

Concentration and annual accumulation values of heavy metals in lake sediments: Their significance in studies of the history of heavy metal pollution

Ingemar Renberg

Department of Ecological Botany, Umeå university, S-901 87 Umeå, Sweden

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Abstract

The first part of the paper discusses the significance of using either concentration or accumulation values for expressing the results of investigations of lake sediment cores aimed at studying the history of heavy metal pollution. Neither the values for heavy metal concentration in the lake sediment, whether expressed per gram dry sediment or per gram soluble (organic) sediment, nor the values for their total annual accumulation per unit area of the lake bottom, can, on their own, provide an accurate picture of past pollution conditions, but when considered in combination they render a fairly reliable and detailed interpretation. The second part of the paper deals with Pb, Cd and Hg analyses of cores of varved sediments from several lakes in N. Sweden. Pb and Cd pollution increased during the second half of the 19th century. In most lakes, Hg pollution seems first to have started during the 20th century. Marked increases in both concentration and accumulation of heavy metals took place during the 20th century. For recent decades, the estimated accumulation rates of heavy metals from anthropogenic sources are: Pb $0.5\text{--}1.5 \mu\text{g cm}^{-2} \text{yr}^{-1}$, Cd $15\text{--}30 \text{ng cm}^{-2} \text{yr}^{-1}$ and Hg $1\text{--}2 \text{ng cm}^{-2} \text{yr}^{-1}$. Higher values were recorded in lakes affected by local emissions.

Introduction

Environmental pollution by heavy metals from mining activities, from industrial and domestic effluents, and from the combustion of fossil fuels, has been much discussed during recent decades. In attempts to estimate the pre-industrial, natural level of heavy metals and to study the historical development of environmental pollution, several different types of naturally-occurring biological and geological records have been analysed (reviews in MARC Report 31). Lake sediments have frequently been used (see e.g. Alderton in MARC Report 35: 1–95). In most cases, the sediment cores have been divided up into consecutive, often half or centimetre-thick samples, which have then been analysed and the results of the heavy metal analyses expressed simply in terms of the dry weight of each sediment sample, e.g. as μg metal per gram dry sediment. This may be a rather imprecise way of expressing the results

for the purpose of ascertaining the history of pollution. A more reliable way is often to express the results on the basis of the content of the organic or acid-soluble fraction of the sediment sample. An alternative approach to the problem is to estimate the net annual accumulation of the heavy metal on the lake bottom, e.g. as the annual accumulation per cm^2 . This method, however, presupposes use of an adequate core-sampling and sub-sampling technique and the possibility of establishing a detailed dating for the sediment core. The present paper discusses: (i) the advantages and disadvantages of using either concentration or accumulation values for expressing the results of investigations of lake sediments aimed at studying the historical course of environmental pollution, and (ii) the history of lake pollution by lead, cadmium and mercury in N. Sweden. Analyses of cores from varved lake sediments, form the basis for these discussions.

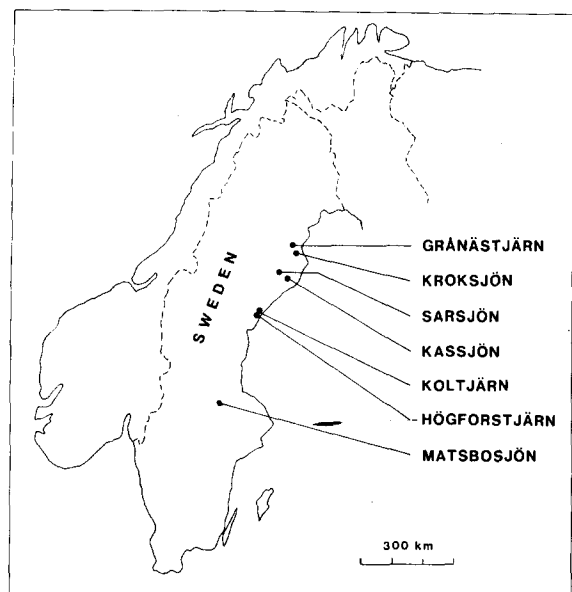


Fig. 1. Map showing the location of the investigated lakes.

Material and methods

In a varved lake sediment (annually laminated sediment) the material deposited on the lake bottom during the course of a single year is preserved intact, no subsequent mixing with the older, underlying, sediment occurring. Each year's deposit is clearly distinguishable and the samples are easily dated by making varve-counts. The type of varved sediment dealt with here has been described in detail in a previous paper (Renberg, 1981a).

Cores of varved sediments, spanning recent centuries, were taken with a crust-freeze sampler, a method which yields undisturbed cores of the unconsolidated surface sediments by freezing the material *in situ* (Renberg, 1981b). The cores were sampled and analysed in 1979 (except Koltjärn which was sampled in 1983). Pre-historic sediment samples from two lakes, taken with a Russian peat corer, have also been analysed.

Consecutive samples, each comprising a known number of years and representing a certain area of the lake bottom, were cut from the frozen cores. Each core extended from the sediment-water interface to 20–30 cm. The sampling and subsampling techniques used have been described in detail elsewhere (Renberg, 1981b, 1985).

Each sediment sample was dried, weighed, and then boiled in a mixture of conc. HNO_3 and HClO_4 , or HNO_3 and a little 4% KMnO_4 -solution. The latter method, used for Hg, broadly follows that described by Håkansson (1975). After wet oxidation each sample was centrifuged and the supernatant used for the heavy metal analyses. Mercury was determined by flameless spectroscopy and lead and cadmium by AAS (graphite furnace). The residue, mainly composed of mineral grains and diatom valves, was carefully washed, dried and weighed. This fraction is termed the 'insoluble' fraction of the sediment. The 'soluble' fraction of each sample is the value given by the difference between the initial dry weight and the dry weight of the insoluble fraction. The soluble fraction consists of organic material and various acid-soluble precipitates such as iron hydroxides.

Results and discussion

As an introduction to the discussion about the reliability of concentration and accumulation values when attempting to ascertain the heavy metal pollution history of an area, the results of analyses of the lead and soluble and insoluble sediment in a core from Lake Gränästjärn are presented in detail. Subsequently, the course of lead, cadmium and mercury pollution of the northern Swedish environment, as indicated by the results from varved sediments from several lakes, is discussed.

Lake Gränästjärn

The annual accumulation rates of both the soluble and insoluble fractions of the lake sediment in any lake vary from year to year, as well as fluctuating over longer periods of time. This is particularly true in recent times, when there has been a great increase in human influence on the lakes and their surroundings, but it is also a natural phenomenon. This has been clearly revealed by studies of varved lake sediments (Segerström *et al.*, 1984; Simola *et al.*, 1984). Ditching, ploughing, road construction, and changes in forestry practice etc, have all resulted, from time to time, in increases in the influx of allochthonous organic and inorganic material to the lakes. The inflow of both agricultural and sewage effluents has led to increases in lake productivi-

ty. These factors have led to changes in the basic composition of the sediments deposited during the past century which have, in turn, affected the concentrations and accumulation rates of heavy metals.

In Lake Grånästjärn, the accumulation of mineral material reached its maximum during the 20th century, with two pronounced peaks, one covering a period of years in the early 1900's and a second around 1940 (Fig. 2b). Both these peaks were due to an artificial lowering of the lake water-level and to ditching operations. The lead content per gram dry weight of the sediment samples from both these periods are the lowest recorded throughout the entire core (Fig. 2c). The reason for this is not that lead pollution of the lake was unusually low during these two periods, but that greater quantities of mineral grains were deposited on the lake bottom, producing a diluted lead content when expressed per gram dry sediment. It is obvious that, since the mineral matter accumulation has varied markedly with time, any results of heavy metal analyses expressed in this manner will yield a false impression of the history of lead pollution in the area.

A second and more reliable picture of the history of lead pollution is obtained when the lead analysis results are expressed in terms of the soluble fraction of the sediment samples (Fig. 2d). But this picture is only valid if no major fluctuations in the annual influx of allochthonous material have taken place, that the lead concentration in this allochthonous

material has always remained constant and, furthermore, that lake productivity has also remained constant. In the case of Lake Grånästjärn, as in most lakes, none of these requirements is fulfilled. For example, the peak in the accumulation of soluble sediment during the period 1930–38 was caused both by a lowering of the lake water-level and by drainage of an adjacent peatland. The latter activity, in particular, must have led to an increased influx into the lake of old organic material, probably with a lower lead content than the contemporaneous material being deposited, and can be expected to have produced a spurious decrease in the lead content when the values are expressed per gram soluble sediment. The same effect could also have been produced by a slight increase in the annual accumulation rate of the autochthonous organic material caused by increased lake productivity. This is because the major part of the lead influx into the lake is derived from atmospheric fall-out, which either accumulates in particulate form, becomes bound to particles suspended in the lake water which is then deposited on the lake bottom, or becomes bound to the allochthonous organic matter. Thus any increase in the amount of autochthonous organic matter or non-polluted allochthonous organic matter in the sediment will result in the dilution of the atmospheric flux of a heavy metal as recorded in the sediment column.

The third way of expressing the results of the lead analyses (Fig. 2e), in terms of its annual accumula-

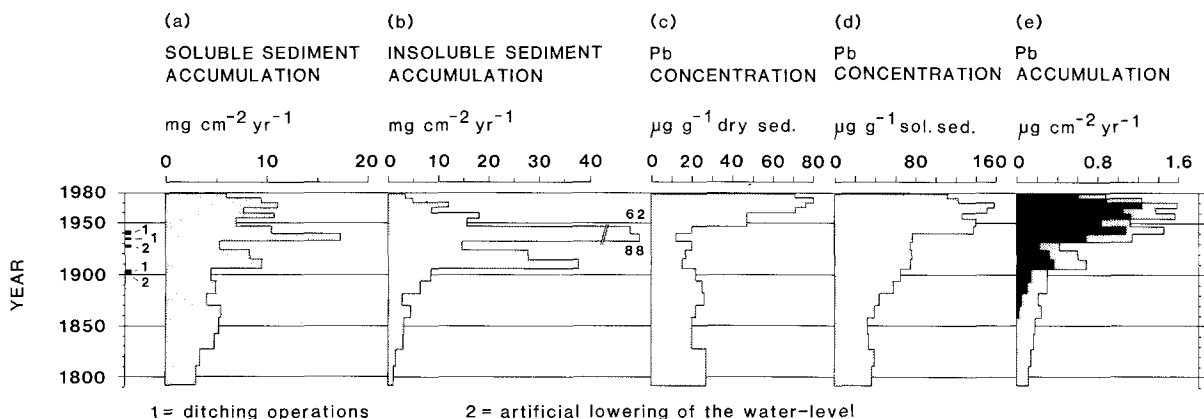


Fig. 2. Results of analyses of a varved lake sediment core from Lake Grånästjärn, N. Sweden, showing: accumulation of soluble sedimentary material, mainly organic matter (a), accumulation of insoluble sedimentary material, mainly mineral matter (b), lead concentration in dry sediment (c), lead concentration in acid-soluble dry sediment material (d) and accumulation of lead on the lake bottom at the sampling site (e). The estimated anthropogenically derived proportion of the total lead accumulation, is shown in black.

tion per unit area of the lake bottom, is independent of any variation in the accumulation rate of the autochthonous organic material, providing that the lead influx to the lake is in the form of direct deposition of particulate lead from the atmosphere, or as lead bound to allochthonous material. However, the accumulation rate of lead will be affected by any variation in the influx of allochthonous material. Any increased accumulation of organic material, such as the above-mentioned peaks which were recorded during the periods 1900–1920 and 1930–38, involves a certain extra accumulation of lead, as shown in Fig. 2e, even when the allochthonous material itself has a very low lead concentration. Values for this naturally-derived lead accumulation cannot be calculated accurately, since the lead concentration in the allochthonous material is unknown. However, for each analysed sample of the core from L. Grånästjärn, a rough value for the natural lead accumulation per cm^2 and year can be obtained by multiplying the ac-

cumulation rate of soluble sediment by what is presumed to be its normal background (pre-industrial) lead concentration (here a mean value from analyses of pre-1850 sediment has been used). A reasonable value for the anthropogenically derived proportion of the annual lead accumulation can then be calculated (Fig. 2e).

To sum up, neither the lead concentration values, expressed per gram dry sediment or per gram dry soluble sediment, nor the total annual lead accumulation values per unit area of the lake bottom, are able, on their own, to provide an accurate picture of the history of lead pollution. But when considered together they enable a fairly reliable and detailed interpretation of the lead analysis results to be made.

Without considering any changes in the lead content of the sediment with time due to mobility and diagenetic processes, the conclusions about lead pollution in the Grånästjärn area that can be drawn from these results are: (i) The lead deposi-

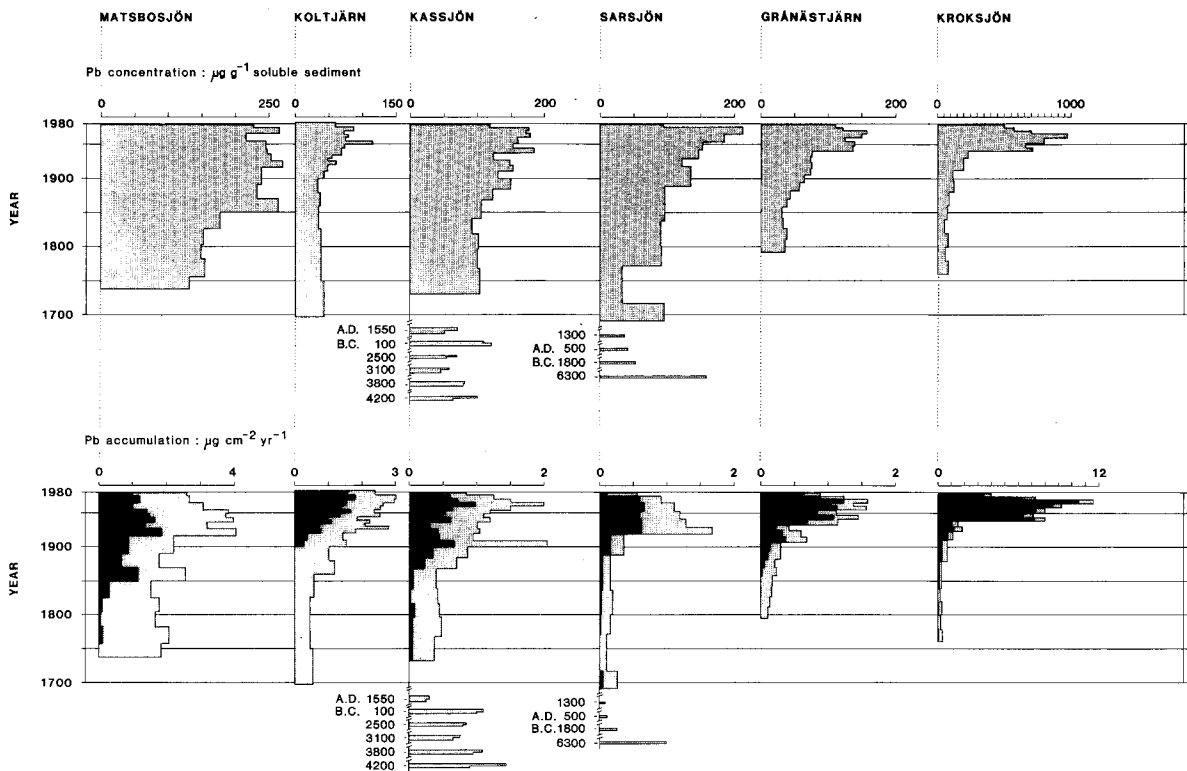


Fig. 3. Results of lead analyses of varved sediments from six Swedish lakes showing: lead concentration in acid-soluble dry sediment (above) and lead accumulation on lake bottom (below). Anthropogenic proportion of lead, shown in black.

tion from anthropogenic sources increased during the later half of the 19th century. A marked increase in the volume of lead in the environment took place between some time in the 1930's and about 1970, whereafter there are signs of a reduction. (ii) Compared to pre-industrial times, the lead concentration in the soluble sediment fraction had doubled by 1900, and quadrupled by 1970. The lead accumulation increased from $0.2 \mu\text{g cm}^{-2} \text{yr}^{-1}$ to a maximum value of $1.6 \mu\text{g cm}^{-2} \text{yr}^{-1}$, of which about $1.2 \mu\text{g cm}^{-2} \text{yr}^{-1}$ is supposed to have been derived from anthropogenic sources. The estimated accumulation values during the late 1970's have declined to below $1 \mu\text{g cm}^{-2} \text{yr}^{-1}$.

Other lakes

Results of analyses of lead, cadmium and mercury in the samples of varved sediments taken from L. Grånästjärn and six other lakes are shown in Figs. 3, 4 and 5.

Both the lead concentration and accumulation values clearly indicate that an increase in lead pollution began in N. Sweden as early as the second half of the 19th century (Fig. 3). Pb curves rised during the 20th century, but with a slight decline being visible during the past few years in most lakes. In all the lakes, the concentration of lead in the soluble sediment fraction has at least doubled between the beginning of the 19th century and the middle of the 20th. During the same period, in most lakes the annual lead accumulation rate per unit area of the lake bottom has increased 2–5 fold, or even more. This was due to increases in the deposition of both organic-bound lead from natural sources and of anthropogenically derived lead. The anthropogenic lead accumulation values for the past few decades lie between 0.5 and $1.5 \mu\text{g cm}^{-2} \text{yr}^{-1}$, except in L. Kroksjön, where values about ten times higher were recorded.

The volume of cadmium deposited in the lakes also increased during the 19th century and has con-

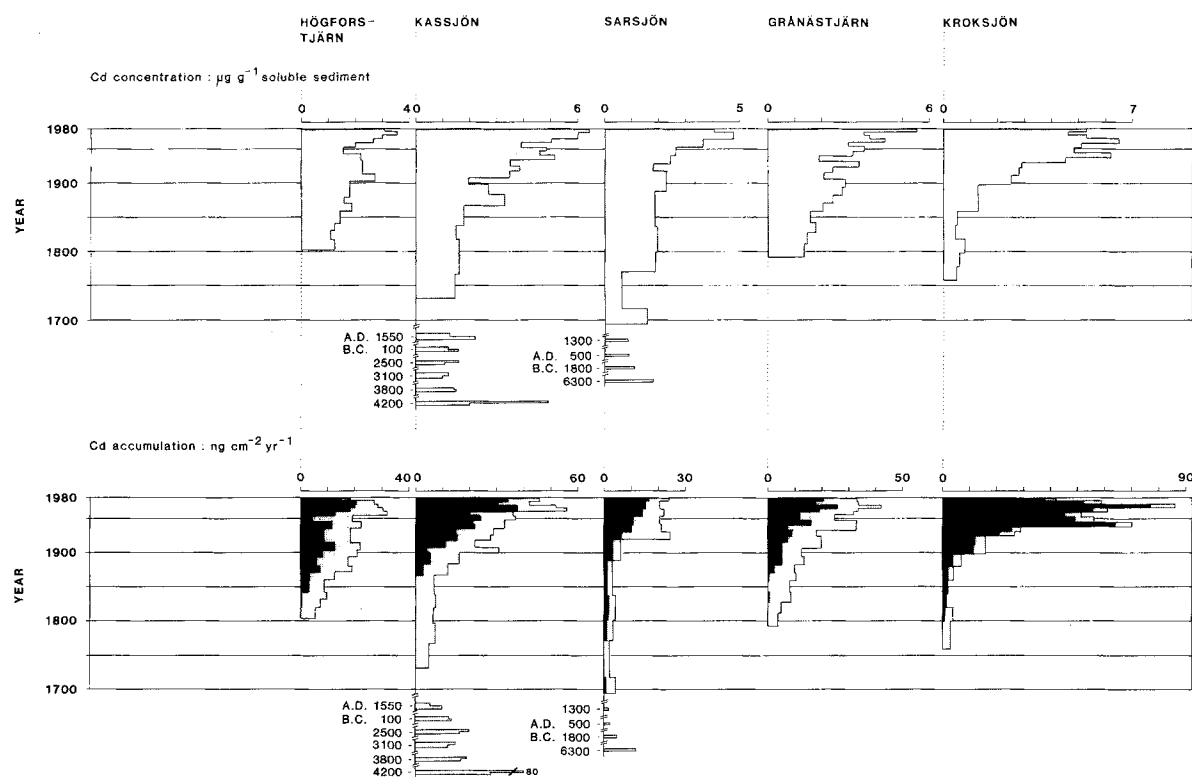


Fig. 4. Results of cadmium analyses of varved sediments from five Swedish lakes showing: cadmium concentration in acid-soluble dry sediment (above) and cadmium accumulation on lake bottom (below). Anthropogenic proportion of cadmium, shown in black.

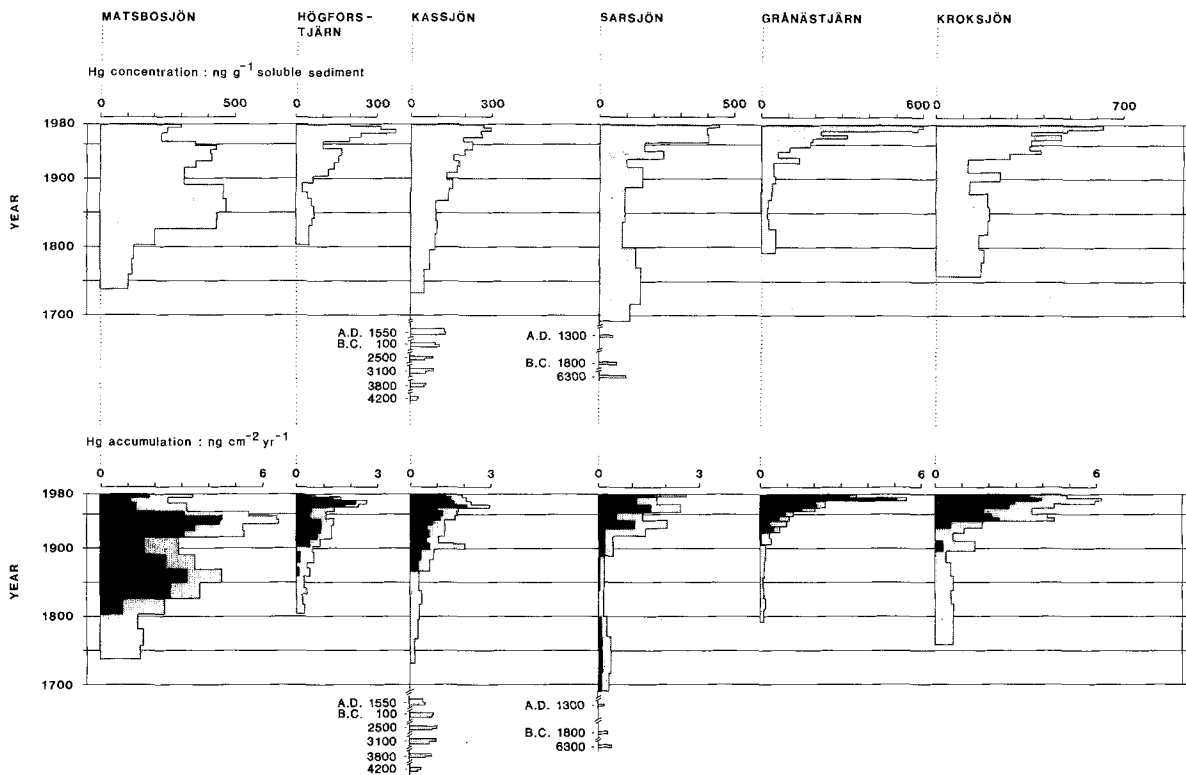


Fig. 5. Results of mercury analyses of varved sediments from five Swedish lakes showing: mercury concentration in acid-soluble dry sediment (above) and mercury accumulation on lake bottom (below). Anthropogenic proportion of mercury, shown in black.

tinued to increase up to the sampling year (1979), except in L. Kroksjön (Fig. 4). The recent values for cadmium per gram soluble sediment are about three times higher than the values for the 18th and early 19th centuries (in L. Kroksjön ten times higher). The increase in the annual accumulation rate of cadmium during the same period of time has been, on average about fivefold, and by an even greater factor in L. Kroksjön. The anthropogenic cadmium accumulation rates during the past few decades have been 15 to 30 $\text{ng cm}^{-2} \text{yr}^{-1}$ in four of the lakes, and slightly higher in L. Kroksjön.

Mercury pollution seems to have started later than the pollution by lead and cadmium (Fig. 5). No significant increase in either the mercury concentration in the soluble sediment fraction, or in the accumulation rate of anthropogenically derived mercury occurs until some time during the present century, although L. Matsbosjön forms an exception, showing high mercury values during the 19th

century. Recent values for mercury concentrations in the soluble sediment are 4–10 times higher than those recorded in 18th and 19th centuries. The annual accumulation rates of mercury have increased 2–10 fold. The anthropogenic mercury accumulation during the past few decades has varied from 1 to 2 $\text{ng cm}^{-2} \text{yr}^{-1}$ in four of the lakes and from 3 to 5 $\text{ng cm}^{-2} \text{yr}^{-1}$ in L. Grånästjärn and L. Kroksjön.

Accumulation of heavy metals in lake sediments during the 19th century probably increased as a consequence of an increase in the fall-out of airborne pollutants, due to the progressive industrialisation of Sweden and Europe. Increased deposition, during the 19th century, of carbonaceous particles characteristic of fossil fuel combustion, has also been recorded in the sediments of L. Grånästjärn and L. Koltjärn (Renberg & Wik, 1985). The marked increase in the accumulation of heavy metals in the lakes during the 20th century is consistent with the known development of industry and with the increased combustion of fossil fuels,

although domestic and agricultural sources within the lake catchment areas also may have contributed to these increases.

The high 19th century value for mercury, and perhaps also that for lead, in L. Matsbosjön may indicate an early onset there of heavy metal pollution. This is a very likely explanation, when it is considered that this lake is situated in an old mining district.

The lakes Kroksjön and Grånästjärn are also almost certainly affected by local emissions of heavy metals, both lakes being situated not very far from a large-scale smelting works, which utilize complex sulphide ores rich in lead, cadmium and mercury. The initial establishment of this industry, during the 1930's, is detectable in the sediments, particularly in L. Kroksjön, which lies in one of the prevailing wind directions from the works. The reduction of lead and cadmium emissions into the atmosphere during the 1970's is also clearly recorded in the sedimentary record.

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