Sediment Chemistry and Atmospheric Contamination [and Discussion]

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Sediment chemistry and atmospheric contamination

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The trace metal, sulphur and polycyclic aromatic hydrocarbon concentration–depth profiles in dated lake-sediment cores are used to establish the history of contamination of the atmosphere above the study lakes. The results from three chemical groups give the same qualitative description of contamination. The atmosphere became contaminated in the areas of high present day acid deposition early last century in Scotland and late last century in southern Scandinavia. Contamination increased this century and the sulphur, polycyclic aromatic hydrocarbon and sometimes the trace metal fluxes to the sediment drop over the past 10–30 years. There was little or no contamination at the low recent acid-deposition sites in both study regions.

Introduction

The concentration–depth profiles of trace metals are frequently used in surface water acidification studies to establish if a lake has received contaminants deposited from the atmosphere (Galloway & Likens 1979; Norton *et al.* 1981; Wong *et al.* 1984; Battarbee *et al.* 1985). This trace metal contamination of the atmosphere and surface waters is part of a global pattern (Rippey *et al.* 1982) and, although the metals do not cause acidification, it is assumed that several trace metals and the acidic components do have the same deposition history. The time when the atmosphere over the lake became contaminated and the change in level of contamination can at least be established from the trace metal profiles.

Sulphur, one of the main components of acid deposition, has been measured in some palaeolimnological studies (Nriagu & Coker 1983; Holdren *et al.* 1984; Mitchell *et al.* 1985) and is potentially a more direct indicator of acid stress on the lake. However, because the main sulphur sedimentation process, sulphate reduction (Nriagu & Soon 1985; Rudd *et al.* 1986), is prone to changes in efficiency as lake conditions change, the concentration–depth or flux–time profiles do not always accurately record the sulphur input history. Polycyclic aromatic hydrocarbons (PAH) have been used as a more reliable record of the deposition history of the products of fossil fuel combustion (Furlong *et al.* 1987). Their main source in the environment is fossil-fuel combustion and they are little altered during transport through the atmosphere or during burial in the sediment (Hites 1981). A few studies have included trace metals, sulphur and polycyclic aromatic hydrocarbons in their palaeolimnological investigation of surface water acidification (Furlong *et al.* 1987; Charles *et al.* 1987).

We also use these sediment properties to establish the timing and extent of contamination of the atmosphere by these chemical species to help provide evidence for the start and change of acid stress on the lakes in the Surface Water Acidification Project (SWAP). Lakes in the United Kingdom, Sweden and Norway were chosen to establish the patterns of atmospheric contamination in areas of high and low present-day acid deposition. The Round Loch of

Glenhead (Galloway), Lochs Tinker and Chon (Trossachs, central Scotland), Verevatn (southern Norway) and Lilla Öresjön (southern Sweden) are in areas of high acid deposition. Loch Doilet and Lochan Dubh (Strontian/Loch Sheil, Northwest Scotland), Lochan Uaine (Cairngorms, Northeast Scotland) and Röyrtjörna (mid-Norway) are in areas of low acid deposition. Site details are given by Battarbee & Renberg (this symposium).

METHODS

In the U.K., sediment cores were taken with a mini-Mackereth corer and in Scandinavia cores were taken with a freeze-corer (for trace metals and S) or a modified Kajak corer (PAH). Laboratory methods are described in Stevenson *et al.* (1987) and are only outlined briefly here. The trace metals were determined by flame atomic absorption spectrophotometry after digestion of the sediment by hydrofluoric, nitric and perchloric acids. Total sulphur was determined by turbidity (Tabatabi 1974) after half fusion of the sediment (Grant & Yeung 1971). The polycyclic aromatic hydrocarbons were determined by liquid chromatography with fluorescence detection after Soxhlet extraction of the freeze-dried sediment with cyclohexane. The extracts were cleaned-up by using neutral alumina. In the U.K. work, one core, which was dated, was used for the trace metal and sulphur analyses and another for the trace organics. This core was cross correlated with the dated one by using dry mass and loss on ignition profiles. In the Scandinavian work, trace metal, sulphur, PAH and ^{210}Pb were analysed on different cores, but these were carefully cross-correlated by using similar techniques.

RESULTS AND DISCUSSION

Figure 1 shows the lead and zinc concentration–depth profiles from a long core from the Round Loch of Glenhead in Galloway. As there is little change in sediment dry mass, loss on ignition and accumulation rate in the core, the shape of the flux–depth and concentration–depth profiles are identical. This core covers the last 9000 years (Jones *et al.* 1986) and shows that zinc and lead contaminate only the most recent sediment. Lead contamination starts above 40 cm (extrapolates to the late 18th century), zinc at 28 cm (extrapolates to around 1820) and the concentrations are highest during the 20th century. As this is a remote lake, the source of contamination is deposition from the atmosphere. The drop in concentration towards the sediment surface indicates that the quality of the atmosphere has improved recently. The lead improvement starts around the 1920s (8.25 cm). However, because the efficiency of zinc sedimentation is less at lower pH values (Tessier *et al.* 1989), the drop in sedimentary zinc concentration above 5.5 cm (1950) is probably due to both lake acidification (Jones *et al.* 1986) and to a real drop in flux from the atmosphere. The deposition flux of trace metals from the atmosphere is known to have dropped recently in the U.K. (Cawse 1987).

The dry mass, loss on ignition, accumulation rate and sediment constitution (grain size and mineralogy) are not always constant in a core and this makes interpretation of the trace metal profiles more difficult. Interpretation of the profiles from Loch Tinker is not as easy as with the Round Loch of Glenhead core. The lead and zinc concentrations in Loch Tinker are constant up to 22.5 cm (extrapolates to early 19th century), and then increase. Lead is constant above 10 cm, whereas zinc drops a little above 5 cm. The broad contamination pattern is similar to that in the Round Loch of Glenhead.

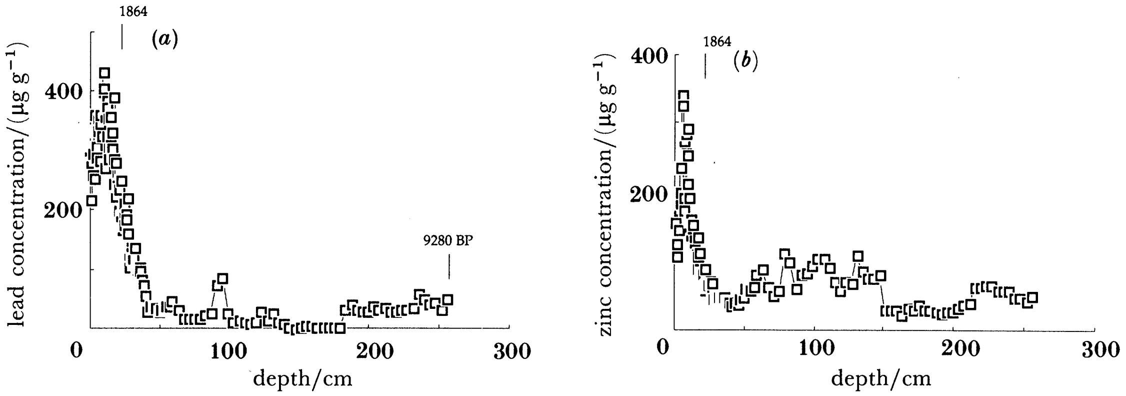

FIGURE 1. The variation of lead (*a*) and zinc (*b*) concentration with depth in the sediments of the Round Loch of Glenhead in Galloway shows that only the most recent sediments are contaminated by material deposited from the atmosphere.

However, superimposed on this pattern there is a trough in the lead and zinc concentrations between 13 and 20 cm. This coincides with changes in sediment composition and accumulation rate. Specifically, the sodium and magnesium concentrations and the sediment accumulation rate are higher in this interval. However, there is a steady increase in lead and zinc fluxes during this interval (figure 2). Although the temporary change in sediment accumulation rate in Loch Tinker did not alter the trace-metal fluxes, this is not always so (Johnston & Nichols 1988). The sulphur and zinc concentration–depth profile shapes are similar and the flux–depth behaviour shows that the input of sulphur to the sediment increased until 3 cm (1960) after which it falls a little (figure 2). In this case, as the zinc and sulphur behaviour is similar, the zinc profile is a good surrogate for acid stress on the lake (Holdren *et al.* 1984).

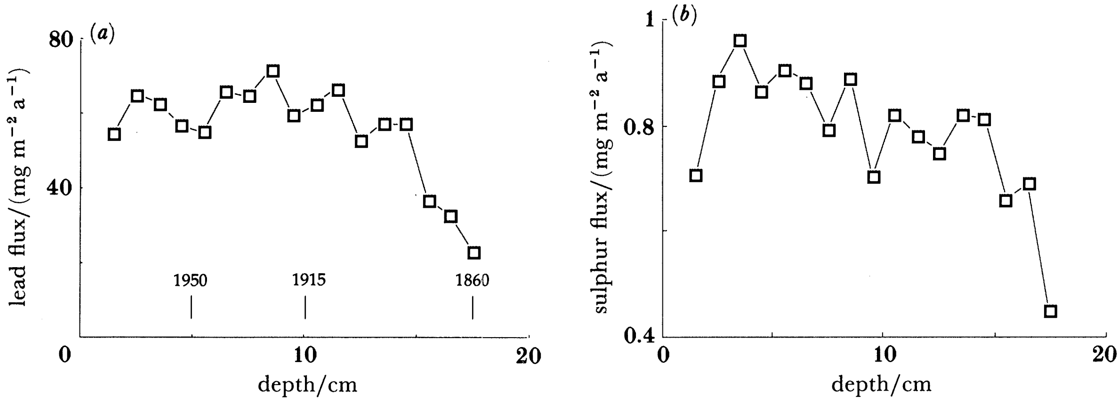

FIGURE 2. The variation of lead (*a*) and sulphur (*b*) fluxes to the sediment with depth in Loch Tinker in the Trossachs, central Scotland.

The behaviour and concentrations of lead and zinc in Loch Chon are similar to nearby Loch Tinker. Contamination started early last century. The results for Lochan Dubh and Loch Doilet in the Strontian–Loch Sheil area of Northwest Scotland and for Lochan Uaine in the Cairngorms show that there is only a little zinc contamination in Lochan Dubh that starts at

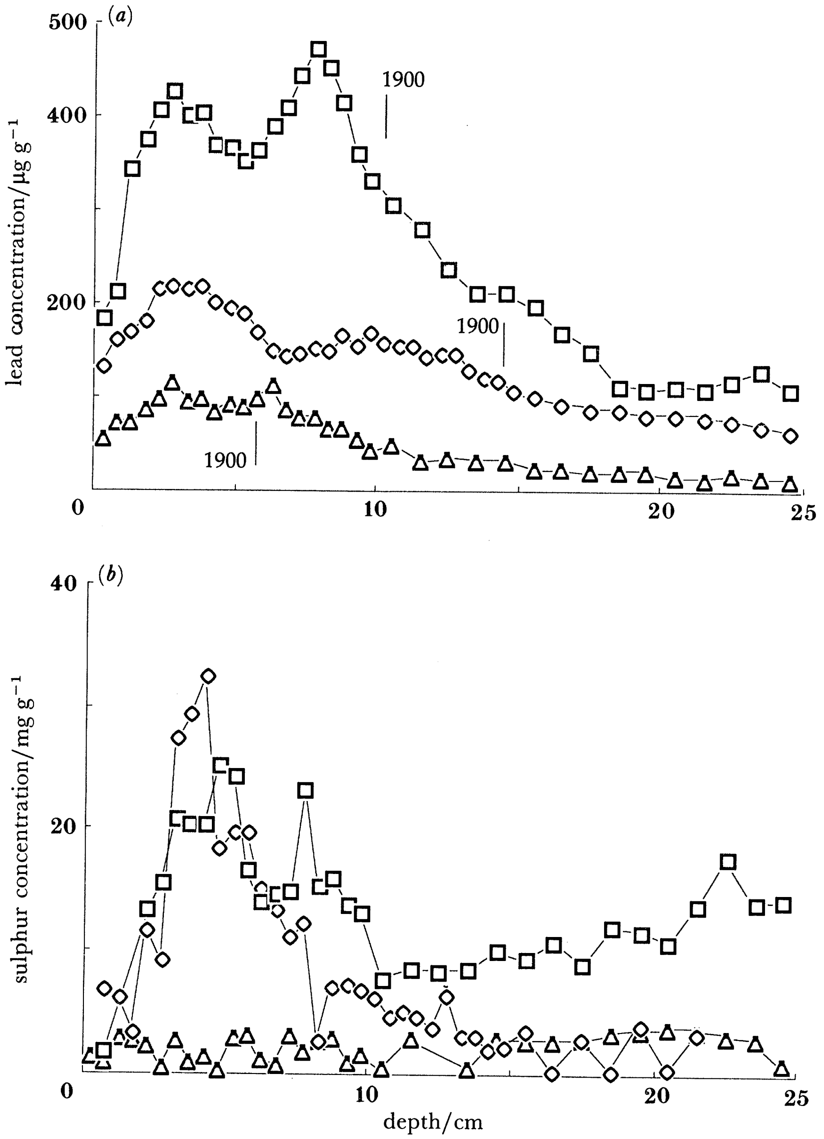

FIGURE 3. The variation of lead (*a*) and sulphur (*b*) concentration with depth in the sediments of Röyrtjörna (△) (mid-Norway), Verevatn (□) (southern Norway) and Lilla Öresjön (◇) (southern Sweden).

10 cm depth (1880s). The lead and zinc concentrations are low in these lakes and do not rise above 100 µg Pb g^{-1} and 150 µg Zn g^{-1} in Lochan Dubh, 80 µg Pb g^{-1} and 130 µg Zn g^{-1} in Loch Doilet and 160 µg Pb g^{-1} and 150 µg Zn g^{-1} in Lochan Uaine (ignoring surface effects). The higher lead concentrations in Lochan Uaine are due to granite in the catchment.

The SWAP lakes in Norway and Sweden were chosen to cover the range from high acid deposition in southern Norway (Verevatn) and southern Sweden (Lilla Öresjön) to low deposition in mid-Norway (Röyrtjörna). The trace metal and sulphur results confirm this contamination pattern (figure 3). Lead and zinc contamination is highest in Lilla Öresjön and Verevatn. Lead and zinc contamination started round 1880 in Lilla Öresjön (16 cm), zinc at the same time (10 cm) and lead earlier in Verevatn. There is a small amount of trace metal contamination in Röyrtjörna. The sulphur profiles show that there is no contamination in

Röyrtjörna but contamination starts in the 1880s in the other two lakes and increases strongly around 1940 (8 cm) in Lilla Öresjön and 1924 (8 cm) in Verevatn. The sulphur concentrations in Lilla Öresjön and Verevatn are quite high (compare with a maximum of 5.2 mg S g^{-1} in Loch Tinker). Although the trace metal and sulphur profiles provide the same qualitative history of atmospheric contamination at these lake sites, there are important quantitative differences. For example, the lead concentration profiles suggest that Verevatn is more contaminated than Lilla Öresjön, whereas the sulphur profiles indicates that there is not much difference. Furthermore, the lead fluxes indicate that there is not much difference between the two lakes, but the sulphur fluxes indicate that Lilla Öresjön is more contaminated.

The trace metal and sulphur results confirm that the atmosphere was contaminated in those areas receiving high present-day acid deposition early last century in Scotland and late last century in southern Scandinavia. There is little or no contamination in the low acid-deposition areas in Scotland and Scandinavia.

We found many polycyclic aromatic hydrocarbons in many of the lake sediments (mostly over 40 compounds). The main compounds, naphthalene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene and dibenz[a,h]anthracene, comprise a group that is found in lake sediments throughout the northern hemisphere (Laflamme & Hites 1978; Furlong *et al.* 1987) and are the result of long-distance transport of the products of fossil fuel combustion (Laflamme & Hites 1978; Bjørseth *et al.* 1979; Hites 1981). The concentrations of PAH in all the lakes examined were highly correlated and one of the compounds found at highest concentration, benzo[a]pyrene, is used to illustrate the degree of PAH contamination between the sites (figure 4). As the concentrations in Verevatn are around twice those in Lilla Öresjön, the concentrations in Loch Tinker and Loch Chon similar, and similar in Loch Doilet and Lochan Dubh, this figure summarizes the relative contamination in areas of high acid deposition in southern Scandinavia (Lilla Öresjön, Verevatn) and central Scotland (Loch Tinker, Loch

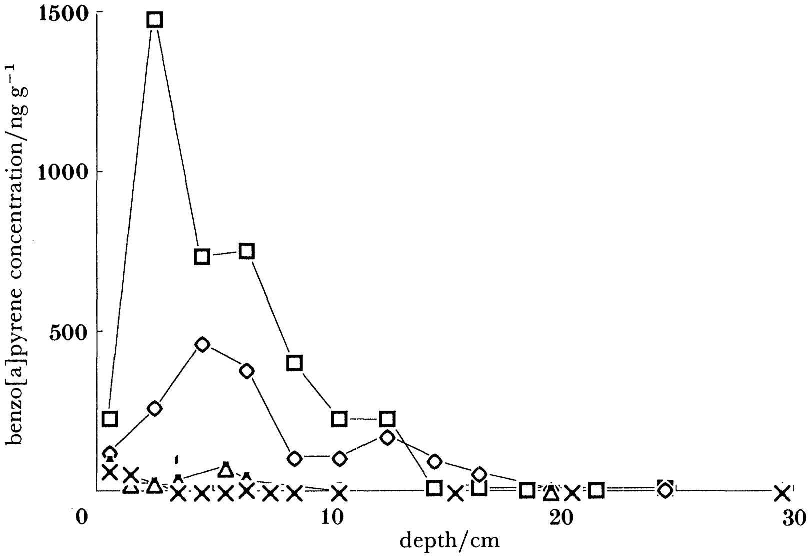

FIGURE 4. The variation of benzo[a]pyrene concentration with depth in the sediments of Lilla Öresjön (southern Sweden), Loch Tinker (Trossachs, central Scotland), Lochan Dubh (northwest Scotland) and Lochan Uaine (Cairngorms, Scotland). (□), Lilla Öresjön; (◇), Loch Tinker; (△), Lochan Dubh; (×), Lochan Uaine.

Chon) and in two areas of low deposition in Northwest Scotland (Loch Doilet, Lochan Dubh) and the Cairngorms (Lochan Uaine). The two areas of low acid deposition have much lower benzo[a]pyrene concentrations, and all other PAH, than the areas of high deposition in Scotland and southern Scandinavia. Loch Doilet, Lochan Dubh and Lochan Uaine do show a small amount of contamination, whereas contamination started early last century in Loch Tinker (and Loch Chon) and late last century in Lilla Öresjön (and Verevatn). There is an improvement at all sites over the past 10–30 years.

The trace metal, sulphur and PAH results give similar qualitative descriptions of the history of atmospheric contamination at the SWAP sites. They all confirm that the atmosphere has been contaminated in the areas of highest recent acid deposition in Scotland since early last century and late last century in southern Scandinavia. Although small, there is a little trace metal contamination at the low deposition sites in both study regions. Contamination by all three chemical groups increased strongly this century and the sulphur, PAH and sometimes the trace contamination drops over the past 10–30 years. Acidification of the lakes coincides with or post-dates the start of atmospheric contamination (Battarbee, this symposium).

REFERENCES

Battarbee, R. W., Flower, R. J., Stevenson, A. C. & Rippey, B. 1985 Lake acidification in Galloway: a palaeoecological test of competing hypotheses. *Nature, Lond.* **314**, 350–352.

Bjørseth, A., Lunde, G. & Lindskoog, A. 1979 Long-range transport of polycyclic aromatic hydrocarbons. *Atmos. Environ.* **13**, 45–53.

Cawse, P. A. 1987 Trace and major elements in the atmosphere at rural locations in Great Britain, 1972–81. In *Pollutant transport and fate in ecosystems* (ed. P. J. Coughtrey, M. H. Martin & M. H. Unsworth), pp. 89–112. Oxford: Blackwell Scientific Publications.

Charles, D. F., Whitehead, D. R., Engstrom, D. R., Fry, B. D., Hites, R. A., Norton, S. A., Owen, J. S., Roll, L. A., Schindler, S. C., Smol, J. P., Uutala, A. J., White, J. R. & Wise, R. J. 1987 Paleolimnological evidence for recent acidification of Big Moose Lake, Adirondack Mountains, N.Y., U.S.A. *Biogeochemistry* **3**, 267–296.

Furlong, E. T., Cessar, L. R. & Hites, R. A. 1987 Accumulation of polycyclic aromatic hydrocarbons in acid sensitive lakes. *Geochim. cosmochim. Acta* **51**, 2965–2975.

Galloway, J. N. & Likens, G. E. 1979 Atmospheric enhancement of metal deposition in Adirondack lake sediment. *Limnol. Oceanogr.* **24**, 427–433.

Grant, C. J. & Yeung, H. L. 1971 A preliminary investigation of a half-fusion method for the determination of total sulphur in acid sulphate soil. *Agric. Sci. Inst. Hong Kong* **4**, 256–264.

Hites, R. A. 1981 Sources and fates of atmospheric polycyclic aromatic hydrocarbons. *ACS Symp. Ser.* **167**, 187–196.

Holdren, G. R., Brunelle, T. M., Matisoff, G. & Whalen, M. 1984 Timing the increase in atmospheric sulphur deposition in the Adirondack Mountains. *Nature, Lond.* **311**, 245–248.

Laflamme, R. E. & Hites, R. A. 1978 The global distribution of polycyclic aromatic hydrocarbons in recent sediments. *Geochim. cosmochim. Acta* **42**, 289–303.

Johnson, M. G. & Nicholls, K. H. 1988 Temporal and spatial trends in metal loads to sediments of Lake Simcoe, Ontario. *Wat. Air Soil Pollut.* **39**, 337–354.

Jones, V. J., Stevenson, A. C. & Battarbee, R. W. 1985 Lake acidification and the land-use hypothesis: a mid-post-glacial analogue. *Nature, Lond.* **322**, 157–158.

Mitchell, M. J., David, M. B. & Uurl, A. J. 1985 Sulphur distribution in lake sediment profiles as an index of historical deposition patterns. *Hydrobiologia* **121**, 121–127.

Norton, S. A., Hess, C. T. & Davis, R. B. 1981 Rates of accumulation of heavy metals in pre- and post-European sediments in New England lakes. In *Atmospheric pollutants in natural waters* (ed. S. J. Eisenrich), pp. 409–421. Ann Arbor: Ann Arbor Science.

Nriagu, J. O. & Coker, R. D. 1983 Sulphur in sediments chronicles past changes in lake acidification. *Nature, Lond.* **303**, 692–694.

Nriagu, J. O. & Soon, Y. K. 1985 Distribution and isotopic composition of sulphur in lake sediments of northern Ontario. *Geochim. cosmochim. Acta* **49**, 823–834.

Rippey, B., Murphy, R. J. & Kyle, S. W. 1982 Anthropogenically derived changes in the sedimentary flux of Mg, Cr, Ni, Cu, Zn, Hg, Pb, and P in Lough Neagh, Northern Ireland. *Environ. Sci. Technol.* **16**, 23–30.

Rudd, J. W. M., Kelly, C. A. & Furutani, A. 1986 The role of sulphate reduction in long term accumulation of organic and inorganic sulphur in lake sediments. *Limnol. Oceanogr.* **31**, 1281–1291.

Stevenson, A. C., Patrick, S. T., Kreiser, A. & Battarbee, R. W. 1987 Palaeoecological evaluation of the recent acidification of susceptible lakes: methods utilised under DoE contract PECD 7/7/139 and the Royal Society SWAP Project. Palaeoecology Research Unit, University College London.

Tabatabai, M. A. 1974 Determination of sulphate in water samples. *Sulph. Inst. Jl* **10**, 11–13.

Tessier, A., Carignan, R., Dubreuil, B. & Rapin, F. 1989 Partitioning of zinc between the water column and the oxic sediments in lakes. *Geochim. cosmochim. Acta* **53**, 1511–1522.

Whalen, M. & Thompson, R. C. 1980 Pollution records from sediments of three lakes in New York State. *Geochim. cosmochim. Acta* **44**, 333–339.

White, J. R. & Driscoll, C. T. 1987 Zinc cycling in an acidic Adirondack lake. *Environ. Sci. Technol.* **21**, 211–216.

Wong, K. T., Nriagu, J. O. & Coker, R. D. 1984 Atmospheric input of heavy metals chronicled in lake sediments of the Algonquin Provincial Park, Ontario, Canada. *Chem. Geol.* **44**, 187–201.

Discussion

D. F. Charles (*United States Environmental Protection Agency, Oregon, U.S.A.*). I understand that the nature, amount and proportion of PAHs varies among PAH emission sources (for example, coal versus oil) and generally from one geographical region to another. Can Dr Rippey interpret the PAH profiles from any of his studied lakes to detect these differences, for example, between the U.K. and Scandinavia?

Secondly, and related to the first question, does Dr Rippey think that any of the decline in PAH concentration in the top 5 cm of some of the cores is due to increased use of emission controls?

B. Rippey. We have not detected any major differences in the relative proportions of the main PAHs either from sample to sample within a core or between sites. The concentrations of the main compounds are highly correlated. As the lakes are contaminated by long-distance transport from the main emission sources in urban and industrial areas, it may be that there is an integration of the various sources during transport through the atmosphere to form a homogeneous mixture.

The decline in PAH concentrations in the top 3–5 cm of some of the cores is probably due to an improvement in atmospheric quality due to improved emission control measures. The improvement starts in the 1950s in Loch Chon and Loch Tinker and this coincides with the introduction of legislation to control emissions in the U.K. The reductions in PAH concentration start around 1960 in Verevatn and in the mid-1970s in Lilla Öresjön.