ENVIRONMENTAL RECORDS OF CARBONACEOUS FLY-ASH PARTICLES FROM FOSSIL-FUEL COMBUSTION

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ABSTRACT

Fossil fuel combustion produces fly-ash particles that are released into the atmosphere and deposited in the environment. A particularly characteristic kind of fly-ash is spheroidal carbonaceous particles. They are composed of an amorphous carbon matrix in which other elements are dispersed. The elemental carbon content makes them very resistant to chemical degradation and these particles can be relatively easily extracted from sediment and soil samples using a method described in this thesis. The distribution of spheroidal carbonaceous particles in lake sediment profiles, surface sediments and forest soils has been studied.

Cores from several Swedish lakes have been analysed and, although the lakes are from different parts of the country, consistent trends in the deposition of the carbonaceous particles have been found. The analyses of dated cores show that the carbonaceous particle deposition in the sediments follows the same general pattern as statistics for Swedish coal and oil combustion over the last two centuries. This indicates that the sediment records reflect the history of the atmospheric deposition of particulate pollutants from fossil fuel combustion.

Analysis of surface sediment samples provides an integrated picture of the deposition over the preceding few years and can be used to indicate the contemporary geographical pattern of deposition from the atmosphere. Two sets of surface sediment samples (0-1 cm) were analysed. One comprised samples from 66 lakes around Sweden's second largest city, Gothenburg, and showed very high carbonaceous particle concentrations within a distance of 50 to 100 km from the city. The second set comprised surface sediment samples from 114 lakes distributed all over Sweden. This survey of Sweden demonstrated a geographical north-south gradient with more than a hundred times higher particle concentrations in the south than in the north. This distribution is similar to the distribution of other air pollutants (data obtained from a moss survey and an air monitoring program) and suggests that carbonaceous particles in palaeolimnological investigations of air pollution, can be used as tracers for pollutants that are otherwise difficult to determine in lake sediments.

Spheroidal carbonaceous particles also accumulate in soils, and forest soil samples can be used for geographical surveys of particle deposition. In Swedish podzol soils the particles mainly accumulate in the thin organic horizon and concentrations in this layer reflect the total deposition since industrialisation, although most will have been deposited during the last few decades.

Since the spheroidal carbonaceous particle record in Swedish lake sediments has a characteristic temporal pattern, carbonaceous particle profiles can be used for indirect dating of recent sediment cores. Analyses of multiple sediment cores from three lakes demonstrate that carbonaceous particles can also be used for studies of sediment distribution in lake basins. Results from Gårdsjön indicate that the acidification of the lake changed sediment distribution processes from a normal sediment focusing regime to a more even distribution of sediments over the lake bottom. Liming of the lake seems to have restored normal sedimentation processes.

Key words: Carbonaceous particles, soot, anthropogenic particles, oil and coal combustion, fossil fuel combustion, lake sediments, lake acidification, forest soils, historical monitoring, atmospheric pollution monitoring.

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- III Wik, M., Renberg, I. & Darley, J. 1986. Sedimentary records of carbonaceous particles from fossil fuel combustion. *Hydrobiologia* 143: 387-394.
- IV Renberg, I. & Wik, M. 1985. Carbonaceous particles in lakes sediments - pollutants from fossil fuel combustion. *Ambio* 14: 161-163.
- V Wik, M. & Natkanski, J. 1990. British and Scandinavian lake sediment records of carbonaceous particles from fossil-fuel combustion. *Phil. Trans. R. Soc. Lond. B* 327: 319-323.
- VI Wik, M. & Renberg, I. 1991. Recent atmospheric deposition in Sweden of carbonaceous particles from fossil-fuel combustion surveyed using lake sediments. *Ambio* 20: 289-292.
- VII Wik, M. & Renberg, I. 1987. Distribution in forest soils of carbonaceous particles from fossil fuel combustion. *Water Air Soil Pollut.* 33: 125-129.
- VIII Wik, M. & Renberg, I. 1991. Spheroidal carbonaceous particles as a marker for recent sediment distribution. *Hydrobiologia* 214: 85-90.

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DISSERTATION MAY 1992

DEPARTMENT OF ECOLOGICAL BOTANY
UNIVERSITY OF UMEÅ

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INTRODUCTION

The natural environment has been affected and changed by human activities to varying degrees since ancient times. With the industrialisation, however, mans activities and pollution have become global in scale. Today environmental issues such as acidification, climate change and contamination by toxic substances are frequently discussed. Anthropogenic emissions into the atmosphere have major impacts on the global and regional cycles of many elements. Fossil-fuel combustion is a major, sometimes even the most important, anthropogenic source for several atmospheric pollutants, e.g. SO₂, NO_x (OECD 1990), CO₂ (Henderson-Sellers 1984) and several heavy metals (Nriagu & Pacyna 1988, Pacyna & Münch 1991).

The environment has an extraordinary ability to accumulate pollutants and increased loading may not be reflected by gradual environmental changes. On the contrary, the effects can be disguised until the ecological system is severely damaged. Often the environmental problem is not observed until this late point, after which monitoring programs are initiated. In this context the lack of historical data are often a crucial drawback. Fortunately, there are natural historical archives such as aquatic sediments, peat, permanent ice sheets and tree rings which can provide information about the past. Among these, lake sediments have become, perhaps, the most important tool for retrospective monitoring. One example, where lake sediments have been very useful, is for the study of lake acidification. Analyses of e.g. diatoms, pollen, chemical substances and carbonaceous particles have provided valuable information about pH changes as well as about the causes for recent acidification (Battarbee et al. 1988, Charles & Whitehead 1989, Battarbee et al. 1990, Charles et al. 1990a, Renberg & Battarbee 1990, Norton & Kahl 1991).

There are several reasons for using lake sediments for retrospective analyses. They are available in most areas, the sampling procedures are reasonably simple and long time-series covering several thousands of years can be obtained. Most lakes have non-laminated sediments which usually are dated by radiometric methods such as ¹⁴C, ²¹⁰Pb and ¹³⁷Cs (Olsson 1986). In certain lakes, varved (annually laminated) sediments can be obtained, that allow exact dating and easy and reliable calculation of net annual accumulation values of various sediment components (Segerström & Renberg 1986). So far, however, varved lake sediments have only been frequently found in northern Fennoscandia and North America (O'Sullivan 1983, Anderson et al. 1985).

However, recent lake sediments are part of the living environment and the sedimentary deposits are liable to post-settlement changes. In ordinary, non-laminated sediments the record is affected by mixing, e.g. by bioturbation and currents, a problem reduced in varved sediments. Additionally, chemical

compounds to a varying extent are liable to transformation and mobilisation in both the water column and the sediment (Livett 1988, Norton et al. 1990, Nelson & Campbell 1991). In fact, pollutants such as NO_x and CO_2 , well-known to have severe impact on the environment, do not leave any reliable records. For sulphur the deposition processes are so complex that for some lake sediments no reliable pollution trends can be found and comparison between different kinds of lakes are difficult (Mitchell et al. 1988, Giblin et al. 1990, Norton & Kahl 1991). It is therefore of great interest to find tracers that are chemically stable. Such a tracer is fly-ash particles that can be used for the historical monitoring of atmospheric deposition of pollutants from fossil-fuel combustion.

The major anthropogenic source of particulate matter in the atmosphere is coal and oil combustion (Goldberg 1985). The quantity, chemical form, size distribution and shape of the emitted particles are dependent on many parameters, such as the amount of inorganic contaminants in the fuel, type of combustion process used, air-to-fuel ratio, residence time and temperature in the combustion zone, and emission control devices.

As much as 90% of the particles generated from high temperature combustion of both oil and coal are spheroidal (Cheng et al. 1976, Shen et al. 1977, Del Monte et al. 1984), a character rarely produced by natural combustion processes. Fly-ash from coal and oil combustion is dominated by different types of particles. Carbonaceous particles constitute an overwhelming portion of the oil fly-ash. They are generated from incompletely burnt oil drops (Peterson 1972, McCrone & Delly 1973), and a vast majority (90 %) of the carbonaceous particles are spheroidal (Shen et al. 1977, Bacci et al. 1983, Del Monte et al. 1984). Coarse carbonaceous particles are also emitted during coal combustion but they only constitute a minor part of the fly-ash (Del Monte & Sabbioni 1984, Griest & Harris 1985) and as they are generated from incompletely burnt irregular coal fragments, only part of these particles obtain a spheroidal shape. The rest remain irregular, resembling particles generated from wood combustion. Fuel coal typically contains 2 to 30% of incombustible mineral material (McElroy et al. 1982) while the mineral content of oil is much smaller, only 0.02-0.08% (Hamilton & Jarvis 1963). Because of the high content of mineral impurities, considerably more particles are generated from coal combustion, and the coal fly-ash is dominated (60-90 %) by spherical particles with an aluminosilicatic glassy matrix (Fisher et al. 1978, Raask 1980, Del Monte & Sabbioni 1984).

Coarse spheroidal carbonaceous particles, which are the focus of this thesis, are composed of an amorphous carbonaceous matrix in which other elements are dispersed. Major elements in particles from oil combustion are S, V, and minor elements are Al, Si, Na, Mg, K, Ca, Fe, Cu (Bacci et al. 1983). In coarse carbonaceous particles from coal combustion the major element is S, and minor elements are V, Al, Si, Ca and K (Del Monte & Sabbioni 1984). The coarse carbonaceous spheres are characterised by a porous surface and many

internal cavities. This gives the particles a density much lower than would be expected if calculated from their inorganic composition (Gay et al. 1984, Raeymaekers et al. 1988). For the same reason these particles have a very large surface area (Raask 1981, Del Monte et al. 1984).

When discussing the picture of particulate emissions from oil and coal combustion it is necessary to mention another type of carbonaceous particles. These are sub-micrometer sized, formed in the gaseous phase by incomplete combustion or by thermal decomposition of hydrocarbons, and often aggregated to form chain like structures (Medalia & Rivin 1982). However, the presence of sub-micrometer sized carbonaceous particles in sediments and soil is beyond the scope of this thesis.

There is no standard terminology concerning carbonaceous particles and the many terms in use are confusing. Names such as carbonaceous particles, carbonaceous cenospheres, coky matter, charcoal, elemental particulate carbon, black carbon, oil soot or just soot have been used. The term carbonaceous particles is frequently used but it has a wide definition, which sometimes includes organic particles. Soot is also a common expression, mostly referring to the sub-micrometer sized particle fraction but occasionally including larger particles as well. The lack of a standard terminology is also reflected in this thesis. "Soot particles" or "soot spheres" were used in papers I, II and IV, changed to "coarse carbonaceous spheres" in papers III and VII, and lastly modified to "spheroidal carbonaceous particles", for convenience shortened to SCP in papers V, VI and VIII.

The elemental carbon matrix of SCP makes them very resistant to chemical degradation. These particles can withstand high temperature treatment, acids, bases and organic solvents. When deposited in sediments, peat and forest soils they are preserved and these materials can be chemically treated in such ways that the particles can be quantified.

OBJECTIVES

The papers included in this thesis describe and discuss how the SCP record in sediments and soils can be used to study fall-out from fossil-fuel combustion, and additionally as a tool for sedimentological studies and dating of sediment cores. The aim was to:

- * develop a simple method for the analysis of SCP.
- * establish relationships between SCP records in lake sediments and historical trends in fossil-fuel combustion.

- * assess whether the SCP content in surface sediment samples could be used to survey the geographical distribution of recent particulate fall-out.
- * test the hypothesis that forest soil samples also could be used for surveys of fall-out.
- * demonstrate that the historical SCP pattern can be used as an indirect dating tool for recent sediment profiles.
- * assess whether SCP can be used as a tool for studies of sedimentation processes in lakes.

REVIEW AND DISCUSSION OF PAPERS I-VIII

PREPARATION AND ANALYSIS METHODS

Goldberg and colleagues were the first to highlight the occurrence in lake sediments of carbonaceous particles from fossil-fuel combustion (Griffin & Goldberg 1979). For the extraction of elemental carbon from sediment samples they used a technique developed by Smith et al. (1975), however, slightly modified to be able to handle sediments with larger amounts of organic material (Griffin & Goldberg 1975). In short, dried sediment was ground and passed through several steps of chemical treatment with KOH, H₂O₂, HCl, and HF. The residue was primarily composed of pyrite, anatase, rutile, zircon and elemental carbon. Infrared spectroscopy was used to determine the amount of elemental carbon in the residue, and results were expressed as per cent carbon g⁻¹ dry mass. This technique was applied on a sediment core from Lake Michigan (Goldberg et al. 1981, Griffin & Goldberg 1981, 1983). They also used light and scanning electron microscopy to examine individual carbonaceous particles produced during the combustion of coal, oil and wood. They found that morphologies, structures and surface textures were indicative of the combustion process and these characters were used to distinguish between particles from different sources (Griffin & Goldberg 1979, 1981).

In Sweden, Renberg & Hellberg (1982) found large amounts of carbonaceous particles in acidified lakes. It was, however, necessary to develop a new method for the analysis, because the infrared technique by Smith et al. (1975) requires very large sediment samples (10 g dry sediment). From recent sediment profiles close-interval sub-sampling is often desired, and it is also advantageous if a single core can be used for several different analyses e.g. SCP, metals, diatoms and pollen. Enough sediment for the infrared method can, therefore, not be obtained using standard sediment coring equipment. Moreover, the infrared method determines the total amount of elemental carbon and if the sediment

contains large amounts of charcoal from forest fires, which is rather common in many Swedish lake sediments, the pattern of anthropogenic carbon may be blurred.

We tried to develop a robust method that only needed small amounts of sediment, was reasonably fast and simple, not requiring expensive or sophisticated instruments (paper I). This method has also been used for soil samples (paper VII). The method, revised slightly, is summarised here. About 0.1 g dry sediment, is oxidised with 32% H_2O_2 at $+55^\circ\text{C}$ to remove organic matter. This step usually takes about four days, but for sediments with very high organic contents it takes longer, up to two weeks. When oxidation has finished, the residue which mainly consists of mineral grains, diatoms and carbonaceous particles, is washed with distilled water. The water suspension is carefully homogenised and small aliquots poured into glass Petri dishes. The water is allowed to evaporate slowly, and then the number of SCP counted under a stereo microscope at $\times 50$ magnification. SCP larger than $5\text{--}10\text{ }\mu\text{m}$ can be identified. The detection limit is slightly variable, depending on the origin of the sedimentary material. For some sediments, and particularly for soils, high mineral grain contents and large amounts of dark minerals reduce the ability to identify the smallest spheres ($5\text{ }\mu\text{m}$). Hydrogen fluoride has been used occasionally to remove mineral matter. When hydrogen fluoride is used, however, a precipitate is formed sometimes, making the counting more difficult. Under the stereo microscope the SCP are black with a shiny lustre and should break easily when touched with a fine-tipped pointer. Other black particles with an appearance similar to SCP are not unusual, but these are much more difficult to disintegrate.

Recently, Rose (1990a) has developed a third method for carbonaceous particle analysis. His method, which digest not only the organic material but also most of the mineral matter, is a modified version of the method presented by Griffin & Goldberg (1975). Sub-samples of the residue are allowed to evaporate onto coverslips and the number of particles counted at $\times 400$ using a light microscope. The great advantage with this technique is the possibility to count particles down to $1\text{ }\mu\text{m}$. However, it is more difficult to identify the particles in the light microscope where the particles appear as dark one-dimensional objects. Under a stereo microscope, surface textures can be studied and if necessary there is a possibility of moving the particles so they can be observed from another angle.

SEDIMENT PROFILES

In the western, industrialised countries the use of fossil fuels has doubled several times since the beginning of this century, with the largest increase taking place since the Second World War (Statistical papers series J 1957-1976, Energy statistics yearbook 1989). In the beginning coal was the major fuel in Europe, but

in modern times the use of oil has increased tremendously. Whether oil has turned to be the major fuel is mainly dependent on the presence of domestic coal resources. In Great Britain, for example, coal is still the main fuel, while Sweden shifted from coal to oil after the Second World War (papers II and V).

Carbonaceous particle analyses of sediment profiles have been done in the USA, Sweden, Great Britain, Norway, Finland and Denmark. A common feature is the close resemblance between the carbonaceous particle pattern and the history of fossil-fuel consumption.

In the USA, cores from Lake Whitney (Bertine & Mendeck 1978), L. Michigan (Goldberg et al. 1981, Griffin & Goldberg 1981, 1983), Green Lake N.Y. (Kothari & Wahlen 1984), and recently from PIRLA-lakes (Charles et al. 1990b, Davis et al. 1990), have been analysed. These studies demonstrated an increasing elemental carbon (Bertine & Mendeck 1978, Goldberg et al. 1981, Griffin & Goldberg 1981, 1983, Kothari & Wahlen 1984) or particulate (Charles et al. 1990b, Davis et al. 1990) content in the most recent sediments, reflecting the increased use of fossil fuels during the 20th century.

The first Swedish sediment profile analysed for SCP was from Lake Gårdsjön, situated in S.W. Sweden, where high particle concentrations were found in the recent sediments (paper I). Moreover, there was an obvious stratigraphic correlation between the pH development as deduced from diatoms and the SCP pattern; the increase in SCP concentration was contemporaneous with the onset of severe acidification (Renberg 1984, Renberg & Wallin 1985), and the SCP pattern showed the same trend as the historical fossil-fuel combustion in Europe. Since then several Swedish lakes with non-laminated as well as varved sediments have been analysed. Results from studies of profiles have been published in papers I, II, III, IV and V. These profiles are, together with a profile published in Renberg & Hultberg (1992) and some unpublished results, presented in a summary figure (Fig. 1). One of the unpublished profiles is from the Baltic Sea.

With varved sediments, an absolute chronology can be established by varve-counting. When quantitative sub-sampling is performed (Renberg 1981, Segerström & Renberg 1986), reliable estimates of the annual accumulation of SCP can be calculated (number of particles $\text{m}^{-2} \text{year}^{-1}$). SCP have been analysed in three lakes with varved sediments; Grånästjärn sampled in 1979, Koltjärn in 1982 and Buvatten in 1981. The latter core was only analysed back to 1953 when varve formation began, while the analyses from the other two lakes go down to the latter part of the 18th century. The SCP diagrams from the varved lakes display several interesting features. The SCP fluxes (number of particles $\text{m}^{-2} \text{year}^{-1}$) show a remarkable resemblance with statistics for the Swedish consumption of oil and coal (see Fig. 4 paper III). Although both Koltjärn and Grånästjärn are situated in areas that were industrialised rather late, SCP accumulation had already begun during the 18th century. During the middle of the 19th century the accumulation rate slowly began to increase reflecting the increased use of coal following the

onset of industrialisation. A sudden increase of short duration took place during the 1930's, which probably reflects the increased industrial activity before the Second World War. The war resulted in a general economic recession, but was followed by a very rapid and stable increase in fuel consumption that is reflected also by the SCP accumulation in the sediments. Both the Swedish fossil-fuel consumption and the SCP accumulation, peak around 1970, before the so-called oil crisis (see Fig. 4 paper III).

When comparing fuel statistics and the sedimentary SCP record it is important to remember that the amounts and distribution of particles emitted from point sources have changed through time. Combustion techniques and emission controls have been improved and emission stacks built taller. If a lake is situated close to a large local source or there is an especially rapid industrial expansion in a region, that will, of course, modify the general SCP pattern. Lake Buvatten, for example, has been influenced by emissions from an oil fired power plant situated 22 km away. However, the combustion in the power plant peaked at the same time as the general Swedish fuel consumption. The abrupt increase in SCP accumulation about 1930 in Koltjärn might be an effect of local sources superimposed on the general pattern; an intensive expansion of the pulp industry took place in the region at that time.

As mentioned in the introduction, non-laminated sediments are to various degrees affected by mixing, such as bioturbation and currents. Despite these modifications, the profiles from Gårdsjön, Lysevatten, Lilla Öresjön, Örvattnet, Funäsdalstjärn, Mellersta Nässjön, Blåmissusjön and Njalakjaure display features characteristic of the SCP pattern in the varved lakes (Fig. 1 and papers I, III, IV and V). However, there are lakes where bioturbation, high sediment accumulation rates or variations in sediment accumulation result in a more indistinct pattern. In Stuvvikesjön and Omnesjön, the trend of increased fossil-fuel combustion followed by a recent decline is still clearly visible, but the fine features can not be recognised.

When comparing SCP profiles from the different lakes it should be noted that the cores have been taken in different years (Fig. 1). There is a 11 year difference between the first lakes, Gårdsjön and Grånästjärn, cored in 1979 and the latest, Njalakjaure, cored in 1990. This time discrepancy explains why the recent decline in SCP concentration seems to be more pronounced in some lakes. Generally, the "1970-peak" has higher concentrations in lakes from S. Sweden than from N. Sweden. Also the total amount of particles deposited per surface area through time is generally higher in southern Sweden than in northern Sweden. The SCP concentration in the profile sampled from the Baltic Sea had surprisingly high concentrations, comparable to lakes in industrialised areas of northern Sweden.

Round Loch of Glenhead situated in Galloway, Scotland, was the first British lake to be analysed (paper III). The SCP concentration in the surficial sediments of Round Loch of Glenhead is high compared to other British lakes and

about three times higher than surface concentrations in the most polluted Swedish lakes. Since the analysis of Round Loch of Glenhead, several other British lakes have been studied (Battarbee et al. 1988, paper V). As with Swedish sites, in Britain the SCP record follows the history of fossil-fuel combustion (Darley 1985, Rose 1990a, paper V). A few particles are present in sediment older than 1900, a sharp increase in concentration occurs at about 1940 and continues to the sediment surface. However, a slight reduction in surface concentration was observed in three lakes from northern Scotland (paper V).

The SCP profiles from Verevatn and Røyrtjörna were the first results published for Norway (Fig. 1, paper V). Lake Verevatn is situated in S. Norway in an area of high sulphur deposition whereas Røyrtjörna is situated in a clean area in central Norway, far from pollution sources. These differences are reflected in the SCP deposition profiles, the maximum particle concentration in the southern lake being about 35 times higher than in the northern. Two further lakes from S.W. Norway have been analysed by Birks et al. (1990). In these lakes the general increase in SCP concentration is clearly visible but the sediments do not display any recent decline in particle deposition as found at Verevatn and Røyrtjörna.

Analyses of SCP in sediment profiles from Finland have recently been published (Tolonen & Haapalahti 1990, Sandman et al. 1990). Tolonen & Haapalahti (1990) report an agreement between historically known consumption of coal and oil and the SCP stratigraphy in varved lakes.

Also in Denmark investigations of SCP have begun. Six lakes have been analysed so far and the SCP pattern in sediment profiles seems to be similar to the Swedish pattern (Bent Odgaard personal communication).

Finally, although it was not within the scope of my study it is of interest to mention that the content of mineral coal fly-ash particles in sediment profiles have been studied, both directly by counting particles (Rose 1990b) and indirectly by magnetic analysis (Hunt 1986, Oldfield & Richardson 1990). The magnetic properties of sediments are mainly controlled by inputs of magnetic minerals from the catchment, but in most cases an anthropogenic record can be successfully distinguished. Both methods have demonstrated increasing concentrations of mineral fly-ash in recent sediments.

SURFACE SEDIMENT

The differences in particle concentration between sediment profiles from different parts of Sweden gave the idea of using surface sediment samples to investigate geographical variations in the most recent deposition of SCP. In 1982 surface sediments were sampled from 66 lakes around Sweden's second largest city, Gothenburg. The resultant map clearly showed how emissions from Gothenburg increased SCP concentrations over a large area. However, when local background

Fig. 1 Diagrams showing spheroidal carbonaceous particle concentrations in sediment cores from thirteen Swedish and two Norwegian lakes, and one core from the Baltic Sea.

concentrations were reached, they were still very high compared to other parts of Sweden (paper IV).

These results initiated a large survey of recent SCP deposition covering the whole of Sweden (paper VI). Besides mapping the SCP distribution, the objective was to test whether SCP could be used as a general indicator for deposition of air pollutants from fossil-fuel combustion. In 1986 surface sediment samples (0-1 cm), i.e. material deposited over the last 5-10 years, were collected from 114 lakes distributed all over Sweden. Care was taken to choose lakes with a similar character: the lakes should be small, relatively deep headwater lakes with forested catchments and situated away from potential SCP sources. The resultant map showed a clear south-north gradient, with the most polluted southern areas having more than a hundred times higher SCP concentrations than clean areas in northern Sweden. When the SCP distribution was compared with the deposition pattern of other air pollutants, using data derived from a moss survey by Å. Rühling (Statens Naturvårdsverk 1987) and the Swedish air pollution monitoring network (Granat 1989), the similarities were obvious. There was a significant correlation between SCP and SO_4^{2-} , and SCP and Pb; both SO_4^{2-} and Pb are considered to be long-range transported pollutants. The SCP pattern also correlated to Swedish SO_2 emissions. Because SCP correlate both with distant pollutants and local emissions, it is not possible to determine to what extent the SCP distribution is influenced by regional and foreign sources respectively (see further discussion in "Concluding remarks"). However, the investigation demonstrated a clear similarity between the geographical distribution of recent SCP deposition and recent deposition of other pollutants in Sweden and indicated that SCP can be used as an indicator for fossil-fuel derived pollutants. A good relationship between measured SCP surface sediment fluxes and sulphur deposition has also been found in Scotland (N. Rose personal communication). Fly-ash particle analysis of surface sediments can contribute with important complementary information to air monitoring programs. While air monitoring is momentary and for economic reasons normally restricted to a limited number of sites, surface sediment samples give an integrated picture of the deposition and numerous sites are available, increasing the spatial coverage and resolution (paper VI).

SOIL

To test the hypothesis that soils could also be used for geographical surveys of SCP deposition, an investigation of the N. Swedish province of Västerbotten (55 430 km²) was made (paper VII). Samples were taken in old (> 100 years) stands of Scots pine (*Pinus sylvestris*), except for a few sites in the mountain region where only sub-alpine birch (*Betula pubescens* subsp. *tortuosa*) forest was growing. Analyses of test samples from podzol soil profiles had shown that the

SCP mainly accumulate in the thin organic horizon (horizons L-F according to Bridges 1986, in older literature and in paper VII called the A-horizon). Samples of the organic horizon with about 0.5 cm of the underlying minerogenic horizon (Ea-horizon), were collected from 164 sites. As SCP are resistant to degradation and the biological activity of Boreal forest soils in general is low, and the soil has a long turnover time, it is likely that the SCP concentration in soil (number of particles m^{-2}) reflects the cumulative deposition since industrialisation. However, the overwhelming amount of particles have been deposited since the Second World War.

The study area comprises both relatively densely populated coastal areas along the Gulf of Bothnia and the mountain wilderness along the Norwegian border. The province has 250 000 inhabitants of which about 50% live in two towns situated along the coast. Some samples that were collected rather close (3-4 km) to towns and industries appear as locally elevated values. More than 15×10^6 particles m^{-2} were found in the industrialised coastal areas and even in the remote mountain area a considerable number of particles were found ($> 0.2 \times 10^6$). The SCP soil distribution in the province, agrees well with the distribution of industry and population and the prevailing wind conditions. However, the main pattern of SCP distribution also agrees well with the distribution of long-range transported pollutants such as wet deposited SO_4^{2-} (Granat 1989) and metals such as Cd, Pb and Zn monitored in the snow pack (Ross & Granat 1986). Even though I believe that the SCP distribution reflects primarily the fall-out from local and regional emissions, the superimposed effect of distant sources cannot be excluded.

Without doubt this investigation demonstrates that soil samples are useful tools in geographical surveys of SCP deposition (paper VII). Soil samples, however, have both advantages and drawbacks compared to sediments. The sampling technique is so simple that it can be undertaken by inexperienced field assistants. The possible sampling sites are innumerable, making this technique very suitable for intensive studies of fall-out in restricted areas, i.e. around a point source. However, the large amounts of charcoal in soil make the SCP analysis demanding, and only the total historical deposition can be studied.

DATING

The SCP content of sediment profiles can be used as an indirect dating method for ordinary non-varved sediments. Two models have been developed. A prerequisite for SCP-dating is the establishment of a master profile, previously dated by independent dating methods or by comparison with emission statistics. The first model for SCP-dating is based on the identification of characteristic changes in the SCP pattern e.g. distinct increases or peaks (papers I and II). Today, SCP profiles have been analysed for many lakes in both Sweden and Great Britain, and

consistent trends in the SCP pattern have been found in both countries (paper V). In Sweden, potential dating points are the slight increase in the middle of the 19th century, the pre-war peak during the 1930's, the post-war increase about 1950 and the peak about 1970. In particular, the post-war increase and the peak about 1970 are very characteristic and can be identified even when the sediment records are blurred by mixing.

The second model for SCP-dating, which in theory makes it possible to derive continuous dates, is based on SCP deposition values (paper II). A prerequisite for using this model is that consecutive sediment samples, each representing a certain area of the lake bottom, are carefully sampled. Then the SCP deposition value is estimated at each level of the sediment core, expressed as cumulative per cent of the total SCP deposition during all times. These values must then be compared to a calibration curve, i.e. a diagram showing at which points in time certain cumulative percentages are reached. The calibration curve should be based on good local records of SCP deposition, obtained either indirectly from coal and oil combustion statistics or preferably, a SCP sediment profile dated by an independent dating method (varve counting, ^{210}Pb).

Indirect SCP-dating has been used in several investigations (papers I and II, Renberg & Hellberg 1982, Birks et al. 1990, Tolonen & Haapalahti 1990, Odgaard personal communication, Renberg & Wik 1989). Additionally, the SCP pattern has been used for correlation between cores from the same lake (Renberg & Hultberg 1992).

SEDIMENT DISTRIBUTION

Knowledge of sediment accumulation and the resultant sediment distribution in lake basins have important implications for the interpretation of palaeolimnological data and for lake geochemistry and biology. In paper VIII the hypothesis that SCP can be used to trace recent (since ca. 1950) sediment distribution in lake basins has been tested. The spatial SCP distribution was studied by multiple sediment coring of lake basins, the temporal accumulation of SCP was studied by sediment traps and a laboratory experiment was undertaken to study the redepositional behaviour of SCP.

Considerable temporal variations in input of SCP to the sediment was demonstrated by the sediment trap sampling, conducted in the dimictic lake, Lövösundet, N.E. Sweden. During the warm summer months the SCP deposition was low. A slight increase was recorded in the autumn when oil combustion increased. In the autumn the stratification in the lake water breaks down and resuspension of material from shallow areas is also taking place. Then with the onset of ice-cover, for about 6 months SCP accumulation in the traps was very low. SCP deposited from the atmosphere during winter, accumulated on the ice

and became aggregated with mineral and organic material. Trap results suggest that a lot of these aggregates melt through the porous spring-ice and settle rapidly just before the ice clearance, resulting in an extremely high SCP deposition rate. From the trap study, it can be concluded that in cold climatic regions, where lakes become ice-covered, considerable amounts of the total annual SCP accumulation take place during a short period in the spring. The temporal variation will be different in climatic regions with no or only a short period of ice-cover.

The redeposition experiment was made using a modified pipette method. Two tests were made, one with and one without a dispersing agent. Although, none of the tests were true reflections of natural conditions, they indicated that SCP settle in a similar manner as other fine inorganic and organic sedimentary components.

The spatial distribution of sedimentary SCP was studied in three small ($\leq 0.3 \text{ km}^2$), dimictic lakes. Gårdsjön and Stora Galten are situated close together in S.W. Sweden while Koltjärn is situated in N.E. Sweden. Multiple cores were collected, using a HON-Kajak corer (Renberg 1991), and the number of SCP m^{-2} was calculated (paper VIII). Core recovery represented at least the 20th century, but as the majority of SCP have been deposited since Second World War the results mainly reflect the post-war particle accumulation. In Koltjärn a total of 39 cores were sampled along transects from the northern half of the lake. In Stora Galten 12 cores were sampled along a profile from a well defined small basin. In both lakes there was a statistically significant correlation between particle accumulation and water depth. These results suggest that SCP and other fine sedimentary components had accumulated in the deep areas in accordance with the concept of sediment focusing (Likens & Davis 1975).

Gårdsjön, in contrast to the other two lakes, acidified during the 1950's and was limed in 1982. The original intention was to make a sediment budget for the post-war period of Gårdsjön using the SCP as a marker for the sediment distribution. Therefore, a total of 55 sediment cores were collected in 1982, before liming. Field observations of a clear gradation in the thickness of total post-glacial sediments, from shallow to deeper water, demonstrated that sediment focusing had occurred earlier. However, in the sediment core collection from 1982 we could not establish any correlation between SCP accumulation and water depth. The particles were more or less evenly distributed over the lake bottom. In agreement with our findings was an investigation of the distribution of soft surficial (0-2 cm) sediments done by Andersson (1985). He found soft sediment all over the lake bottom and fine-grained organic particles dominated even in shallow areas. Extensive bottom areas in Gårdsjön were at that time covered by a mat of filamentous algae and *Sphagnum* spp, a feature typical for acidified lakes in Sweden (Lazarek 1982, Grahn 1985). Andersson (1985) suggested that the normal sedimentation pattern was disturbed because of the rapidly growing filamentous algae and *Sphagnum* beds. The liming in 1982 severely reduced the abundance of

Sphagnum spp and filamentous algae, and the dead material started to decompose. In 1985, three years after liming, 30 new cores were sampled along the same profiles as in 1982. This time a significant correlation between SCP accumulation and depth was found for one of three profiles. In a second profile, some change, although not statistically significant, was observed. The results indicate that normal sedimentation processes had begun to work.

The results from Koltjärn, Stora Galten, Gårdsjön and the resuspension test demonstrate that SCP can be used as a marker to study recent sediment distribution. The contrasting sediment distribution in the acidified lake is probably caused by the trapping, incorporation and stabilisation of material by the *Sphagnum*-algae mat. This phenomenon has important implications for nutrient cycling, faunal habitats and surface-sediment processes. If the sediment distribution is disturbed similarly in all acidified lakes that have bottom growths of *Sphagnum* and filamentous algae, many lakes are affected.

CONCLUDING REMARKS

The potential of fly-ash particles has long been overlooked by palaeolimnologists. When this project was started in the beginning of the 1980's only few papers dealing with fly-ash particles had been published, mainly by Griffin, Goldberg and co-workers. Despite the work presented in this thesis, and increasing interest in other countries in the use of carbonaceous particles, the full potential of the particles remains unexplored.

The next important step will be to develop a method for the analysis of smaller particles ($> 0.1\text{-}1.0\ \mu\text{m}$) called the accumulation mode, known for their long-range transport in the atmosphere. This analytical advance might be achieved by adding hydrogen fluoride treatment to the sediment extraction procedure, as done by Griffin & Goldberg (1975) and Rose (1990a). Such an approach should result in a residue of greater purity. The carbonaceous particles might then be separated into two different size fractions, smaller than $1\ \mu\text{m}$ and larger than $1\ \mu\text{m}$, using filtration techniques. Filtration will also make it possible to concentrate a large volume of the residue onto a small area, thereby reducing the time required for counting coarse particles and allowing other qualitative methods to be applied. The possibility to use automatic image analyses for the final quantification of the particles is certainly attractive. However, it will be extremely difficult to produce a residue that is pure enough, as there is always some mineral matter left in the residue. Furthermore, I have observed the formation of a precipitate when some sediments are treated with hydrogen fluoride. The skill of an experienced person using a scanning electron microscope or a stereo microscope, will probably be

unsurpassed for reliable separation of carbonaceous particles from other particles, at least until advanced computer programs for image analysis are developed.

To what extent the Swedish SCP distribution is influenced by international sources is still an open question. Both the soil survey (paper VII) and the surface sediment survey of Sweden (paper VI), display similarities between the geographical deposition of SCP and domestic emissions as well as long-range transported pollutants. Coarse particles, such as SCP, are considered to have a short atmospheric life-time and not susceptible to long-range transport (van Aalst 1985). However, the porous structure and low density of SCP gives them a lower settling rate than would be expected from their geometric diameter. My results indicate that SCP can in fact be transported over considerable distances. The particles are frequently present in surface sediments even in remote areas in northern Sweden. SCP were also found in sediments deposited before northern Sweden was industrialised, and the SCP concentration in a core from the Baltic Sea, sampled ca. 100 km from the nearest possible source, was comparable to the concentrations found in samples taken from lakes in industrialised parts of northern Sweden. There is also other evidence suggesting that, under particular weather conditions, SCP can be transported over long distances. For example, coarse ($> 5 \mu\text{m}$) mineral coal fly-ash particles (with densities higher than SCP) have been found in marine sediments and in snow far from their sources (Doyle et al. 1976, Deuser et al. 1983, Davies et al. 1984). The atmospheric transport of coarse dust particles from the African continent to Sweden is a further example (Franzen 1987). Long-distance transport of pollen from the Baltic states to northern Sweden is also taking place (Wallin et al. 1991). Coarse particles transported over long-distances have also been detected in the atmosphere above the Arctic (Bailey et al. 1984, Sheridan & Musselman 1985). Therefore, it is likely that the pattern of SCP distribution in Sweden is a result of deposition from domestic sources, with internationally derived deposition superimposed. Foreign influence is especially likely for the southern parts Sweden, where the distance to e.g. central Germany is only about 500 km.

When a technique for the analysis of sub-micrometer sized particles has been developed, the distribution of these particles can be compared with the SCP distribution. Differences in the distribution might shed some light on the transportation distances of SCP. Moreover, different fuels and combustion techniques are used in various parts of Europe, and valuable information about the transport distances from the point of emission would also be obtained if particles from different sources and/or different combustion processes could be identified and separated. A separation based on particle morphology (Griffin & Goldberg 1981) is far too crude and insecure. A new technique for the separation of particles from oil and coal has recently been developed by N. Rose and colleagues at University College London and J. Watt at Imperial College (Rose et al. in press, Rose in press). This technique is based on chemical characterisation of individual

particles using automated scanning electron microscopy and energy dispersive X-ray spectroscopy, and has been applied to sediment profiles and surface samples. The use of coal for energy production is limited in Sweden (paper V), whereas it is important in most other European countries. An estimate of the proportion of SCP derived from coal in different parts of Sweden would indicate to what extent the SCP deposition in Sweden is influenced by emissions from other countries. A preliminary study to test this hypothesis in Sweden has been initiated in cooperation with colleagues in London.

This thesis has focused on carbonaceous particles as an indicator for the deposition of airborne pollutants derived from the combustion of fossil-fuel. However, SCP also deserve attention because they are carriers of metals, S (Cheng et al. 1976, Bacci et al. 1983), and PAH (Dunstan et al. 1989, Broman et al. 1990), and because they have an indirect influence on chemical processes. Carbonaceous particles can act as catalysts of chemical reactions, and in the atmosphere the catalytic oxidation of SO_2 to SO_4^{2-} is of special importance (Chang & Novakov 1983). Carbonaceous particles are also strong adsorbents of PAH, and PAH adsorbed on carbonaceous particles are stabilised towards photodegradation (Dunstan et al. 1989). Carbonaceous particles also have a crucial catalytic effect on the decay of buildings and monuments made of calcareous stone (Del Monte & Vittory 1985). The possibility of carbonaceous particles interfering with natural weathering processes in soils is also worth considering.

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REFERENCES

- Anderson, R. Y., Dean, W. E., Bradbury, J. P. & Lowe, D. 1985. Meromictic lakes and varved sediments in North America. US Geological Survey bulletin 1067, pp. 19.
- Andersson, B. I. 1985. Properties and chemical composition of surficial sediments in the acidified Lake Gårdsjön, S.W. Sweden. *Ecol. Bull.* 37: 251-262.
- Bacci, P., Del Monte, M., Longhetto, A., Piano, A., Prodi, F., Redaelli, P., Sabbioni, C. & Ventura, A. 1983. Characterization of the particulate emission by a large oil fired power plant. *J. Aerosol. Sci.* 14: 557-572.
- Bailey, I. H., Radke, L. F., Lyons, J. H. & Hobbs, P. V. 1984. Airborne observations of Arctic aerosols. *Geophys. Res. Lett.* 11:397-400.
- Battarbee, R. W., Anderson, N. J., Appleby, P. G., Flower, R. J., Fritz, S. C., Haworth, E. Y., Higgitt, S., Jones, V. J., Kreiser, A., Munro, M. A. R., Natkanski, J., Oldfield, F., Patrick, S. T., Richardson, N.G., Rippey, B. & Stevenson, A. C. 1988. Lake acidification in the United Kingdom 1800-1986. ENSIS, London, pp. 66.
- Battarbee, R. W., Mason, B. J., Renberg, I. & Talling, J. F. 1990. Palaeolimnology and lake acidification. Proceedings of a Royal Society Discussion Meeting, London, pp. 219.
- Bertine, K. K. & Mendeck, M. F. 1978. Industrialization of New Haven, Conn., as recorded in reservoir sediments. *Environ. Sci. Technol.* 12: 201-207.
- Birks, H. J. B., Berge, F., Boyle, J. F. & Cumming, B. F. 1990. A palaeoecological test of the land-use hypothesis for recent lake acidification in south-west Norway using hill-top lakes. *J. Paleolim.* 4: 69-85.
- Bridges, E. M. 1986. World soils. Cambridge University Press, New York , pp. 128.
- Broman, D., Näf, C., Wik, M. & Renberg, I. 1990. The importance of spheroidal carbonaceous particles (SCPs) for the distribution of particulate polycyclic aromatic hydrocarbons (PAHs) in an estuarine. *Chemosphere* 21: 69-77.
- Chang, S.-G. & Novakov, T. 1983. Role of carbon particles in atmospheric chemistry. In *Trace Atmospheric Constituents: Properties, Transformations, & Fates* (ed. S. E. Schwartz), John Wiley & Sons, New York: 191-219.

- Charles, D. F. & Whitehead, D. R. 1989. Paleocological Investigation of Recent Lake Acidification (PIRLA): 1983-1985. EPRI EN-6526, Interim Report.
- Charles, D. F., Battarbee, R. W., Renberg, I., Van Damm, H. & Smol, J. P. 1990a. Paleocological analyses of lake acidification trends in North America and Europe using diatoms and chrysophytes. In *Acid precipitation*, vol 4 (eds S. A. Norton, S. E. Lindberg & A. L. Page), Springer Verlag, New York: 207-276.
- Charles, D. F., Binford, M. W., Furlong, E. T., Hites, R. A., Mitchell, M. J., Norton, S. A., Oldfield, F., Paterson, M. J., Smol, J. P., Uutala, A. J., White, J. R., Whitehead, D. R. & Wise, R. J. 1990b. Paleocological investigation of recent lake acidification in the Adirondack Mountains, N.Y. *J. Paleolim.* 3: 195-241.
- Cheng, R. J., Mohnen, V. A., Shen, T. T., Current, M. & Hudson, J. B. 1976. Characterization of particulates from power plants. *J. Air Pollut. Control Ass.* 26: 787-790.
- Darley, J. 1985. Particulate soot in Galloway lake sediments; its application as an indicator of environmental change and as a technique for dating recent sediments. Dept. of Geog., University College London. B301 Project.
- Davis, R. B., Anderson, D. S., Whiting, M. C. Smol, J. P. & Dixit, S. S. 1990. Alkalinity and pH of three lakes in northern New England, U.S.A., over the past 300 years. *Phil. Trans. R. Soc. Lond. B* 327, 413-421.
- Davies, T. D., Abrahams, P. W., Tranter, M., Blackwood, I., Brimblecombe, P. & Vincent, C. E. 1984. Black acidic snow in the remote Scottish Highlands. *Nature* 312: 58-61.
- Del Monte, M. & Sabbioni, C. 1984. Morphology and mineralogy of fly ash from a coal-fueled power plant. *Arch. Met. Biocl. B* 35: 93-104.
- Del Monte, M. & Vittori O. 1985. Air pollution and stone decay: the case of Venice. *Endeavour* 9: 117-122.
- Del Monte, M. Sabbioni, C., Ventura, A. & Zappia, G. 1984. Crystal growth from carbonaceous particles. *Sci. Total Envir.* 36: 247-254.
- Deuser, W. G., Emeis, K., Ittekkot, V. & Degens, E. T. 1983. Fly-ash particles intercepted in the deep Sargasso Sea. *Nature* 305: 216-218.

- Doyle, L. J., Hopkins, T. L. & Betzer, P. R. 1976. Black magnetic spherule fallout in the eastern Gulf of Mexico. *Science* 194: 1157-1159.
- Dunstan, T.D.J., Mauldin, R.F., Jinxian, Z., Hipps, A.D., Wehry, E. L. & Mamantov, G. 1989. Adsorption and photodegradation of pyrene on magnetic, carbonaceous, and mineral subfractions of coal stack ash. *Environ. Sci. Technol.* 23: 303-308.
- Energy statistics yearbook 1989. United Nations, New York.
- Fisher, G. L., Prentice, B. A., Silberman, D., Ondov, J. M., Biermann, A. H., Ragaini, R. C. & Mcfarland, A. R. 1978. Physical and morphological studies of size-classified coal fly ash. *Environ. Sci. Technol.* 12: 447-451.
- Franzen, L. 1989. A dustfall episode on the Swedish west coast, October 1987. *Geografiska Annaler* 71A: 263-267.
- Gay, A. J., Littlejohn, R. F. & van Duin, P. J. 1984. Studies of carbonaceous cenospheres from fluidised-bed combustors. *Sci. Total Envir.* 36: 239-246.
- Giblin, A. E., Likens G. E., White, D. & Howarth, R. W. 1990. Sulfur storage and alkalinity generation in New England lake sediments. *Limnol. Oceanogr.* 35: 852-869.
- Goldberg, E. D. 1985. Black carbon in the environment. John Wiley & Sons, New York, pp. 198.
- Goldberg, E. D., Hodge, V. F., Griffin, J. J., Koide, M. & Edgington, D. N. 1981. Impact of fossil fuel combustion on the sediments of Lake Michigan. *Environ. Sci. Technol.* 15: 466-471.
- Grahn, O. 1985. Macrophyte biomass and production in Lake Gårdsjön - an acidified clearwater lake in S.W. Sweden. *Ecol. Bull.* 37: 203-212.
- Granat, L. 1989. Luft och nederbörds-kemiska stationsnätet inom PMK, rapport från verksamheten 1988. Statens Naturvårdsverk SNV PM 3649, pp. 64 (in Swedish).
- Griest, W. H. & Harris L. A. 1985. Microscopic identification of carbonaceous particles in stack ash from pulverized-coal combustion. *Fuel* 64: 821-826.
- Griffin, J. J. & Goldberg, E. D. 1975. The fluxes of elemental carbon in coastal marine sediments. *Limnol. Oceanogr.* 20: 256-263.

- Griffin, J. J. & Goldberg, E. D. 1979. Morphologies and origin of elemental carbon. *Science* 206: 563-565.
- Griffin, J. J. & Goldberg, E. D. 1981. Sphericity as a characteristic of solids from fossil fuel burning in a Lake Michigan sediment. *Geochim. Cosmochim. Acta* 45: 763-769.
- Griffin, J. J. & Goldberg, E. D. 1983. Impact of fossil fuel combustion on sediments of Lake Michigan: A reprise. *Environ. Sci. Technol.* 17:244-245.
- Hamilton, E. M. & Jarvis, W. D. 1963. The identification of atmospheric dust by use of the microscope. Monograph published by the Central Electricity Generating Board, Balding & Mansell, pp. 32.
- Henderson-Sellers, B. 1984. Pollution of our atmosphere. Adam Hilger, Bristol, pp. 210.
- Hunt, A. 1986. The application of mineral magnetic methods to atmospheric aerosol discrimination. *Phys. Earth Planet. Int.* 42: 10-21.
- Kothari, B. J. & Wahlen, M. 1984. Concentration and surface morphology of charcoal particles in sediments of Green Lake, N.Y.: Implications regarding the use of energy in the past. *Northeastern Environ. Sci.* 3: 24-29.
- Lazarek, S. 1982. Structure and function of a cyanophyten mat community in an acidified lake. *Can. J. Bot.* 60:2235-2240.
- Likens, G. E. & Davis, M. B. 1975. Post-glacial history of Mirror Lake and its watershed in New Hampshire, USA: An initial report. *Int. Ver. Theor. Angew. Limnol. Verh.* 19: 982-993.
- Livett, E. A. 1988. Geochemical monitoring of atmospheric heavy metal pollution: theory and applications. *Adv. Ecol. Res.* 18: 65-177.
- Medalia, A. I. & Rivin, D. 1982. Particulate carbon and other components of soot and carbon black. *Carbon* 20: 481-492.
- McCrone, W. G. & Delly, J. G. 1973. The Particle Atlas, II. Ann Arbor Science, Ann Arbor, pp. 267.
- McElroy, M. W., Carr, R. C., Ensor, D. S. & Markowski, G.R. 1982. Size distribution of the fine particles from coal combustion. *Science* 215: 13-19.

- Mitchell, M. J., Schindler, S. C., Owen, J. S. & Norton, S. A. 1988. Comparison of sulfur concentrations within lake sediment profiles. *Hydrobiol.* 157: 219-229.
- Nelson, W. O. & Campbell, P. G. C. 1991. The effects of acidification on the geochemistry of Al, Cd, Pb and Hg in freshwater environments: A literature review. *Environ. Pollut.* 71: 91-130.
- Norton, S. A. & Kahl J. S. 1991. Progress in understanding the chemical stratigraphy of metals in lake sediments in relation to acidic precipitation. *Hydrobiol.* 214: 77-84.
- Norton, S. A., Dillon, P. J., Evans, R. D., Mierle, G. & Kahl, J. S. 1990. The history of atmospheric deposition of Cd, Hg, and Pb in North America: Evidence from lake and peat bog sediments. In *Acidic precipitation*, vol 3 (eds S. E. Lindberg, A. L. Page & S. A. Norton), Springer-Verlag, New York: 73-102.
- Nriagu, J. O. & Pacyna, J. M. 1988. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. *Nature* 333: 134-139.
- Oldfield, F. & Richardson, N. 1990. Lake sediment magnetism and atmospheric deposition. *Phil. Trans. R. Soc. Lond. B* 327: 99-104.
- Olsson, I. U. 1986. Radiometric dating. In *Handbook of Holocene Palaeoecology and Palaeohydrology* (ed. B. E. Berglund), John Wiley & Sons, New York: 273-311.
- Organization for Economic Co-operation and Development (OECD). 1990. *Emission Inventory of Major Air Pollutants in OECD European Countries*. OECD: Paris.
- O'Sullivan, P.E. 1983. Annually-laminated lake sediments and the study of quaternary environmental changes - a review. *Quat. Sci. Rev.* 1: 245-313.
- Pacyna, J. M. & Münch, J. 1991. Anthropogenic mercury emission in Europe. *Water Air Soil Pollut.* 56: 51-61.
- Peterson, K. F. 1972. *Stoftbildning vid oljeeldning*. Ph.D. thesis, The Royal Institute of Technology, pp. 229 (in Swedish).
- Raask, E. 1980. Quartz, sulphates and trace elements in pf ash. *J. Inst. Energy* 53: 70-75.

- Raask, E. 1981. Surface properties of pulverized coal ash and chimney solids. *Power Ind. Res.* 1: 233-251.
- Raeymaekers, B., Demuyne, M., Dorrine, W. & Adams, F. 1988. Characterization of oil fly ash particles by electron probe microanalysis. *Intern. J. Environ. Anal. Chem.* 32: 291-312.
- Renberg, I. 1981. Improved methods for sampling, photographing and varve-counting of varved lake sediments. *Boreas* 10: 255-258.
- Renberg, I. 1984. Sot och kiselalger visar: Förbränning och försurning går hand i hand. *Forskning och Framsteg* 4/84: 36-40 (in Swedish).
- Renberg, I. 1991. The HON-Kajak sediment corer. *J. Paleolim.* 6: 167-170.
- Renberg, I. & Hellberg, T. 1982. The pH history of lakes in southwestern Sweden, as calculated from the subfossil diatom flora of the sediments. *Ambio* 11: 30-33.
- Renberg, I. & Wallin, J.-E. 1985. The history of the acidification of Lake Gårdsjön as deduced from diatoms and *Sphagnum* leaves in the sediment. *Ecol. Bull.* 37: 47-52.
- Renberg, I. & Wik, M. 1989. En paleolimnologisk undersökning av pH utvecklingen i tre sjöar i Rogenområdet i Härjedalen. Report 15 pp. (in Swedish).
- Renberg, I. & Battarbee, R.W. 1990. The SWAP Palaeolimnology Programme: a synthesis. In *The Surface Waters Acidification Programme* (ed. B. J. Mason), Cambridge University Press, Cambridge, 522 pp.
- Renberg, I. & Hultberg, H. 1992. A paleolimnological assessment of acidification and liming effects on diatom assemblages in a Swedish lake. *Can. J. Fish. Aquat. Sci.* 49: 65-72.
- Rose, N. L. 1990a. A method for the extraction of carbonaceous particles from lake sediment. *J. Paleolim.* 3: 45-53.
- Rose, N. L. 1990b. A method for the selective removal of inorganic ash particles from lake sediments. *J. Paleolim.* 7: 61-67.

- Rose, N. L. Characterisation and distribution of carbonaceous particles in lake sediments. European university centre for the cultural heritage. Man-made and volcanic particles and gases: their impact on different environments and effects on the cultural heritage. European workshop at Villa Rufolo, Ravello, 1990 (in press).
- Rose, N. L., Watt, J., Juggins, S, Munro, M. A. R. & Battarbee, R. W. The characterisation of carbonaceous particles derived from fossil-fuel combustion. European university centre for the cultural heritage. Airborne particles and their negative effects on the cultural heritage, the environment and man. European workshop at Villa Rufolo, Ravello, 1989 (in press).
- Ross, H. B. & Granat, L. 1986. Deposition of atmospheric trace metals in northern Sweden as measured in the snowpack. *Tellus* 38B: 27-43.
- Sandman, O., Eskonen, K. & Liehu, A. 1990. The eutrophication history of Lake Särkinen, Finland and the effects of lake aeration. *Hydrobiol.* 214: 191-199.
- Segerström, U. & Renberg, I. 1986. Calculating net annual accumulation rates of sediment components exemplified by pollen. *Hydrobiol.* 143: 45-47.
- Shen, T. T., Cheng, R. J., Mohnen, V. A., Current, M. & Hudson, J. B. 1977. Characterization of differences between oil-fired and coal-fired power plant emissions. International Clean Air Congress, 4. Tokyo: 386-391.
- Sheridan, P. J. & Musselman, I. H. 1985. Characterization of aircraft-collected particles present in the Arctic aerosol; Alaskan Arctic, spring 1983. *Atmos. Envir.* 85: 2159-2166.
- Smith, D. M., Griffin, J. J. & Goldberg, E. D. 1975. Spectrometric method for the quantitative determination of elemental carbon. *Anal. Chem.* 47: 233-238.
- Statistical papers series J. 1957-1976. World energy supplies. United Nations, New York.
- Statens Naturvårdsverk. 1987. Monitor 1987. Liber förlag, Stockholm, pp. 182 (in Swedish).
- Tolonen, K. & Haapalahti, R. 1990. Comparison of varve dated soot ball chronology and lead-210 dating in Finland. INQUA Commission for the Study of the Holocene. Working Group on Laminated sediments. Workshop at Lammi Biological Station, Finland.

- van Aalst, R. M. 1985. Dry deposition of aerosol particles. In *Aerosols: Research, risk assessment and control strategies* (eds S. D. Lee, T. Schneider, L. D. Grant & P. J. Verkerk), Lewis Publishers, Chelsea, Michigan: 933-949.
- Wallin, J.- E., Segerström, U., Rosenhall, L., Bergmann, E. & Hjelmroos, M. 1991. Allergic symptoms caused by long-distance transported birch pollen. *Grana* 30:265-268.