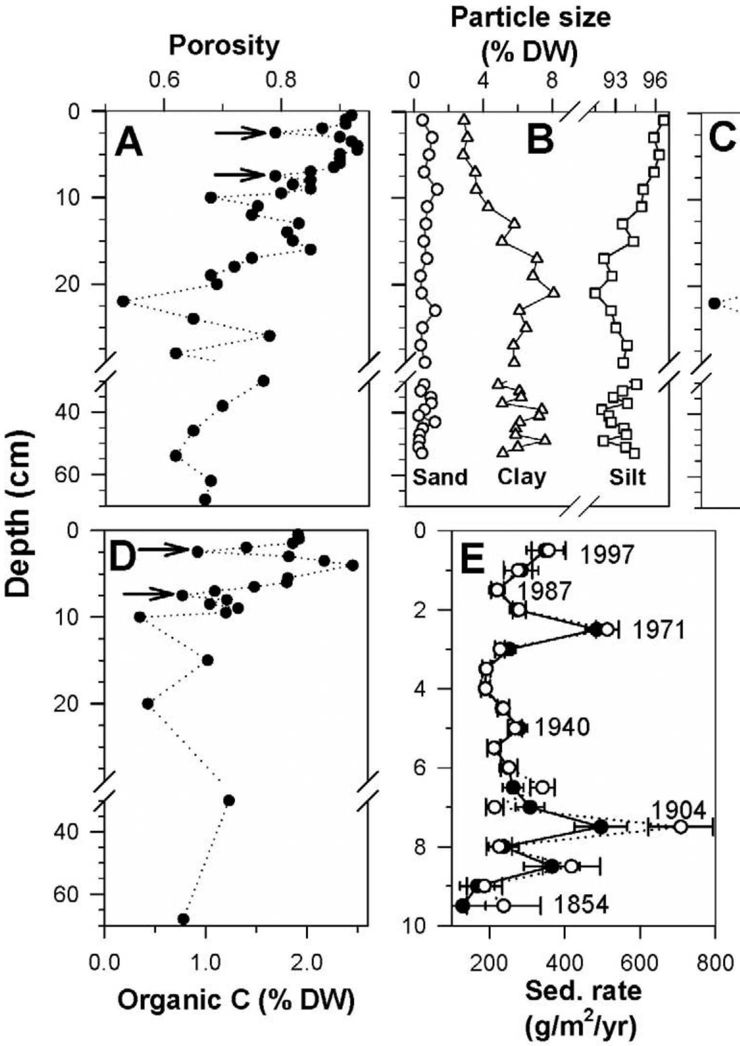

Fig. 2. Down-core sediment profiles of (A) porosity, (B) particle size, (C) water content, (D) organic carbon, and (E) sedimentation rate in Lake DV-09. (In (E), note different Y-axis scale; black circles denote core 1 and open circles core 2, while error bars represent ± 1 S.D. around sedimentation estimates. Dates shown in (E) are based on CRS model estimates from core 1 (see Fig. 1). In (A), (C), and (D), arrows indicate low values caused by elevated sedimentation in 1904 and 1971).

Mercury concentrations exhibited a pattern unique among all the elements with an increasing trend to the surface starting at about 15 cm corresponding to the late 18th Century, accelerating sharply at 7.0–7.5 cm depth or the first decade of the 20th Century (Fig. 5l). Over the past 400 years, this pattern was similar to that shown by total diatom concentrations (Fig. 6a), which underwent an exponential increase from about 10^5 to 3×10^9 cells/g DW over the last 100 years. Linear regression analysis found that Hg and diatom concentrations from 1600 A.D. to the present were significantly correlated ($F=93.8$, $r^2=0.84$, $P < 0.0001$, total df=19). Diatom abundance therefore accounted for about twice as much explained variance in Hg as did organic carbon. Northern Hemisphere temperature anomaly data (Fig. 6a), reconstructed from proxy archives by Bradley and Jones (1993) and Folland et al. (1990), were significantly correlated with diatom abundance in DV-09 since 1600 A.D. ($F=23.8$, $r^2=0.56$, $P < 0.001$, total df=19).

3.2. Amituk Lake

The pre-1989 ^{210}Pb profile and sediment chronology for Amituk Lake sampled in 2003 was almost identical to that resulting from the 1989 sampling (P. Wilkinson, pers. comm.). Based on the linear dating model for core AML-1, the average sedimentation rate in 2003 was 418 g/m^2/yr, compared to 363 and 389 g/m^2/yr from two 1989 cores (Lockhart et al. 1998; P. Wilkinson, pers. comm.). Diatoms were undetectable in most samples of Amituk Lake sediments up until about 1955, but afterwards increased rapidly to 2×10^7 cells/g DW at the top of the core (Fig. 6b). Mercury concentrations increased after 1910 but the largest and most rapid increase occurred after 1970; maximum concentrations were attained in 1989. Mercury and diatom concentrations over the past four centuries were significantly correlated ($F=27.7$, $r^2=0.65$, $P < 0.001$, total df=16).

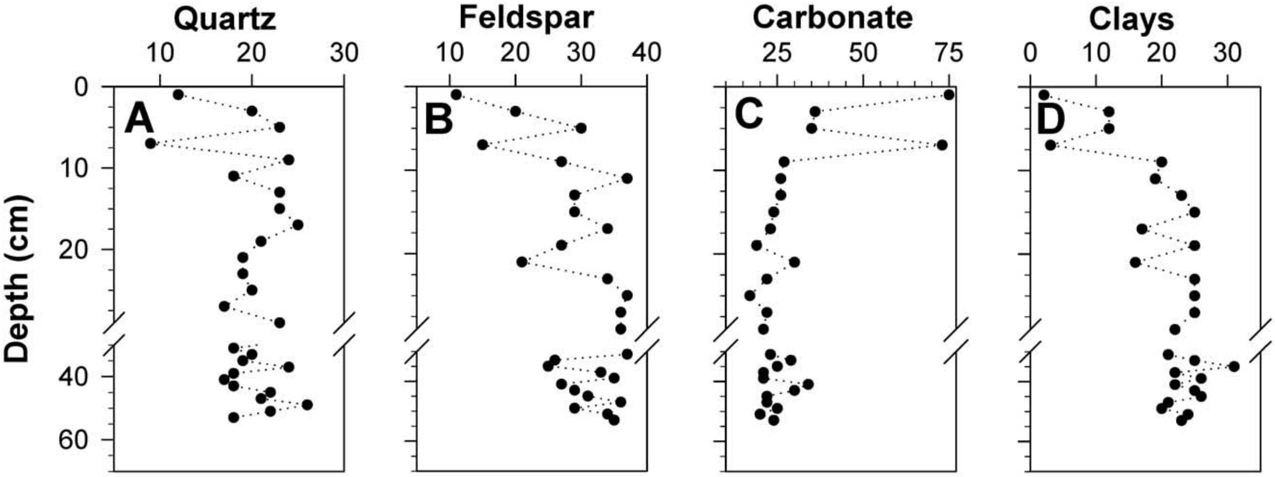

Fig. 3. Mineralogical composition of Lake DV-09 sediment as a function of depth. (Units are percentage dry wt).

3.3. Metal Fluxes in Lake DV-09

Calculated fluxes of Hg, Cd, Cu and Zn in DV-09 over the past 150 years, based on the CRS model sedimentation rates calculated for each core slice, show that much of the variation in these parameters was significantly associated with the changing inputs of Ca, Al and La (Fig. 7 and Table 2). This is also true when the high sedimentation and metal flux events of 1904 and 1971 were excluded (see Table 2). Except for these two events, Cd, Cu and Zn fluxes were relatively constant from 1880 onwards. Unlike Cd, Cu and Zn, however, there was an overall increase in Hg flux through much of the 20th Century from 2.5–5.9 μg/m^2/yr in the late 19th Century to 6.8–10.9 μg/m^2/yr in 1987–1997, a 2.3-times increase on average. Mercury flux was also correlated with diatom flux ($F=7.15$, $r^2=0.44$, $P < 0.05$) when analysed as a simple linear regression. Forward stepwise regression analysis of Hg variations as a possible combined function of diatoms, Ca, Al and La found that diatoms ($r^2 = 0.33$, P for inclusion in model $= 0.006$) and Ca ($r^2 = 0.47$, P for inclusion $= 0.005$) were the only variables accounting for significant amounts of variance, and together accounted for 81% of the variation in Hg flux (model $r^2=0.81$, $P=0.001$). Aluminum and La did not significantly add to the explained variance of the model, and no other element fluxes besides Hg were correlated with diatom flux.

4. DISCUSSION

4.1. Mercury Profiles

No other Arctic lake with varved sediments has been studied specifically from the aspect of atmospheric metal deposition, and as such this integrated study of historical trends in the biological productivity, geochemistry and mineralogy of Lake DV-09 presents a unique perspective on the question of whether sedimentary metal profiles provide an unambiguous record of atmospheric metal deposition in high-latitude lakes. Lake DV-09 has undergone marked limnological changes over the past century or more which appear to be related to climate warming. The changes include a four orders-of-magnitude increase in total diatom abundance, higher species diversity, a coincident shift to larger benthic and periphytic species (Gajewski et al. 1997), and an increase in the silt fraction of sediments deposited since 1750 with a corresponding decline in the finer clay fraction. The trend towards larger sediment par-

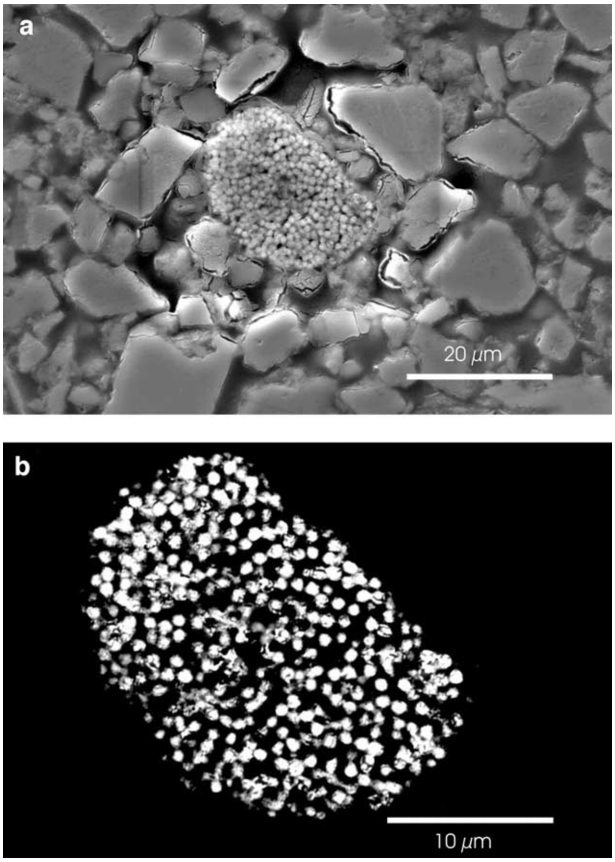

Fig. 4. (a) SEM photomicrograph of sediment sample at 30–32 cm in DV-09 sediment, showing isolated patches of framboidal pyrite surrounded by medium- to coarse-grained silt particles of dolomite, quartz and K-feldspar (secondary electron image); and (b) close-up view of framboidal pyrite (backscattered image).

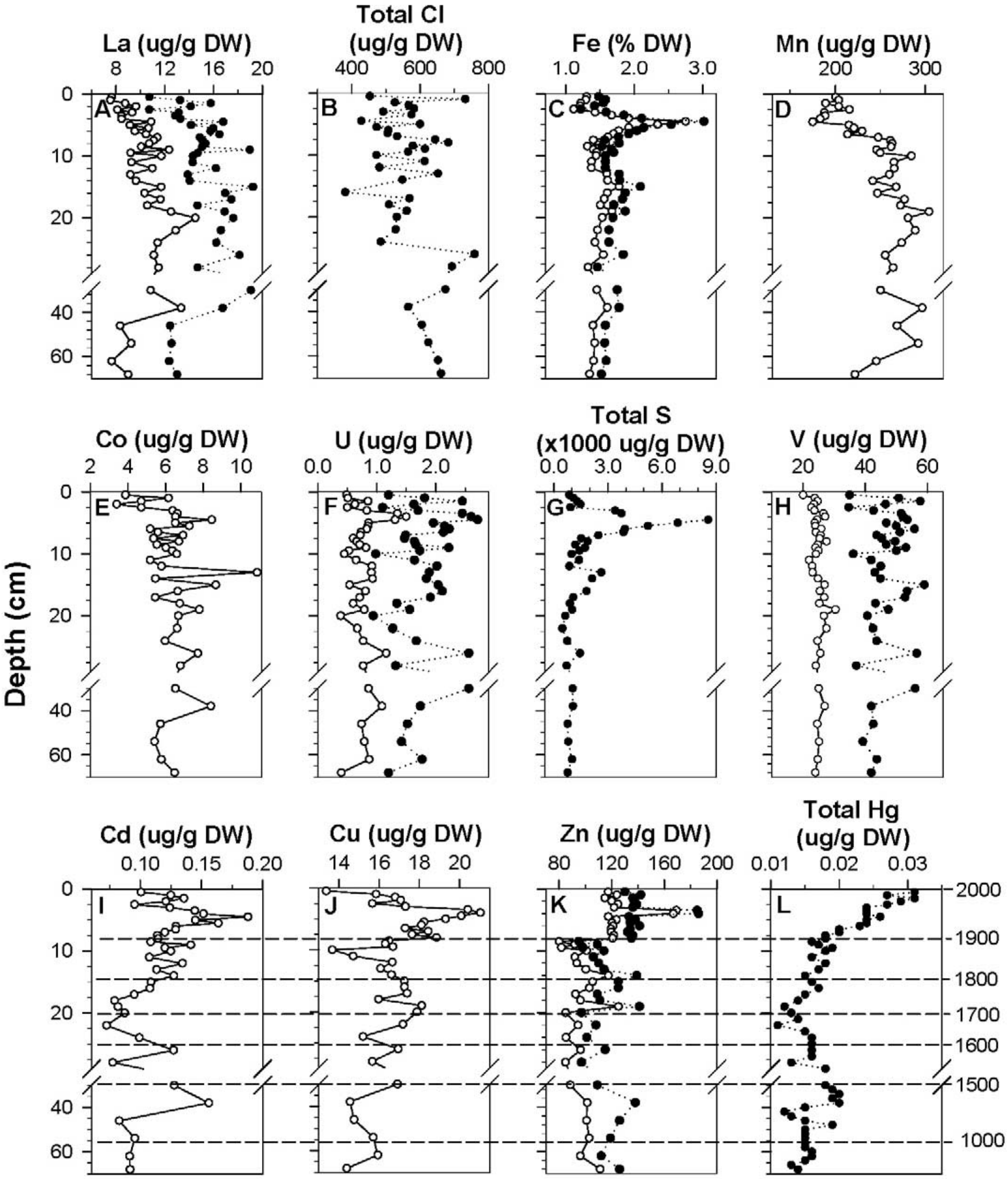

Fig. 5. Down-core elemental profiles of Lake DV-09 sediment. (Total concentrations (dilute acid-leachable + residual fractions) indicated by solid circles, dilute acid-leachable concentrations by open circles. Elements for which only open circles are shown were detectable only in the leachable fraction; elements for which only solid circles are shown were determined only as total concentrations. ^{210}Pb-based linear model dates are shown to the right of the bottom panel).

ticle size is consistent with higher energy inflows to the lake during spring thaw, which may be related to warmer springtime temperatures in recent centuries. Similar diversity and productivity increases in diatom flora over the last ~150 yrs have been reported in 12 other lakes and small ponds in the Canadian High Arctic (Douglas et al. 1994; Wolfe 2000; Smol et al. 2005) as well as Amituk Lake in the present study, showing that the changes in DV-09 are part of a widespread pattern (see also Overpeck et al. 1997; Magnuson et al. 2000). Ponds and shallow lakes in the High Arctic seem particularly sensitive to climate warming compared with lakes at lower latitudes, often exhibiting (as in Amituk) an entirely new establishment of diatom assemblages believed to have been previously light-limited by perennial ice (Overpeck et al. 1997; Smol et al. 2005).

The down-core profiles of Hg and diatom concentrations in both study lakes, but especially in DV-09, generally follow the average surface temperature trend in the northern hemisphere over the past 400 years and particularly in the 20th Century (see Fig. 6). These parameters in DV-09 showed a gradual increase commencing in the late 18th Century and a larger, more rapid increase during the 20th Century commencing about 1910. A levelling-off or slight decline in Hg and diatom concentrations occurred during 1940–1970. While this period of relative con-

Table 1. Correlation co-efficients and F-values for linear regressions between organic C, leachable Fe, and selected trace metals in the DV-09 sediment core.

	Organic C			Leachable Fe		
Parameter	r^2	F-value	P-value	r^2	F-value	P-value
Cd (leachable)	0.36+	11.4	**	0.21+	5.48	*
Co (leachable)	0.04	0.80		0.41+	13.8	**
Cu (leachable)	0.16	3.86		0.39+	12.9	**
Fe (leachable)	0.04	0.90		—	—	—
Fe (total)	0.10	2.1		0.96+	906	***
Hg (total)	0.43+	18.3	***	0.06	0.28	
La (leachable)	0.40−	13.4	**	0.05	1.81	
La (total)	0.04	0.84		0.11+	4.62	*
Mn (leachable)	0.62−	33.0	***	0.01	0.14	
S (total)	0.32+	8.59	**	0.54+	31.8	***
U (leachable)	0.49+	19.3	***	0.23+	5.81	*
U (total)	0.57+	26.0	***	0.19+	4.78	*
V (leachable)	0.01	0.62		0.34+	10.4	**
V (total)	0.24+	6.25	*	0.20+	5.07	*
Zn (leachable)	0.30+	8.46	**	0.08	1.69	
Zn (total)	0.36+	11.2	**	0.08	1.75	

Significance level:

For significant outcomes, "+" and "−" show the direction of correlation. Note that 100% of Cd, Co, Cu and Mn were present in leachable forms, and none in the residual fraction. "−" indicates the correlation was not tested).

* $-P < 0.05$;

** $-P < 0.01$;

*** $-P < 0.001$.

stancy could be the result of dilution by temporarily increased sedimentation, after 1980, Hg and diatom concentrations increased concurrently with sedimentation (see Figs. 1, 2e, 6a). Also, the period of relatively stable Hg and diatom abundance began 30 yrs before the high sedimentation event around 1971. Overall, this pattern of Hg and diatoms coincides with the recent cycle of the Arctic Oscillation, a decadal-scale climatic phenomenon which produces warmer temperatures in much of the Arctic and which appears to be superimposed over an overall long-term warming trend (Serreze et al. 2000). In Amituk Lake, where sedimentary diatom abundance was always lower than in DV-09, the diatom increase occurred later, beginning during the 1950s when diatom populations in DV-09 were stable. The explanation for this difference is uncertain, although the larger and deeper dimensions of Amituk may have made it less responsive to the initial phases of climate warming.

Mercury fluxes in Lake DV-09 over the last 150 years were correlated with fluxes of diatoms and Ca. This association includes a coincident increase during the 1990s of Hg and Ca as well as Hg and diatoms. Calcium fluxes, like those of other elements such as Al and La which are believed to have few or no significant global anthropogenic sources, probably represent material transported into the lake from local geological sources by weathering and runoff from melting snow. The correlation between the fluxes of Hg and these geogenic elements suggests local geology may have been the ultimate source of much of the Hg in Lake DV-09. While the indication of a local geogenic source effect is not a surprising finding, the association between Hg and diatom concentrations and fluxes is novel, and may be suggestive of a previously-unrecognized phenomenon at work superimposed over the geogenic input fluctuations.

The significant Hg—diatom correlations in DV-09 and Amituk could be a coincidence, given that fossil fuel combustion is one of the major atmospheric sources both of the greenhouse gases which drive much of the recent warming (Prentice et al. 2001) and of Hg (Pacyna and Pacyna 2001). Also, there is a geographically-broad consistency to the pattern of long-term increases of sedimentary Hg across the North American, Russian and Greenland Arctic and sub-Arctic, which is similar in magnitude to that seen in these study lakes and which has been interpreted as being due to anthropogenic Hg emissions during the 20th Century (Lucotte et al. 1995; Landers et al. 1998; Lockhart et al. 1998; Rognerud et al. 1998; Bindler et al. 2001). This explanation remains a valid hypothesis. However, as an alternative hypothesis for DV-09, Amituk and similar lakes in the High Arctic where climate warming has had a pronounced impact, we postulate that substantial increases of algal productivity over the past century or more, linked to a longer ice-free growing season, may have driven the recent increase of sediment Hg through more efficient scavenging of Hg from the water column during spring melt. In effect, recent warming may have increased the Hg flux between water and sediment compartments by establishing a new mechanism for Hg transfer in previously unproductive lakes.

High-latitude lakes often exhibit an ice-free moat around their littoral zones in late spring, zones which in some lakes have developed a productive diatom flora over recent decades. Incoming spring meltwater from the catchment enters the littoral moat. Thus, Hg in meltwater may enter lakes at a time of year when algal productivity is at or near maximum. Algae rapidly concentrate both inorganic and organic Hg forms from water (Pickhardt et al. 2002), and a close association has been reported between the spatial patterns of total and methyl Hg concentrations in sediments and those in suspended particulate matter of algal origin (Jackson 1986). In High Arctic lakes, accumulation or adsorption of Hg by littoral algae, followed by their senescence, wind- and wave-induced transport offshore and subsequent sedimentation, would provide a pathway for an

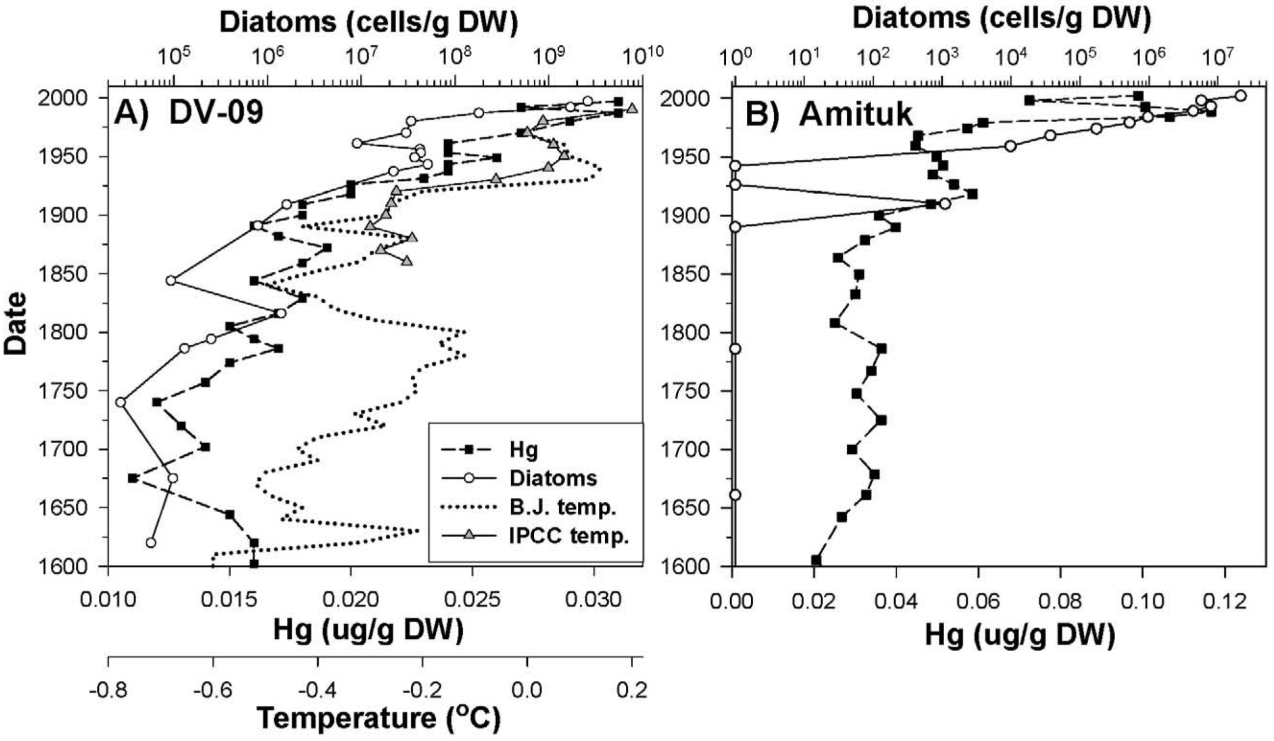

Fig. 6. (A) Historical trends of Hg and diatom concentrations in Lake DV-09 sediment, and anomalies in average Northern Hemisphere surface temperature, and (B) trends of Hg and diatom concentrations in Amituk Lake, over the past 400 years. (Source of temperature data: "B.J. temp."—Bradley and Jones (1993, Fig. 9, and "IPCC temp."—Folland et al. (1990, Fig. 7.6a), as adapted by Pang and Yau (2002, Fig. 1c)).

enhanced flux of Hg into sediments which is not directly driven by trends in atmospheric Hg deposition. Corroborative evidence for a diatom scavenging phenomenon in Lake DV-09 was recently provided by Stern et al. (2005), in a study of the sedimentary fluxes of persistent organic pollutants (POPs) in this lake. Between 1940 and the 1970s, during a period of relative stability in diatom abundance, most POPs profiles closely matched the global or continental production/emission histories, showing increases up to the 1960's–70's with subsequent declines as production was curtailed. However, between the early 1980's and late 1990's, a period when diatom populations expanded by two orders of magnitude, the sedimentary fluxes of some POPs (PCBs, toxaphene, polychlorinated alkanes, chlordane) again increased despite the continuing decline or elimination of their global production. In some cases, maximum fluxes were recorded in the most recent sediments (median age of upper slice: 1997). While this pattern could be the result of "black market" or remobilized historical emissions, the fact that Arctic biota continue to exhibit declines in these POPs up to the present time (Braune et al. in press) indicates that atmospheric POPs fluxes in the Arctic have not increased again; rather, it is more likely that the recent DV-09 pattern did not reliably reflect atmospheric POPs trends.

One potentially powerful test of the hypothesis that diatom scavenging, rather than anthropogenic emissions, contributed to the recent Hg increase in DV-09 is to examine Hg and diatom trends in sediment laid down during previous periods of relatively warm temperatures, such as the Medieval Warm Period (MWP). This natural climatic event is generally considered to have lasted from the 11th to the 14th Centuries (Folland et al. 2001) but may have occurred slightly later in west Greenland (Crowley and Lowery 2000). The current consensus is that MWP did not occur in a globally or hemispherically synchronous pattern but was regionally variable and also relatively mild, being only about 0.2°C warmer than the 15th–19th Centuries compared with the putative 0.6°C average global increase during the 20th Century (Folland et al. 2001). In Lake DV-09, Hg levels were higher by about 30% in sediment at 32–38 cm depth compared to that deposited immediately before and afterwards (see Fig. 5l). These depths are estimated to correspond to the 15th Century, but given the bias of the linear ^{210}Pb model towards more recent dates (noted in the Results) the elevated Hg may lie within the 14th Century, coinciding with the end of the MWP. Paradoxically, diatoms in DV-09 did not exhibit an increase during the MWP but were consistently $<10^6$ cells/g DW from the bottom of the core (estimated at about the 7th Century) until the end of the 19th Century. Either the MWP effect was negligible in this part of the Arctic or its signal was obliterated by the dissolution of diatom valves, which is observed in the present-day sediment record of a few coastal Arctic lakes (Hamilton et al. 2000) and in the deeper parts of some sediment cores (Barker 1992; Gell et al. 1994). In any case, the results neither support nor refute the scavenging hypothesis.

A test of the competing hypothesis for the Hg concentration and flux patterns (i.e. reflective of distant anthropogenic emis-

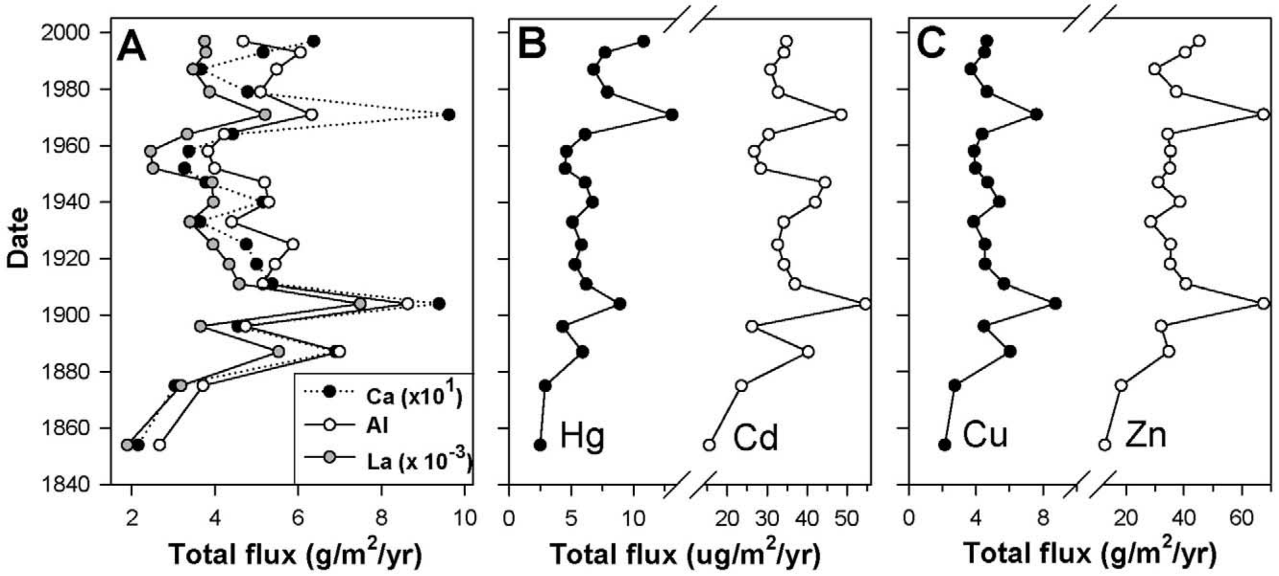

Fig. 7. Trends since 1854 in sedimentary fluxes of (A) Ca, Al and La, (B) Hg and Cd, and (C) Cu and Zn, in Lake DV-09.

sions) is a comparison of the DV-09 profile against the history of global industrial Hg emissions and likely trends of atmospheric Hg in the Northern Hemisphere over recent decades. Over the long-term, the several-times increase of Hg concentrations above pre-industrial background in DV-09 and Amituk, and the 2.3-times increase of flux in DV-09 over 150 years, is consistent with other Arctic and sub-Arctic lakes and peat bogs (see Fitzgerald et al., 1998 and INAC, 2003 for summaries of the evidence) and with inventories of the relative Hg emissions from natural and anthropogenic sources (Pacyna and Pacyna 2001).

In recent decades, however, the Hg concentration and flux record in DV-09 has deviated from global emission trends and from sub-Arctic and temperate latitude records of atmospheric Hg deposition. Atmospheric Hg concentrations in remote locations should be coupled with significant global changes in industrial emissions owing to the relatively long residence time (believed to be >1 yr) of gaseous Hg in the atmosphere and its capacity to be rapidly transported long distances (Schroeder and Munthe 1998; Banic et al. 2003). These factors are believed to explain the spatially-homogeneous pattern of atmospheric Hg over the Northern Hemisphere including the High Arctic (currently 1.4–1.8 ng/m^3 total gaseous Hg; Ebinghaus et al. 2002; Banic et al. 2003; Kellerhals et al. 2003). Global emission inventories indicate that between 1983 and 1995, the anthropogenic Hg contribution to the atmosphere declined by 37% (Pacyna and Pacyna 2001). Mercury in a glacier ice core from four km altitude in the western United States showed a decrease of about 40% of the anthropogenic component from a maximum at 1984 to 1998 (Schuster et al. 2002), in good agreement with the emission inventories. Given that Hg is geographically homogeneous, and vertically homogeneous in the Northern Hemispheric atmosphere up to seven km altitude except over Arctic Hg depletion events and in the vicinity of cities (Ebinghaus and Slemr 2000; Banic et al. 2003), these decadal-scale emission reductions are likely to have been reflected throughout the lower troposphere. The next question is whether there is any evidence of recent declines in atmospheric Hg fluxes, especially in remote areas at low elevation. Decreases in Hg flux which roughly agree with the emissions data and the ice core record have been observed in temperate North American lakes (Engstrom and Swain 1997; Lamborg et al. 2002), two western Greenland coastal lakes (Bindler et al. 2001) as well as peat bogs in Denmark and southern Greenland (Shoytk et al. 2003). The historical records from peat bogs showed that Hg deposition has been declining since the early 1950's whereas the lake sediments showed decreases since the 1970's or 1980's; the difference may be due to ombrotrophic peat recording only an atmospheric Hg input which has a very low natural background compared to sediments (Shotyk et al. 2003). In any case, clearly, Hg profiles in the temperate and sub-Arctic sediments and peat bogs were probably influenced by Hg variations in the lower troposphere. However, this is not

Table 2. Correlation co-efficients for linear regressions between fluxes of total Hg, Cd, Cu and Zn and the geogenic elements Ca, Al and La in Lake DV-09 sediment since 1854.

	Hg	Cd	Cu	Zn
(A) All core slices				
Ca	0.70***	0.69***	0.87***	0.79***
Al	0.52***	0.76***	0.77***	0.62***
La	0.46**	0.79***	0.79***	0.56***
(B) Excluding 1904 and 1971				
Ca	0.60***	0.56***	0.79***	0.66***
Al	0.47**	0.69***	0.69***	0.50**
La	0.37**	0.67***	0.69***	0.38**

(A) All core slices (total df = 18), (B) Core slices excluding the high sedimentation events of 1904 and 1971 (total df = 16). Significance level:
** −P < 0.01;
*** −P < 0.001).

the case in Lake DV-09; the continuing increases of Hg concentrations and fluxes here are in contrast with the other archives, and with declining global industrial emissions. While the transient 1971 peak in flux may appear to be partly consistent with other archives when taken at face value, as discussed above, this peak probably resulted from high sedimentation input of local geogenic Hg. Thus, in contrast to the long-term average data, recent decadal patterns are inconsistent with the hypothesis that increasing Hg in DV-09 is reflective of anthropogenic Hg inputs, unless atmospheric Hg in this region is decoupled by some means from the rest of the Northern Hemisphere and has had a different trend in the past two or three decades.

Amituk Lake results showed that the Hg—diatom correlation observed in DV-09 is not unique to this lake. However, the geographical extent and strength of the association remains to be determined, and studies on other lakes in the High Arctic are underway. If the scavenging phenomenon is dependant on establishment of an abundant diatom flora in previously unproductive lakes, then it is likely to be limited to lakes where recent climate-driven limnological changes have been equally as dramatic as in DV-09 and Amituk (see Smol et al. 2005). At lower latitudes, where warming has not impacted lake productivity to the same degree as in the High Arctic (Smol et al. 2005), another explanation must be invoked to explain the large body of evidence from lake sediments, peat bogs and ice cores which shows historical increases and recent declines of atmospheric Hg flux (e.g. Engstrom and Swain 1997; Schuster et al. 2002; Lamborg et al. 2002; Shoytk et al. 2003). The changing temporal pattern of anthropogenic Hg emissions is the most likely explanation for these trends. Nonetheless, even if the scavenging hypothesis is relevant only to the High Arctic, it would affect environmental assessments concerning the relative importance of natural and anthropogenic Hg in the Arctic atmosphere (e.g. AMAP 1998, 2002; INAC 2003) because the relative anthropogenic contribution to this region would be over-estimated compared with local, natural sources.

Climate warming may be affecting Hg dynamics in Arctic lakes in other ways as well. Elevated algal productivity may increase the Hg reservoir within Arctic lakes by producing a larger algal biomass containing more biologically-incorporated Hg, with deleterious consequences for Hg biomagnification in lake food-webs. High-latitude lakes are often inefficient at trapping chemical inputs (Freitas et al. 1997; Diamond et al. 2003) and thus even a relatively small increase of bioavailable Hg at the bottom of food-chains could yield proportionately large increases of Hg throughout lake ecosystems. Alternately, where greater algal biomass is associated with limited dissolved Hg, Hg content on a per cell basis may be reduced, resulting in lower concentrations in upper trophic levels (Pickhardt et al. 2002). Higher algal productivity may also increase the organic matter content of lake sediments, as demonstrated by the correlation between diatoms and organic carbon in DV-09. Higher organic content, in conjunction with warmer water temperatures, may provide more favourable conditions for sedimentary bacterial populations that methylate inorganic Hg. Organic matter content and methyl Hg concentrations at the sediment-water interface of lakes have been found to be significantly correlated (Regnell and Ewald 1997; Kainz et al. 2003).

4.2. Profiles of Cd, Cu and Zn

With respect to other metals, their profiles are more likely to be the product of variable geogenic inputs from the local catchment, coupled with post-depositional remobilization or association with organic matter inputs to sediment, rather than of atmospheric deposition affected by long-range anthropogenic sources. Cadmium and Zn were strongly correlated with organic carbon down-core, whereas Cu was correlated with leachable Fe. Distinct sub-surface peaks of Cd, Cu and to a lesser extent Zn coincided with those of other elements which are known to undergo redox-related migration, such as Fe, S, Co, U and Cr (Boyle 2001), which is suggestive of a redox-related effect on Cd, Cu and Zn distribution. Similar Fe-associated patterns of Co, Cu and Ni were reported for Toolik Lake in Alaska, and attributed to migration of dissolved metals followed by precipitation at the redox boundary (Cornwell 1986). The mechanism by which the peaks were produced in DV-09 is unclear. Two possibilities are co-precipitation or adsorption of dissolved metals onto Fe oxides at the redox boundary, or precipitation of metal sulphides. The coincidence of maximum Fe and S concentrations with those of Cd, Cu and Zn suggests the latter mechanism, but metal concentrations were too low to permit mineralogical analysis by XRD. There was no evidence here of extensive in situ metal sulphide formation because only trace amounts of framboidal pyrites were found, unlike organic-rich, strongly-reducing sediments (e.g. Percival et al. 1999). Sulphide formation in DV-09 may be limited by low organic matter content.

A second line of evidence that suggests the Cd, Cu and Zn profiles do not reflect atmospheric deposition is the lack of agreement with another nearby archive of atmospheric metals and with industrial emission trends. Owing to the good temporal resolution of the DV-09 core, it was apparent that the peak concentrations of Cd, Cu and Zn at about 1950 (see Fig. 5) and the subsequent abrupt 30–50% declines do not agree with the history of atmospheric metal deposition onto the Greenland Summit icefields (see Boutron 1995). The Cd, Cu, and Zn maxima in DV-09 occurred about two decades earlier than on Summit, and the subsequent declining trends in the ice core were gradual, unlike those in sediment but similar to Northern Hemisphere industrial emissions (Boutron et al. 1991, Pacyna and Pacyna 2001). Furthermore, by 1990 the concentrations of Cd and Cu in DV-09 sediment had returned to long-term background (pre-1700 A.D.) levels, but their rates of atmospheric deposition at Greenland Summit were still four-times and two-times background levels, respectively (Boutron 1995). Corroboratively, concurrent emission inventories estimated that global industrial sources of Cd and Cu to the atmosphere were contributing 230% and 93%, respectively, of natural sources at this time (Pacyna and Pacyna 2001). The metal flux profiles also disagree with Greenland ice core and emission inventory data. Indeed, aside from the two peaks associated with high sedimentation events around 1904 and 1971, the flux profiles were remarkably constant throughout the 20th Century. Although the magnitude of atmospheric metal deposition may vary between Lake DV-09 at sea-level and the high-altitude (3,230 m) Summit glacier, relative long-term trends are expected to be similar. The air catchments of both areas are influenced by Eurasian air masses, and although Greenland also receives atmospheric inputs from North America (Sturges and Barrie 1989; Raatz 1991) the magnitude of declining metal emissions in recent decades was similar in Europe and North America (Pacyna and Pacyna 2001).

A third line of evidence regarding sediment reliability concerns the absence of anthropogenic Pb from DV-09 and other High Arctic lake sediments (Outridge et al. 2002), despite its unequivocal presence in the Canadian Arctic atmosphere (Sturges and Barrie 1989). Arctic airborne Pb (like other metals except for Hg and Se) is believed to occur predominantly as fine particulate aerosol (Dietz et al. 1998). Outridge et al. (2002) argued that low precipitation rates at high latitudes limited the scavenging of airborne aerosols so that the atmospheric input of anthropogenic Pb was negligible compared to natural Pb inputs from catchment geology. Aerosol-associated Cd, Cu and Zn fluxes from the atmosphere may be likewise limited, and similarly negligible.

Thus, while the predominant mechanisms involved in controlling the flux and distribution of Hg, Pb, Cd, Cu and Zn may differ between elements, the overall conclusion from the present study and Outridge et al. (2002) is that none of the metal profiles examined in Lake DV-09 are unequivocally reflective of deposition of anthropogenic-source metals from the atmosphere. For Cd, Cu, Pb and Zn, the hypothesis that sedimentary profiles in this lake record an atmospheric deposition history can be rejected, whereas for Hg the data are as yet inconclusive. This result is not due to the lake being particularly insensitive to atmospheric metal inputs, as Outridge et al. (2002) demonstrated for Pb. The late 19th Century Hg fluxes in DV-09, which ranged from 2.5 to 5.9 μg/m^2/yr, are in the low to middle part of the range of pre-industrial or historical period fluxes in other North American and West Greenland Arctic lakes (see Lockhart et al. 1995, 1998; Landers et al. 1998; Hermanson 1998; Bindler et al. 2001).

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