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T.A. Jackson

Aquatic Ecosystem Restoration Branch
National Water Research Institute (NWRI)
P.O. Box 5050
Burlington, Ontario L7R 4A6, Canada

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Introduction.

It appears to be the consensus among environmental scientists who have studied the regional and global distribution of mercury (Hg) that the following conclusions are supported by the available evidence: (1) winds transport Hg (mainly as gaseous Hg^{o} and particulate Hg(II)) thousands of kilometers from its points of origin; (2) the anthropogenic component of this Hg flux is comparable in magnitude to the natural component; and (3) the rates of emission of Hg into the atmosphere and subsequent deposition of this Hg in natural environments have increased progressively over time as a result of human activities (especially the burning of fossil fuels) since the onset of the Industrial Revolution, accelerating noticeably in the mid-twentieth century (although there are indications that in some regions, at least, anthropogenic emissions peaked some time in latter part of the 20th century and are now declining).

However, some Canadian geologists question the quantitative significance of pollution (i.e. emissions resulting from human activities) in the long-range atmospheric distribution of Hg, claiming that insufficient attention has been paid to the assessment of natural sources of Hg in the Earth's crust (Rasmussen, 1994). They have also challenged the widely accepted proposition (Johnson *et al.*, 1986) that the elevated Hg concentrations observed in the uppermost strata of many lake sediment cores indicate a relatively recent temporal increase in Hg loading due to pollution, countering this interpretation with the hypothesis that diagenetic redistribution of Hg can account for the patterns of variation (Rasmussen, 1994). But, as outlined below, there is an impressive weight of evidence, comprising different kinds of data, in favour of the conclusion that the anthropogenic contribution to the atmospheric flux of Hg rivals the natural contribution in quantitative importance; and, as attested by the literature, the idea that environmental scientists have generally failed to take natural sources

of Hg into account is unfounded (Heit *et al.*, 1981; Johnson *et al.*, 1986; Nriagu, 1989; Lindqvist *et al.*, 1991; Nater and Grigal, 1992; Nater *et al.*, 1992; Rognerud and Fjeld, 1993). Furthermore, there are grounds for concluding that Hg profiles in cores of undisturbed fine-grained lake sediments are reliable records of temporal variations in Hg loading and that alteration of the sediments by diagenesis has only negligible effects on the vertical distribution of Hg.

The division of opinion about the effects of long-range atmospheric transport of Hg seems to resolve itself into two principal questions: To what extent is long-range atmospheric transport responsible for the Hg found in remote areas (e.g. the Arctic), and to what extent are human activities responsible for the long-range atmospheric transport of Hg to these areas? A third question which has an important bearing on the other two is, How should Hg profiles in lake sediment cores be interpreted? The question of whether the long-range atmospheric Hg contamination is having appreciable ill effects on organisms is, of course, especially important, but it is beyond the scope of this report. It should be mentioned in passing, however, that methyl Hg levels in fish inhabiting ill-buffered lakes in remote areas have been rising, probably as a result of air pollution, although the mechanisms are as yet unknown. Acidification due to "acid rain" is a prime suspect owing to a general inverse corrrelation between lake pH and the Hg content of fish, but the process is probably complex, and other factors appear to be involved (Johansson, 1985; Jackson, 1987; Richman *et al.*, 1988; Winfrey and Rudd, 1990). These other factors may well include atmospheric Hg pollution, which, of course, is connected with the acid rain phenomenon since both result largely from the burning of coal and other fossil fuels (Richman *et al.*, 1988).

The purpose of this review is to attempt to answer these questions about the quantitative significance of airborne Hg in general and anthropogenic airborne Hg in particular, and to address the issue of the correct interpretation of Hg profiles in lake sediment cores, by summarising relevant published information, drawing inferences from different lines of evidence, and attempting to develop a coherent synthesis in consultation with colleagues at the National Water Research Institute. The evidence marshalled for this brief overview should provide a reasonably firm foundation for conclusions and recommendations regarding Canada's official position on the UN ECE protocol for Hg.

The evidence discussed below demonstrates that (1) large quantities of anthropogenic Hg as well as Hg from natural sources are continually being introduced into the atmosphere; (2) significant long-range atmospheric transport of Hg (regional and global transport over distances on the order of hundreds to thousands of kilometers) takes place; (3) a large proportion of this airborne Hg is anthropogenic; and (4) vertical profiles of Hg in lake cores primarily reflect temporal variations in Hg loading, not post-depositional redistribution due to diagenesis, which appears to have only a minor effect, if any, on the patterns of variation.

I. ESTIMATES OF GLOBAL Hg EMISSIONS TO THE ATMOSPHERE.

Using calculations based on various empirical data, a number of workers have estimated that human activities introduce thousands of metric tons (tonnes) of Hg into the Earth's atmosphere every year (Weiss and Goldberg, 1971; Lantzy and MacKenzie, 1979; Jaworowski *et al.*, 1981; Nriagu and Pacyna, 1988; Lindqvist *et al.*, 1991; Hudson *et al.*, 1995). According to the data of Nriagu and Pacyna (1988), the largest single cause of global atmospheric Hg pollution in the year 1983 was combustion of coal, and incineration of municipal refuse was a close second. Similarly, D'Itri *et al.* (1978) reported that the largest anthropogenic contribution in the U.S.A. in 1973 was from "energy related activities." Some published estimates of the annual emission of natural and anthropogenic Hg into the atmosphere are shown in the following table:

Source of information	Geographic scope	Hg emission (tonnes/yr)		% Anthropogenic	Comments
		Natural	Anthropogenic		
Weiss *et al.* (1971)	Global	25,000-150,000	6,700	4.3-21	
Lantzy & Mackenzie (1979)	Global	29,300,000	11,500,000	28.2	Based partly on data from Weiss *et al.* (1971)
Nriagu & Pacyna (1988); Nriagu (1989)	Global	2,500 (100-4,900)	3,600 (910-6200)	59	Data for 1983 (median & range)
Lindqvist *et al.* (1991)	Global	3,000	4,500[1]	60	Based on modification of data from Nriagu (1989) & Nriagu & Pacyna (1988)
Hudson *et al.* (1995)	Global	2,700	2,000	43[2]	
D'Itri *et al.* (1978)	U.S.A. (not including Alaska & Hawaii)	1,019	475	32	Data for 1973 compiled by U.S. Environmental Protection Agency

[1]Diffuse sources as well as point sources were taken into account.

[2]Conservative estimate. Might be as high as 60% if "natural" emissions include reemitted anthropogenic Hg (Hudson *et al.*, 1995).

The table demonstrates that the more recent estimates of Hg fluxes to the atmosphere (data published in the 1980's and 1990's) agree well with each other but differ greatly from the older estimates (data published in the 1970's) except for the anthropogenic Hg data of Weiss *et al.* (1971). Most of the numbers from the two oldest publications are one to four orders of magnitude higher than the more recent ones! In view of the technical improvements and the expansion and updating of scientific information which have been taking place over the years, it would not be unreasonable to assume, on general principles alone, that the most recent estimates tend to be the most reliable ones. However, Nriagu and Pacyna (1988) have given more explicit reasons for believing that the older estimates in general, and the estimates of Lantzy and Mackenzie (1979) in particular (see table), are inaccurate; for instance, they pointed out that Lantzy and Mackenzie made an incorrect assumption about the percentage of the heavy metal content of coal and oil that is released to the atmosphere on combustion. Another reason for doubting the reliability of the two oldest sets of numbers is that both are based in part on Greenland ice data (Weiss *et al.*,

1971) whose validity is questionable (see section 2.3, below). The discrepancies between the older and more recent data sets in the table probably reflect differences in the assumptions on which the models were based, in the choice of the parameters and geochemical pathways represented in the calculations, and in the estimated values of certain parameters (Nriagu and Pacyna, 1988; Rasmussen, 1994). Technical problems connected with sample collection, handling, and analysis (e.g. sample contamination, instrument sensitivity, etc.) could also have been contributing factors, although some workers suspect that dubious estimates of Hg fluxes have more to do with a lack of representative analytical data than with poor-quality data (Geological Society of Canada, 1995). One very important point made by Hudson *et al.* (1995) may be relevant here and is worth emphasising: Anthropogenic Hg emissions into the atmosphere amount to about 40% of the total according to their calculations (see table, above), *but there are grounds for thinking that an additional 20% comes from past anthropogenic emissions being reemitted from the land and oceans*. Consequently, much of the "natural" flux may actually consist of anthropogenic Hg undergoing recycling.

As may be surmised from the disparities in the estimates put forward by different workers, none of the calculated values of the global Hg emissions can be regarded as exact; at best they are rough approximations. Nevertheless, important and fundamental inferences may be drawn from these data. It must be emphasised that in spite of the wide differences between the absolute values of the Hg emissions as estimated by different investigators, all data sets are essentially in agreement to the extent that they support the following major conclusions: (1) thousands of tonnes of anthropogenic as well as natural Hg are introduced into the Earth's atmosphere every year, the amounts having been estimated from actual measurements; and (2) the anthropogenic and natural emissions are of comparable magnitude (not counting the data of Weiss *et al.* (1971)), the anthropogenic component being on the order of 30-60% of the total. From the standpoint of our inquiry into the significance of long-range atmospheric transport of Hg and the relative importance of the anthropogenic and natural components of airborne Hg, the fundamental agreement between the various data sets is of greater interest and relevance than the differences.

Another matter related to the modelling of Hg emissions should be mentioned. As the reader may have noticed, the work of Jaworowski *et al.* (1981) is not represented in the table. The reason for this omission is that their data do not include estimates of total natural and total anthropogenic Hg emissions. Jaworowski *et al.* estimated the total flux to the atmosphere as 190,000 tonnes/yr (based on glacier ice for the years 1950-1978) and the total flux of particulate anthropogenic Hg as 11,000 tonnes/yr, but such information alone is not sufficient for the purposes of this review.

It should also be noted that published estimates of the natural Hg emissions to the atmosphere have been reviewed in a recent report issued by the Geological Survey of Canada (1995) (see Figure 3 in the report). Regretably, however, the following remarks have to be made about their treatment of the subject: (1) The global Hg emission into the atmosphere according to Jaworowski *et al.* (1981) (190,000 tonnes/yr) is incorrectly designated as the "natural" emission. In fact, it is the total emission and therefore undoubtedly includes a substantial anthropogenic component. (2) The natural Hg emission according to Weiss *et al.* (1971) is recorded as 150,000 tonnes/yr. In reality, this is only the highest value in a wide range of possible values (25,000-150,000) calculated by Weiss *et al.* (see table above). (3) The value of the natural Hg emission which was adopted by Lindqvist *et al.* (1991) is treated as an independent estimate. In truth, as Lindqvist *et al.* stated in their monograph, this value was derived directly from Nriagu (1989) (see table above). The number calculated by Nriagu was 2,500, and Lindqvist *et al.* simply rounded it off to 3,000.

II. SPATIAL VARIATIONS IN Hg CONCENTRATIONS AND FLUXES.

1. Systematic long-range variations in the concentrations of Hg and associated airborne pollutants, and measurements of Hg fluxes, in terrestrial and aquatic environments.

1.1 Scandinavia. A number of different, independent sets of data representing various environmental compartments, including vegetation, show the existence of a distinct north-south Hg gradient in Scandinavia, with high Hg levels in the south and low levels in the north (Johansson, 1985; Iverfeldt, 1991; Johansson *et al.*, 1991; Lindqvist *et al.*, 1991; Steinnes and Andersson, 1991; Rognerud and Fjeld, 1993; Iverfeldt *et al.*, 1994; Steinnes, 1994). Moreover, measurements of the dynamics of atmospheric Hg demonstrate that winds are carrying Hg into the region from European sources to the south (Lindqvist *et al.*, 1991), and Hg in rain is correlated with a number of well known air pollutants (Iverfeldt, 1991; Lindqvist *et al.*, 1991). Scandinavian - especially Swedish - investigators have accumulated a large mass of evidence establishing the importance of long-range atmospheric transport of anthropogenic Hg to Scandinavia; and their achievement is all the more convincing because it demonstrates agreement between many different kinds of data. More specifically, the evidence is as follows:

-Hg concentrations in precipitation grade from higher in the south to lower in the north. This applies to Norway and Denmark as well as to Sweden (where the most detailed Scandinavian research seems to have been done) (Lindqvist *et al.*, 1991). Although the distribution of Hg in Sweden is roughly comparable to the distribution of point-sources of Hg pollution within Sweden, a detailed examination reveals that the correspondence is actually rather poor; and the occurrence of a north-south gradient throughout Scandinavia, not just in Sweden, demonstrates that the gradient is not primarily the result of local pollution. The fact that the prevailing winds in that part of the world blow from southwest to northeast, and the presence of major heavily industrialised, densely populated sources of air pollution in European countries to the south and southwest of Scandinavia, together with results of "trajectory analysis" which reveal south-to-north movement of airborne Hg over Sweden, strongly support the conclusion that most of the Hg was transported into Scandinavia by winds from sources of pollution in other European countries.

-In Norway and Sweden the north-south gradient described above is reflected in Hg data for soil organic matter, moss, peat bogs, and lake sediment cores as well as rain water (Johansson, 1985; Iverfeldt, 1991; Johansson *et al.*, 1991; Lindqvist *et al.*, 1991; Steinnes and Andersson, 1991; Rognerud and Fjeld, 1993; Iverfeldt *et al.*, 1994; Steinnes, 1994). In sediment cores from Swedish lakes Hg is generally highest at the top and decreases downward, but the proportion of surface Hg to the background Hg at deeper horizons is much higher in the south than in the north. High Hg levels in soil humus sampled in central Norway has been attributed to local natural (i.e. geological) sources, and high levels in southeastern Norway have been blamed on local chlor-alkali plants; nevertheless, the general south-to-north gradational decrease in Hg across Norway and Sweden is regarded as the result of long-range atmospheric transport. It is extremely unlikely that the simple pattern of south-to-north gradational decrease in Hg levels observed in natural environments throughout Scandinavia could have been produced by geological sources of Hg in such a geologically diverse and complex region: At the most, one would expect natural Hg from geological formations to produce a more patchy pattern, with anomalously high environmental Hg levels (if any) occurring only in certain isolated, unevenly distributed localities (Evans, 1986; Painter *et al.*, 1994), as in central Norway, not the large-scale regional gradient described above. Nor do there appear to be any grounds for believing that natural emissions upwind from Scandinavia caused such a gradient, whereas major sources of air pollution are *known* to be located in areas which, during the greater part of each year, are situated upwind from Scandinavia; and, as discussed in the next paragraph, Hg in Swedish rain samples is *known* to correlate with typical air pollutants generated by the burning of fossil fuels.

-Hg levels in rain water collected in Sweden correlate with concentrations of other airborne pollutants, including soot, sulphate, acids, Cd, and Pb (Lindqvist *et al.*, 1991). This constitutes further evidence that the Hg introduced into Sweden by atmospheric circulation is largely anthropogenic; and the soot, sulphate, and acids, in particular suggest that combustion of fossil fuels (which is known to be a major contributor to atmospheric Hg pollution in general (Nriagu and Pacyna, 1988; Pacyna and Keeler, 1995) is the principal cause of the airborne Hg problem in Scandinavia.

1.2 Canada and the United States. Nater and Grigal (1992) and Nater *et al.* (1992) reported that Hg concentrations in surface soil and forest litter tend to increase along a transect running from northwestern Minnesota to eastern Michigan - i.e. toward sites of more intensive industrialisation and greater density of sources of pollution (e.g. Detroit). Paralleling the gradient in Hg levels were comparable gradients in wet sulphate deposition and Pb, Cd, and S concentrations. Furthermore, estimated background Hg from geological sources did not show this tendency, and subtraction of background Hg from the total Hg revealed an even more striking gradational west-to-east increase. The observed regional trend is clearly a result of atmospheric Hg emanating from sources of pollution east of the field area, not from natural sources.

There are indications that the situation in Canada is similar to that in Scandinavia. Thus, radioactively dated cores from lakes in Arctic and subarctic regions of Canada far from any industrial sources of pollution show surface enrichment in Hg (see below) and decreasing concentrations with depth, strongly suggesting atmospheric pollution from distant sources as a result of the combustion of fossil fuels (Lockhart *et al.*, 1994). This interpretation is strongly supported by the presence of a near-surface concentration of polycyclic aromatic hydrocarbons, which are combustion products. Similar Hg profiles have been recorded for "pristine" lakes in Alaska (Engstrom *et al.*, 1994). Centres of intense industrial activity in the U.S.A., southern Canada, Europe, and Asia are the likely sources of Hg and other air pollutants deposited in the North (Pacyna and Keeler, 1995).

As in Scandinavia, the uppermost sections of cores from lakes in the Boreal forest zone of northern Québec showed Hg enrichment suggesting a temporal increase in deposition (starting about 1940) because of atmospheric pollution (Lucotte *et al.*, 1995). But, unlike the Scandinavian data, Hg concentrations in the Hg-enriched surficial sediment (normalised with respect to background Hg in the deeper layers or with respect to organic C) showed no correlation with latitude; yet Pb data normalised with respect to organic C showed a definite gradational decrease toward the north (as with Hg in Scandinavia). The reason for this discrepancy is unknown. Since the Hg was deposited far from the industrial sources of pollution where it is thought to have originated, Lucotte *et al.* speculated that the atmospheric Hg over northern Québec is mainly in the form of Hg^{o} vapour and submicron aerosols which have a long residence time in the atmosphere, with the result that Hg is deposited evenly over a wide area of the continent. This may be true, but it remains to be determined why there is a distinct south-north Hg gradient in Scandinavia but not in Québec.

Direct measurements of Hg fallout from the atmosphere have confirmed the indirect evidence obtained from lake sediment cores. As part of a research project on the dynamics and mass balance of Hg in a remote seepage lake in northern Wisconsin, Fitzgerald *et al.*(1992) performed direct measurements of Hg in air, rain, and snow collected over the lake surface or on the shore of the lake using ultra-clean protocols. Their results showed that the Hg concentrations and atmospheric inputs were similar to those observed in the open ocean regions of the northern hemisphere. But, on computing the mass balance of Hg for the lake, they found that the measured total annual rate of atmospheric Hg deposition readily accounted for the total mass of Hg in the fish, water, and sediments of the lake. They concluded that airborne Hg makes up an important part of the Hg introduced into lakes and lacustrine organisms of the temperate zone.

In summary, the results of lake core analysis, soil and forest litter analysis, and direct measurement of Hg fluxes together with mass balance calculations all support the conclusion that long-range atmospheric transport of Hg has had a significant impact on lakes and terrestrial environments; furthermore, the evidence from cores, soils, and forest litter, including the the association of the Hg with other common air pollutants generated by combustion of fossil fuels, implies that air pollution accounts for much of the Hg input. Thus, in North America, as in Scandinavia, the convergence of quite different, independent lines of evidence all pointing in the same direction makes a far stronger case than any one class of evidence by itself.

1.3 Long-range atmospheric transport of Hg to the ocean. Mason *et al.* (1994) estimated that about 90% of the Hg in the ocean has come from wet and dry atmospheric deposition. In a study of the distribution of gaseous Hg in the air overlying the Atlantic Ocean, Slemr and Langer (1992) found that the Hg levels were considerably higher in the heavily industrialised Northern Hemisphere than in the less industrialised Southern Hemisphere; moreover, Hg levels in the Northern Hemisphere increased from the equator to higher latitudes (from 0° to 60°). Besides demonstrating long-range atmospheric transport of Hg, these results suggest that the Hg was mainly anthropogenic. In general, atmospheric trace element emissions and fallout are known to be much higher in the Northern Hemisphere than in the Southern Hemisphere because most of the world's industrial activity is concentrated in the Northern Hemisphere (Nriagu, 1992).

III. VARIATIONS IN Hg LEVELS OVER TIME.

1. Hg levels in the atmosphere.

-In some instances, changes in the atmospheric transport of Hg have coincided with specific documented events altering the emission of Hg from distant sources, or suspected sources, of the pollution. Thus, Iverfeldt *et al.* (1994) reported that a drop in the concentrations of Hg in air and precipitation was observed in Sweden after the closing of Hg-emitting East German factories (especially chlor-alkali plants in the Halle-Leipzig-Bittefeld region) following the reunification of Germany. This constitutes strong evidence that considerable quantities of Hg introduced into the air from these factories had been polluting environments in Sweden as a result of atmospheric transport.

-The investigation of gaseous Hg in air over the Atlantic Ocean for the period 1977-1990 revealed a 1.46% increase per year in the Northern Hemisphere and a 1.17% increase per year in the Southern Hemisphere - rates of increase that are consistent with results of independent soil, peat bog, and lake sediment data (Slemr and Langer, 1992). These observations strongly suggest that anthropogenic rather than natural sources of Hg dominate the cycle of atmospheric Hg. As shown in lake cores and other data, they demonstrate that pollution has been increasing over time, and they also reflect the fact that industrial pollution has been more severe in the Northern than in the Southern Hemisphere.

2. Vertical Hg profiles in sediment, ice, and peat deposits.

2.1 Lake sediment cores. A large body of literature stretching back many years documents vertical variations in Hg concentration in cores of undisturbed fine-grained lake sediments collected from lakes situated in widely separated regions of the Northern Hemisphere (e.g. Scandinavia, Canada, and the U.S.A.) which have not been polluted by local point sources of Hg. Such cores typically show Hg enrichment in the uppermost (youngest) horizons, the Hg concentrations declining and finally levelling off with increasing depth (i.e. age). Absolute dating by means of radioactive isotopes such as ^{210}Pb has usually revealed that the Hg content of the sediment rose steadily and sharply after the onset of the Industrial Revolution (starting, in some cases, as late as the mid-twentieth century) and either continued to rise to the present day or peaked in the late

twentieth century and then started to come back down. The generally accepted interpretation of these core profiles is that they reflect temporal variations in Hg loading and that the Hg enrichment of the uppermost strata signifies atmospheric pollution originating in distant centres of industrial activity, whereas the relatively low Hg concentrations which are found deeper in the core, and which do not show any significant variation as a function of age, represent the natural background Hg.

Before inquiring into the validity of this interpretation, let us survey a few examples of core data on the assumption that the conventional interpretation is sound. In a separate section (no. 2.4) the case for concluding that the conventional explanation of the core profiles is indeed the correct one will be presented. In brief, the examples of lake core evidence are as follows:

-A series of cores taken from forest lakes along a transect from southern Sweden to the northern extreme of the country show a greater or lesser degree of Hg enrichment at the top of the core (Johansson, 1985; Lindqvist *et al.*, 1991). The degree of surface enrichment with respect to background Hg in deeper horizons is very high in the south and decreases gradationally toward the north (almost disappearing in the far north). These observations are in agreement with the results of a study conducted in Norway (Rognerud and Fjeld, 1993). From other kinds of data (see above) it is known that atmospheric Hg emanating from sources of pollution in European countries south of Scandinavia is transported across Sweden by the prevailing southwest-northeast winds, creating a north-to-south gradational increase in the severity of Hg contamination in the Swedish environment. There is little doubt, then, that the core data represent recent atmospheric Hg pollution; and there are no grounds for suggesting that the observed regional pattern seen in the cores is due to natural sources of Hg.

-Lockhart *et al.* (1995) collected cores from lakes in the Boreal forest zone (Northwestern Ontario) and widely separated areas in the Canadian Arctic (from Ellesmere Island to the Yukon), far from any known industrial source of Hg. Core slices were analysed for Hg and polycyclic aromatic hydrocarbons (PAH's) and were dated by means of ^{210}Pb and ^{137}Cs (the earliest recorded date being 1850 A.D.). In all cases in which ^{210}Pb declined exponentially with depth, as would be expected if little or no mixing had occurred, Hg content increased toward the top of the core (i.e. increased with decreasing age). The PAH's, which are anthropogenic combustion products of fossil fuels, showed similar profiles except that they commonly peaked below the sediment-water interface, whereas Hg continued to increase right up to the top. In a comparable study, Engstrom *et al.* (1994) found that ^{210}Pb-dated cores from two "pristine" lakes in Alaska showed a 2.5-fold increase in Hg content following the onset of industrialisation. The results of both of these studies lead to the conclusion that the Hg profiles were produced by deposition of airborne Hg emitted by distant centres of pollution in the temperate zone.

-Hultberg *et al.* (1994) reported that sediments in Swedish lakes known to be polluted by atmospheric deposition of Hg showed profiles indicating a large increase in Hg contamination from 1950 to 1980, after which the Hg levels decreased with time owing to a sharp decline in Hg emissions from East Germany following the reunification of Germany (see above). Moreover, the core sections showing increases in Hg content over time also show parallel increases in soot, acidity (inferred from diatom fossils), and Pb. These data prove beyond reasonable doubt that the Hg profiles represent trends in atmospheric deposition of anthropogenic Hg.

-Dominik *et al.* (1991) recorded the results of a very exact, high-resolution analysis of Hg profiles in ^{210}Pb- and ^{137}Cs-dated cores from Lake Geneva, Switzerland. As with the data of Lockhart *et al.* (1995), the ^{210}Pb measurements show a smooth, exponential decrease with depth and hardly any scatter as far back as the year 1890, testifying to uniform conditions of sedimentation and a relatively constant rate of sedimentation over a time scale on the order of 100

years; moreover, a ^{137}Cs maximum generated by nuclear bomb tests in 1964 strongly confirms the accuracy of the ^{210}Pb age scale. The Hg profiles reveal a gradual, progressive increase with decreasing age (i.e. decreasing depth), starting at the end of the nineteenth century and continuing until about 1950, when the Hg concentration rose sharply to a prominent maximum, which is ascribed to a pollution event; thereafter the Hg levels declined just as abruptly and tended to continue declining with decreasing age, but superimposed on this trend is a small secondary maximum with a ^{210}Pb date of 1973 which is attributed to a second pollution event that has actually been documented. As Rhone River sediments of the Alpine region have been subject to yearly monitoring since 1970, the 1973 Hg peak in the Lake Geneva sediments can be attributed, with confidence, to an important episode of pollution which is known to have occurred during the period 1971-1972 (Dominik *et al.*, 1991). The Hg content of the sediment decreases with distance from the mouth of the Rhone River, providing a further indication that the river is the source of the Hg pollution. Also note that the two buried Hg peaks appear to be unique to Hg, as other heavy metals do not show this pattern of variation (Dominik *et al.*, 1991).

-Other evidence for the deposition of airborne anthropogenic Hg in lakes far from the sources of pollution, causing surficial sediments to have anomalously high Hg levels with respect to the natural background levels in deeper strata, include Hg profiles in ^{210}Pb-dated cores from the Turkey Lakes (Northwestern Ontario) (Johnson *et al.*, 1986), ^{137}Cs-dated cores from lakes in southern Québec (Ouellet and Jones, 1983), and ^{210}Pb-dated cores from lakes in both northern and southern Québec (Louchouarn *et al.* (1993), as well as Hg and PAH profiles in cores from lakes in the Adirondack Mountains (New York) (Heit *et al.*, 1981), and Hg profiles in cores from lakes in south-central Ontario (Evans, 1986), north-central Wisconsin (Rada *et al.*, 1989), and both northern and southern Québec (Louchouarn *et al.*, 1993; Lucotte *et al.*, 1995). In these cases, a number of lakes show the typical decrease in Hg concentration with depth, although certain others vary rather erratically and show no consistent trend. A few of the Hg profiles show a buried Hg maximum, probably owing to a recent decrease in the rate of loading (Ouellet and Jones, 1983). The reasons for the erratic variations are unknown; assuming that sample contamination and analytical error can be ruled out, possible explanations include post-depositional mixing (e.g. by benthos), erosion by currents, and temporal variations in the composition or texture of the sediment or the rate of sedimentation (e.g. because of occasional intrusion of turbidites into the stratigraphic sequence (Dominik *et al.*, 1991)). In any event, such inconsistencies serve to warn us that not all fine-grained stratigraphic sequences in lakes are suitable for the study of temporal variations in Hg loading. Only cores from sites where there have been no major changes in the nature and deposition rate of the sediment over time, and no major post-depositional disturbance, can be relied upon. Consequently, it is necessary to be discriminating and cautious in the use of lake core data as records of temporal variations in Hg loading and to be aware of possible complications due to local conditions of sedimentation and post-depositional changes which may obscure the effects of Hg loading from the atmosphere. As pointed out by Lockhart *et al.* (1994), a smooth exponential increase in age (as determined, say, by ^{210}Pb analysis) with increasing depth in the core is probably diagnostic of an undisturbed sequence.

2.2 <u>Peat cores</u>. Peat deposits in ombrotrophic bogs are regarded as excellent media for the preservation of records of atmospheric deposition of heavy metals provided they are situated above the water table (Damman, 1978; Madsen, 1981; Urban *et al.*, 1990; Jensen and Jensen, 1991; Steinnes and Andersson, 1991). Cores from peat bogs have revealed Hg profiles similar to those of sediment cores from lakes; and, as with lake cores, there have been important differences in the results from different sampling sites, suggesting that local environmental and biological factors (e.g. the position and fluctuations of the water table, the growth of the plants from which the peat is formed, etc.) affect the vertical distribution of Hg and may mask, distort, or even obliterate any effects of temporal variations in Hg loading. As with lake cores, peat core data can be

used to investigate temporal variations in atmospheric loading, but caution and discrimination are required to avoid erroneous interpretations: It would be a serious mistake to assume that all Hg profiles in peat deposits are records of Hg loading, pure and simple. Let us consider the results of two independent studies conducted in Scandinavia:

-Madsen (1981) analysed a core from each of two widely separated ombrotrophic peat bogs in Denmark. The plants whose remains are the source materials of the organic deposits in such bogs are known to depend on atmospheric fallout for their nutrients, and, in adapting themselves to the bog environment, they have evolved the ability to retain heavy metals strongly (Madsen, 1981; Jensen and Jensen, 1991). The ages represented by the cores ranged from the middle or latter part of the eighteenth century (i.e. the beginning of the Industrial Revolution) to about 1980 according to ^{210}Pb dating (confirmed by ^{14}C dating of a subsample from one of the cores). The position of the water table was not recorded, but at both sites the ^{210}Pb age exhibited a very smooth exponential increase with depth, suggesting that there has been no significant post-depositional redistribution of heavy metals nor any radical variation in the conditions of deposition and peat formation. The Hg deposition rate (based on measurements of Hg content, bulk density, and age) showed a long-term increase from the middle or late nineteenth century to 1980 paralleling an increase in the estimated rate of Hg consumption in countries of the European Community based on independent data compiled by another worker. Superimposed on the trends observed in the cores are episodic short-term increases which could be due to natural causes (e.g. volcanic eruptions and elevated temperatures and increases in precipitation), but these fluctuations are not large enough to mask the overall temporal trend, which is attributable to pollution (Madsen, 1981).

-Jensen and Jensen (1991) estimated temporal variations in Hg deposition rates using ^{210}Pb-dated cores taken from six ombrotrophic peat bogs at widely separated localities in Norway and Sweden. The ages of the stratigraphic sequences represented by the cores fell in the range late eighteenth or early nineteenth century to 1988. Comparison of cores from different sampling sites revealed widely differing patterns of temporal variation in Hg deposition rate. At one extreme was a core from a bog at Øverbygd in the far north of Norway, which gave a particularly close approximation of the general pattern of variation that is so frequently seen in lake cores: a large maximum at the surface declining sharply and progressively with increasing depth. A secondary late nineteenth century peak, which also occurs in the Danish peat sequences described by Madsen (1981), is superimposed on this trend. Thus, in this case, as in the Danish core profiles, there is actually a zigzag pattern of temporal variation comprising a minor maximum in the late nineteenth century, declining to a minimum in the mid-twentieth century, followed by a steady increase to a major late twentieth century maximum. Ostensibly, the major increase toward the top of the sequence began about a century later at Øverbygd than in the Danish bogs, but the discrepancy may reflect uncertainties in the data rather than a real disagreement: Without more refined and detailed stratigraphic work it is not possible to tell exactly when the trend began in either case; and even if we had more refined data, the short-term fluctuations superimposed on the major trend would probably limit our ability to pinpoint the beginning of the trend. Lake cores profiles, too, differ among themselves in this regard, the trend beginning much earlier in some cases than in others (see above).

Diametrically opposed to the Øverbygd core profile was a core profile representing a locality in southern Sweden, where the Hg deposition rate was lowest at the <u>top</u> and increased with depth (Jensen and Jensen, 1991). Between these two opposite extremes were profiles of intermediate or less well defined character: in three of them there was a tendency for the Hg deposition rate to increase toward the surface, as in the Øverbygd core, but it was weakly developed or was partly overshadowed by other variations superimposed on the trend (e.g. by an anomalously high value near the bottom of the sequence in one of the cores). In one core there was no systematic change whatsoever with depth. These

highly inconsistent results suggest that environmental and biological variables have obscured or obliterated any record of atmospheric Hg loading except at certain favourable localities. As Jensen and Jensen (1991) recorded the depth of the water level at his sampling sites, there is some basis for determining whether remobilisation and loss beneath the water table has had a significant effect on the Hg profiles. Examination of the data of Jensen and Jensen suggests that the position of the water table has not caused appreciable mobilisation of Hg. In each case the Hg profile crosses the water table, and there is no indication of an abrupt change in the pattern on passing below that boundary. Thus, trends cross the boundary unaltered. Except at Øverbygd, the water table was 10-37 cm below the surface, placing it below the stratigraphic interval in which the upward increase, if any, occurs. The Øverbygd core is exceptional, because the water table was only 5 cm below the surface, lying just below the horizons where the Hg deposition rates (and total Hg concentrations) were highest, suggesting possible Hg depletion below the water table; however, the smooth downward decrease in Hg deposition rate, which begins above the water table, continues without apparent interruption or change in slope as it crosses the water table, coming to an end far below it. Thus, there is no discontinuity at the water table. It is conceivable that there were systematic errors in dating owing to depletion of ^{210}Pb below the water table (Damman, 1978; Urban *et al.*, 1990), but there is no definite indication that the position of the water level has had an appreciable effect on the Hg profiles in the peat cores. This is not surprising, as Hg is not only bound very strongly by humic matter (the main constituent of peat) but is preferentially associated with the higher molecular weight humic fractions, which are much less mobile than the lower molecular weight fractions (Jackson *et al.*, 1980; Jackson, 1989; Louchouarn *et al.*, 1993).

In summary, data for peat cores from ombrotrophic bogs tend to corroborate lake core data; but, as with lake sediments, Hg profiles of peat cores from different localities differ widely, probably owing to variations in local conditions and related variations in plant growth. Fluctuations in the water table and remobilisation of metals below it cause significant redistribution of metals in peat deposits (Damman, 1978; Urban *et al.*, 1990), but there seems to be no definite evidence that the position of the water table has had an appreciable effect on the vertical distribution of Hg. Whatever the causes of the site-specific variations, it would seem that some peat sequences are highly suitable for the measurement of temporal variations in Hg loading from the atmosphere whereas others are not; but in all cases one has to be alert to possible complications due to environmental and biological factors unrelated to Hg fallout from the atmosphere.

2.3 Ice deposits in Greenland and Antarctica. Undisturbed ice and snow deposits of great age, such as the Greenland and Antarctic ice caps, should, in theory, be excellent media for the preservation of a long-term record of Hg deposition from the atmosphere. Hg sealed in subsurface snow, firn, or solid ice is not subject to the diagenetic processes that may cause remobilisation in sediments (although Hg in surficial snow is subject to redistribution by melting and wind erosion). Therefore, if ice cores and lake cores were found to have similar vertical Hg profiles, the ice data would tend to validate the theory that the vertical variations seen in lake cores reflect variations in loading rather than diagenetic remobilisation. Unfortunately, however, research on Hg in ice-cap samples has yielded dubious results. A pioneering investigation of Hg in ^{210}Pb-dated samples taken at different depths in the Greenland ice cap revealed a vertical distribution of Hg similar to the typical profiles seen in lake cores, suggesting effects of recent atmospheric pollution (Weiss *et al.*, 1971). But soon afterwards Dickson (1972) and Carr and Wilkniss (1973) raised serious questions about the validity of the supposed temporal variation in Hg concentration, and subsequent research on samples of Greenland ice failed to confirm the original results, revealing no temporal trends whatsoever (Weiss *et al.*, 1975; Appelquist *et al.*, 1978). Research on Hg in Antarctic snow and ice has not been much more successful, as the results are considered suspect owing

to the likelihood that samples were contaminated despite the use of refined ultra-clean sampling techniques (Dick *et al.*, 1990; Sheppard *et al.*, 1991). Because of the extremely low Hg concentrations in the Antarctic and Greenland ice caps, the problem of contamination looms very large (especially in Antarctica, since the impact of Hg pollution has been greater in the Northern Hemisphere than in the Southern); consequently, technical difficulties constitute a major barrier to progress in this area of research. The suitability of snow and ice deposits for this kind of study - at any rate, the suitability of particular sampling localities - is another question that may have to be considered. More research, and possibly further technical advances, will be needed to obtain reliable information on Hg in remote ice fields.

2.4 The controversy over the meaning of lake core data: The case for accepting the conventional interpretation of Hg profiles. The following observations strongly support the conclusion that the typical Hg profiles seen in cores of lake sediments were caused by long-range atmospheric transport of anthropogenic Hg, not by post-depositional redistribution of Hg as suggested by Rasmussen (1994):

-A paper by Gobeil and Cossa (1993) on the geochemistry of mercury in the lower estuary of the St. Lawrence River has an important bearing on the lake core issue. Gobeil and Cossa analysed core slices not only for total Hg but also for dissolved Hg in pore water and Hg extractable with "hydroxylamine" (presumably hydroxylamine hydrochloride) and acetic acid ($NH_2OH{\cdot}HCl$/HAc), a reagent mixture of a type commonly used to extract "amorphous" Mn and Fe oxyhydroxides from sediments. The critical significance of this is that these three sets of data make possible a direct test of the hypothesis that the vertical distribution of Hg is controlled by diagenesis - an hypothesis that cannot be properly tested unless the composition of pore water is taken into account (J. Azcue, verbal communication). (Also note that although the data presented in this paper represent an estuarine environment, they demonstrate basic principles which are applicable to lakes.) As the work of Gobeil and Cossa (1993) is worth examining in detail, three of their diagrams are reproduced here. These diagrams illustrate the profiles for total Hg, pore-water Hg, and $NH_2OH{\cdot}HCl$/HAc-extractable Hg at one particular sampling site (Fig. 1). Total Hg forms a well-defined buried peak (Fig. 1A); pore-water Hg (Fig. 1B) shows a comparable distribution in the depth range 6-32 cm but a completely unrelated pattern of variation in the depth range 0-6 cm; and $NH_2OH{\cdot}HCl$/HAc-extractable Hg (Fig. 1C) varies independently of total Hg but shows a marked inverse relationship with pore-water Hg, especially in the upper half of the core. Also note that the total Hg is one to two orders of magnitude more abundant than the $NH_2OH{\cdot}HCl$/HAc-extractable Hg and about four to five orders of magnitude more abundant than the pore water. Also note that the range of total Hg values in the St. Lawrence estuary core studied by Gobeil and Cossa is similar to the range of values seen in some cores from remote lakes in both northern and southern Québec (Louchouarn *et al.*, 1993; Lucotte *et al.*, 1995).

The inverse relationship between $NH_2OH{\cdot}HCl$/HAc-extractable Hg and pore-water Hg demonstrates that some postdepositional redistribution of Hg has occurred as a result of dissolution of colloidal Mn or Fe oxyhdyroxides, with release of adsorbed or coprecipitated Hg into the pore water. However, comparison of the three diagrams (Fig. 1, a-c) proves that diagenetic remobilisation of Hg has affected only a very small fraction of the total sedimentary Hg. This conclusion is based on the following grounds: (1) The vertical profile of total Hg is distinctly different from the vertical profiles of the two Hg fractions ($NH_2OH{\cdot}HCl$/HAc-extractable Hg and pore-water Hg) which demonstrate effects of diagenesis; (2) neither $NH_2OH{\cdot}HCl$/HAc-extractable Hg nor pore-water Hg amounts to more than a tiny fraction of the total Hg; and (3) the total Hg maximum is below the surface instead of right at the surface, as would be expected if (as in the case of $NH_2OH{\cdot}HCl$/HAc-extractable Hg) the overall vertical distribution of Hg had been determined by diagenesis. In brief, the three sets of data prove conclusively that diagenesis has had no appreciable effect on the vertical

distribution of total Hg. Thus, the work of Gobeil and Cossa supports the view that Hg profiles in undisturbed cores primarily reflect temporal variations in Hg loading and that any alteration of the pattern of variation by diagenesis is negligible.

Lindberg and Harriss (1974) and Bothner *et al.* (1980) carried out comparable studies of total Hg and interstitial Hg in cores of estuarine sediment, although they did not take the oxide-bound Hg fraction into account. Like Gobeil and Cossa (1993), they found that the relationship between total Hg and interstitial Hg could be highly variable even within a single core, indicating that the two parameters often vary independently of each other. Thus, there were examples of positive and negative correlations between total Hg and pore-water Hg occurring in different segments of the same core, with the result that there was no significant overall correlation. In other cores, however, the profiles of total Hg and pore-water Hg showed weakly to strongly developed parallel trends throughout the length of the core. As in the system studied by Gobeil and Cossa, the vertical variation in total Hg content was probably determined almost entirely by the rate of Hg loading; apparently post-depositional remobilisation, as represented by the interstitial Hg, affected only a very small fraction of the sediment-bound Hg. Moreover, Bothner *et al.* (1980) observed, as did Gobeil and Cossa, that Hg was more soluble under anoxic conditions than in a well oxygenated environment, probably owing to release of the soluble species HgS_2^{2-} from anoxic sediment and the coprecipitation or sorption of Hg by FeOOH and MnOOH formed in the presence of dissolved O_2 (cf. Jackson, 1993). But in the environments studied by Lindberg and Harriss (1974), the Hg in the pore water was in the form of dissolved organic (probably humic) complexes, and their data suggest that the molecular size range of the humic matter determined the relationship between interstitial Hg and total Hg.

One other study could be mentioned for the sake of comparison with the work of Gobeil and Cossa. Louchouarn *et al.* (1993) examined vertical profiles of total Hg and citrate/dithionite/bicarbonate-extractable Fe oxide and other sediment constituents in cores from four widely separated lakes in Québec, although they did not include data for interstitial Hg. From their results they concluded that there was no indication of a strong tendency for Hg to be associated with Fe oxide. (Actually, it would be more correct to say that there was no *consistent* tendency, as two of the lakes showed no apparent correlation between total Hg and Fe oxide, whereas in the other two lakes inspection of the core profiles revealed a definite tendency toward positive correlation.) The authors inferred that there was either a lack of post-depositional remobilisation of Hg from Fe oxide or else remobilsation followed immediately by highly effective scavenging of the released Hg by other particulate binding agents - most probably organic matter. Analytical data for pore water would probably have helped to resolve the uncertainty regarding the processes controlling the distribution of Hg.

Unfortunately, the interstitial Hg and oxide-bound Hg fractions of sediments seem to have been neglected in most of the research that has been done on Hg in cores. Clearly there is a need for more work in this area - in particular, comparative studies of lakes - to determine how widely the conclusions based on the findings of Gobeil and Cossa (1993) are applicable to Hg in sediments.

-In Sweden cores have revealed a <u>buried</u> Hg maximum corresponding in time to an historical event which greatly reduced the emission of Hg by major sources of atmospheric pollution in Germany (Hultberg *et al.*, 1994). The fact that there was an increase in Hg concentration over time followed by a sudden reversal of that trend coinciding with an abrupt decline in Hg loading from an important known source of the atmospheric Hg pollution in Sweden makes a strong case for concluding that the Hg profiles record variations in the rate of Hg loading, not postdepositional alteration of the sediment. Equally persuasive evidence has been furnished by a study of high-resolution Hg profiles in very accurately dated cores which record the history of Hg pollution in Lake Geneva since the late nineteenth century (Dominik *et al.*, 1991). The Hg profiles reveal two distinct

buried Hg maxima attributable to pollution events in the Rhone River upstream from the lake. As the more recent of the two peaks was formed after annual monitoring of the Rhone had been initiated, it is possible to relate the peak to independently recorded events occurring in the river. Accordingly, Dominik *et al.* (1991) were able to establish that the Hg maximum in the lake sediment was formed immediately after a recorded episode of Hg pollution in the Rhone River. (Furthermore, Dominik *et al.* (1991) claimed that the two buried maxima in the Hg profiles were not detected in the profiles of other metals; this adds additional weight to the already compelling evidence that the Hg profiles in the core were shaped by temporal variations in Hg loading, not by diagenesis.)

Analogous examples of buried Hg maxima in cores have been reported for the Hg-polluted Wabigoon River system of Northwestern Ontario, in which a sharp reduction in the discharge of Hg from the point source of pollution (a chlor-alkali plant) led to a decline in the rate of Hg deposition in the river and a riverine lake; as a result, cores collected several years later showed Hg concentrations rising toward the top of the core, peaking, and then coming back down (Jackson and Woychuk, 1980; Rudd *et al.*, 1983). Striking examples of buried Hg maxima have also been observed in the west basin of Lake Ontario, and they have been ascribed to a decrease in Hg loading from the Niagara River (Mudroch, 1983). Similarly, dated cores from two lakes in southern Québec show buried Hg maxima tentatively attributed to a decrease in total particulate emissions from coal-fired power plants (Ouellet and Jones, 1983). In the same cores Pb increases steadily from deeper levels right up to the sediment-water interface, possibly owing to continuing pollution from cars (Ouellet and Jones, 1983). The marked difference between the Hg and Pb profiles casts doubt on the hypothesis that such core profiles are controlled by diagenesis but is entirely consistent with the view that they are controlled by the rate of loading. Furthermore, cores from lakes in Minnesota and Wisconsin (in contrast to certain lakes in Alaska) show a buried Hg maximum suggesting a regional decline in atmospheric Hg pollution (whereas global Hg pollution, which is thought to be represented by the Alaskan cores, has not declined) (Engstrom *et al.*, 1994).

-The suite of Swedish lake cores showing a north-to-south gradational increase in the degree of surface enrichment in Hg with respect to the background Hg deeper in the cores (Johansson, 1985; Lindqvist *et al.*, 1991) strongly supports the conclusion that the core profiles represent a geographic trend in the severity of pollution. An exactly analogous series of cores from the west basin of Ontario has been described by Mudroch (1983); her data show a progressive decrease in the intensity of a buried Hg maximum with distance northwest from the mouth of the Niagara River, which had introduced the Hg into the lake. But because of the pattern of currents in the lake (which are known independently from other studies) no gradational decrease in Hg away from the source of pollution is seen in cores taken north and northeast of the mouth of the river (Mudroch, 1983). Thus, there can hardly be any doubt that the core profiles reflect both temporal and spatial variations in the rate of Hg deposition, not diagenesis, and there is every reason to suppose that this applies to the Swedish cores as well. Furthermore, the inferences drawn from the Swedish core data have been confirmed independently by a wealth of other kinds of data, such as the geographical distribution of Hg, soot, acids, sulphate, and Pb in rain water, results of trajectory analysis, and Hg data for moss, peat, and soil organic matter (Lindqvist *et al.*, 1991; Steinnes and Andersson, 1991). Consequently, the weight of evidence overwhelmingly supports the conclusion that the core profiles represent a record of Hg loading and that the surface enrichment is a result of air pollution.

-Hg profiles in cores are comparable to the profiles of associated substances which, like Hg itself, are known to be diagnostic of air pollution caused by the combustion of fossil fuels. Thus, in cores from certain lakes in Sweden the tendency of Hg levels to increase toward the top correlated with similar trends in soot, Pb, and fossil diatoms indicative of acidic conditions (Hultberg *et al.*, 1994). Obviously, diagenesis cannot account for the distribution of soot and

diatoms. Furthermore, the correspondence between the vertical variations of all these sediment constituents, as well as the fact that atmospheric soot and strong acids and much of the Hg in the atmosphere have a common origin as products of fossil fuel combustion, strongly suggests that all the trends have a common cause. Therefore, the only plausible conclusion seems to be that air pollution, not diagenesis, accounts for the observed trend in Hg concentrations. By the same token, cores from remote areas (e.g. the Arctic) have revealed a progressive increase in both Hg and PAH's (which, like Hg, are products of fossil fuel combustion) toward the top (Lockhart *et al.*, 1994), implying that all of these substances were deposited as a result of long-range atmospheric pollution, and that the core profiles represent an increase in the rate of loading over time.

-Cores showing the typical surface enrichment in Hg and a progressive decrease in Hg with depth also show a parallel exponential decline in ^{210}Pb, demonstrating that there has not been appreciable postdepositional redistribution of trace metals by diagenesis or physical mixing or erosion (Lockhart *et al.*, 1994).

-The vertical variations in Hg deposition rate recorded for some ombrotrophic peat bog cores strongly resemble the Hg profiles of lake cores that show surface enrichment and a steady decrease in Hg with depth (Madsen, 1981; Jensen and Jensen, 1991), suggesting a common mechanism for both. The question then arises whether Hg deposited in peat is subject to remobilisation. Published data for certain metals other than Hg, including Pb and Zn, indicate that the metals are strongly immobilised in well drained peat hummocks above the water table but are mobilised and leached to a considerable extent below the water table (Damman, 1978; Urban *et al.*, 1990). In contrast, however, the Hg profiles in the peat cores described by Jensen and Jensen (1991) cross the water level without showing any sign of a discontinuity, suggesting that Hg is not subject to appreciable solubilisation below the water table. In view of the strong affinity of Hg for humic matter, especially the relatively insoluble higher molecular weight humic acid fractions (Jackson *et al.*, 1980; Jackson, 1989), it seems probable that Hg in peat is immobilised by humic acids, both above and below the water table.

-Hg is not highly susceptible to post-depositional remobilisation in lake sediments because it tends to be bound stongly by refractory organic matter such as humic substances (Jackson *et al.*, 1980; Jackson, 1989; Louchouarn *et al.*, 1993; Lucotte *et al.*, 1995). Hg is bound preferentially by the relatively insoluble higher molecular weight humic acids with respect to the more soluble lower molecular weight fulvic acids (Jackson *et al.*, 1980, 1982).

<u>Conclusions</u>. The weight of evidence provided by the many different kinds of data assembled independently by different investigators in different parts of the world strongly supports the following conclusions:

1. Thousands of tonnes of Hg are introduced into the atmosphere every year as a result of various human activities, especially the combustion of fossil fuels (notably coal) and incineration of solid wastes.

2. Substantial amounts of anthropogenic Hg are transported over vast distances by atmospheric circulation, resulting in pollution of natural environments thousands of kilometers from the points of origin. The abundance of anthropogenic Hg in the atmosphere is of the same order of magnitude as the abundance of Hg from natural sources. Thus, long-range atmospheric transport of anthropogenic Hg is a major global and regional environmental problem.

3. Anthropogenic Hg is accompanied by other products of fossil fuel combustion, including the acids responsible for "acid rain." It is important to bear this in mind when pondering the biological effects of the Hg and Canada's position on the UN ECE protocol, because the associated acids interact with Hg and organisms in poorly buffered freshwater environments in ways that are not yet understood, causing substantial increases in the concentrations of methyl Hg in fish. Thus, effects of associated pollutants as well as the Hg itself must be taken into

account in the investigation of biological impact of Hg pollutions.

4. The evidence available to date militates strongly against the hypothesis that Hg profiles in lake sediment cores are determined primarily by diagenetic redistribution of the Hg. A minute amount of postdepositional redistribution does occur, but its effects on the overall distribution of Hg appear to be neglible. Different lines of evidence support the conclusion that vertical Hg profiles in fine-grained, undisturbed lake sediments primarily reflect temporal variations in Hg loading, provided that the sediment texture and composition and the rate of deposition have not changed drastically over time.

5. Atmospheric Hg pollution is an international problem that must be dealt with by reducing or eliminating emissions. The Geological Survey of Canada are right to insist, with Rasmussen (1994), that natural sources of Hg be taken into account in the study and modelling of Hg pollution and the biogeochemical cycling and environmental effects of Hg; but there is ample proof in the literature that environmental scientists have been doing this all along as a matter of course.

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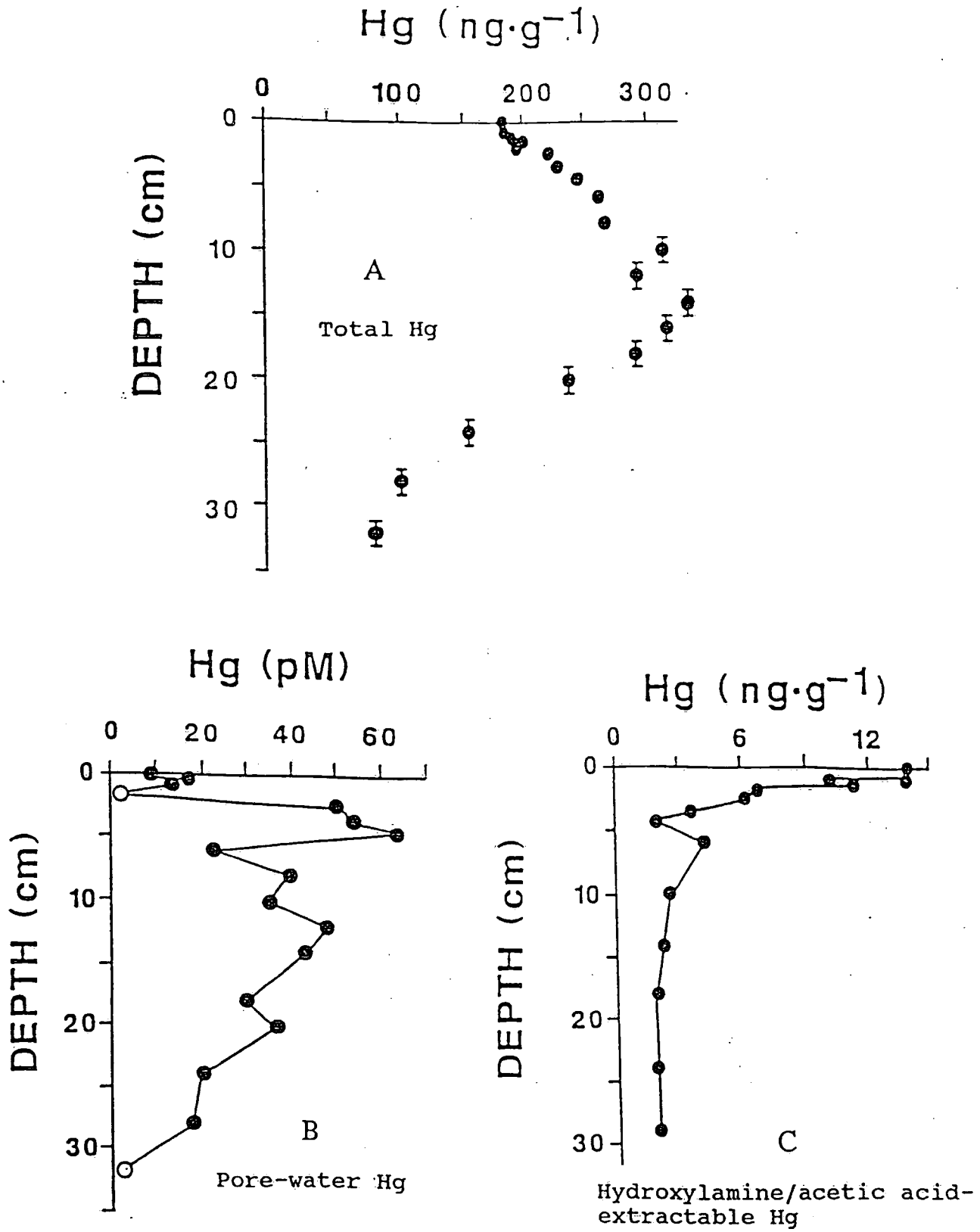

Fig. 1. The vertical profiles of (A) total Hg, (B) pore-water Hg, and (C) hydroxylamine/acetic acid-extractable Hg in sediments at a site in the Laurentian Trough (data from Gobeil and Cossa, 1993). The two white symbols in Fig. 1B represent concentrations below the detection limit. (Note: Presumably "hydroxylamine" stands for hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$), a widely used reagent for extracting "amorphous" oxides and oxyhydroxides of Mn and Fe.)

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NATIONAL WATER RESEARCH INSTITUTE
P.O. BOX 5050, BURLINGTON, ONTARIO L7R 4A6

Environment Canada Environnement Canada

Canada

INSTITUT NATIONAL DE RECHERCHE SUR LES EAUX
C.P. 5050, BURLINGTON (ONTARIO) L7R 4A6