

Environmental records of carbonaceous fly-ash particles from fossil-fuel combustion

A summary

Maria Wik¹ & Ingemar Renberg^{2*}

¹*Department of Ecological Botany, Umeå University, S-901 87 Umeå, Sweden*

Present address: Environmental Protection Agency, Skellefteå Municipality, S-931 85 Skellefteå, Sweden

²*Department of Environmental Health, Umeå University, S-901 87 Umeå, Sweden*

* *Author for correspondence*

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Abstract

Analysis of fly-ash particles in lake sediments has become increasingly important in studies of environmental pollution and lake acidification history. Most fly-ash studies have concerned black spheroidal carbonaceous particles (SCP) (>5 µm) produced from oil and coal combustion. This review paper provides a summary of this technique and its application, and focusses on our investigations in Sweden between 1979 and 1993. It consists of five parts: i) preparation and analysis methods, ii) historical trends in atmospheric deposition, iii) geographical surveys of atmospheric deposition, iv) sediment dating, and v) studies of sedimentation processes in lakes. Methods for preparation and analyses of SCP have been developed and applied to investigations using sediment, soil and snow samples. Stratigraphic trends of SCP concentrations in lake-sediment cores reflect the consumption history of fossil fuels. A characteristic temporal SCP pattern, with a marked concentration increase beginning after the 1940's and a peak in the early 1970's, has been recognized in most Swedish lakes and elsewhere in Europe. A survey of SCP concentrations in surface sediments of >100 lakes covering Sweden demonstrated that polluted areas in southern Sweden had >100 times higher SCP concentrations than clean areas in the north. The spatial distribution of SCP over Sweden is similar to the deposition pattern of long-range transported airborne pollutants, such as excess sulphate monitored by network stations. SCP also accumulate in soils, and soil analyses can be used for determining the integrated historical deposition of SCP at the local or regional scale. Finally, SCP have been used for indirect dating of sediment cores and as a marker to assess sediment distribution patterns within lake basins.

Introduction

Fossil fuel combustion is a major source of anthropogenic particulate emissions into the atmosphere (Goldberg, 1985). When these fly-ash particles are deposited on lakes or are transported there by water, they collect in the sediments, provided that the particles are insoluble in water. Fly-ash particles accumulate also in surface soils. Studies of fly-ash particles in sediments and soils are relevant because: (i) the particles contain heavy metals and sulphur from the

fuel (Bacci *et al.*, 1983; Del Monte & Sabbioni, 1984) and also organic pollutants such as PAH (Polycyclic Aromatic Hydrocarbons) produced at the combustion processes (Dunstan *et al.*, 1989), and, most importantly, (ii) the particles can be used as indicators of atmospheric deposition of pollutants from fossil-fuel combustion. Pollutants such as NO_x and SO₂, well-known for their environmental impact, do not leave reliable historical records in lake sediments or other natural archives. Poor sedimentary records result because nitrogen and sulphur are involved in various

chemical and biological processes in both terrestrial and aquatic environments. Fly-ash particles are, on the other hand, less reactive and are not chemically mobile in lake sediment deposits.

Coal and oil combustion produces three types of insoluble fly-ash particles. First, spherical particles with an aluminosilicate glassy matrix (Fisher *et al.*, 1978; Raask, 1980; Del Monte & Sabbioni, 1984). These particles dominate coal fly-ash. Second, sub-micrometer carbonaceous particles formed in the gaseous phase by incomplete combustion or by thermal decomposition of hydrocarbons. These particles are produced during oil and coal combustion, and the particles are commonly aggregated to form chain like structures (Medalia & Rivin, 1982). Third, coarse carbonaceous particles from coal and oil which may be irregular or spheroidal. These carbonaceous particles constitute an overwhelming portion of oil fly-ash, and the vast majority (90%) are spheroidal (Cheng *et al.*, 1976; Shen *et al.*, 1977; Del Monte *et al.*, 1984).

Although fly-ash particles are very abundant in recent sediments from lakes in industrialized regions, the potential of fly-ash particles has been underutilized by palaeolimnologists. Pioneering work was done by Griffin & Goldberg (1979, 1981, 1983) and Goldberg *et al.* (1981). At investigations of the sediments from the severely acidified lake Gårdsjön in southwestern Sweden in 1979 (Renberg & Hellberg, 1982), large amounts of spheroidal carbonaceous particles were found in recent sediments. This discovery initiated work on these particles in lake sediments and surface soils in Sweden. Here, we summarize this work.

The Spheroidal Carbonaceous Particles (SCP)

There is no standard terminology concerning carbonaceous particles. Names such as carbonaceous particles, carbonaceous cenospheres, cokey matter, charcoal, elemental particulate carbon, black carbon, oil soot, soot balls, and soot have been used. The term 'carbonaceous particles' is frequently used but it has a broad definition. Soot is also a common expression, mostly referring to the sub-micrometer sized particle fraction. The lack of a standard terminology is also reflected in our papers; the terms soot particles, soot spheres, coarse carbonaceous spheres, and finally spheroidal carbonaceous particles (SCP), have been used.

Spheroidal carbonaceous particles are generated from incompletely burned oil drops or from coal par-

ticles (Peterson, 1972; McCrone & Delly, 1973), but SCP only constitute a minor part of the coal fly-ash (Del Monte & Sabbioni, 1984; Griest & Harris, 1985). The SCP are composed of an amorphous carbonaceous matrix in which other elements are dispersed (Fig. 1). Major elements in particles from oil combustion are S, V; minor elements include Al, Si, Na, Mg, K, Ca, Fe and Cu (Bacci *et al.*, 1983). In coarse carbonaceous particles from coal combustion the major element is S, and minor elements include V, Al, Si, Ca and K (Del Monte & Sabbioni, 1984). The coarse carbonaceous spheres have a porous surface and many internal cavities. Consequently the particles have a low density (Gay *et al.*, 1984; Raeymaekers *et al.*, 1988) and a very large surface area (Raask, 1981; Del Monte *et al.*, 1984).

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. After deposition in sediments, peat, and forest soils they remain well preserved and these materials can be chemically treated in such ways that the particles can be quantified.

Preparation and analysis methods

Griffin & Goldberg (1979) were the first to properly demonstrate the occurrence in lake sediments of carbonaceous particles from fossil-fuel combustion. 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. Infrared spectroscopy was used to determine the amount of elemental carbon in the residue, and results were expressed as percent carbon g⁻¹ dry mass. This technique was applied to 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 characteristic morphologies, structures, and surface textures for different combustion processes (Griffin & Goldberg, 1979, 1981).

The infrared analysis method of Smith *et al.* (1975) requires large sediment samples (10 g dry sediment was used by Griffin & Goldberg). For palaeolimnology

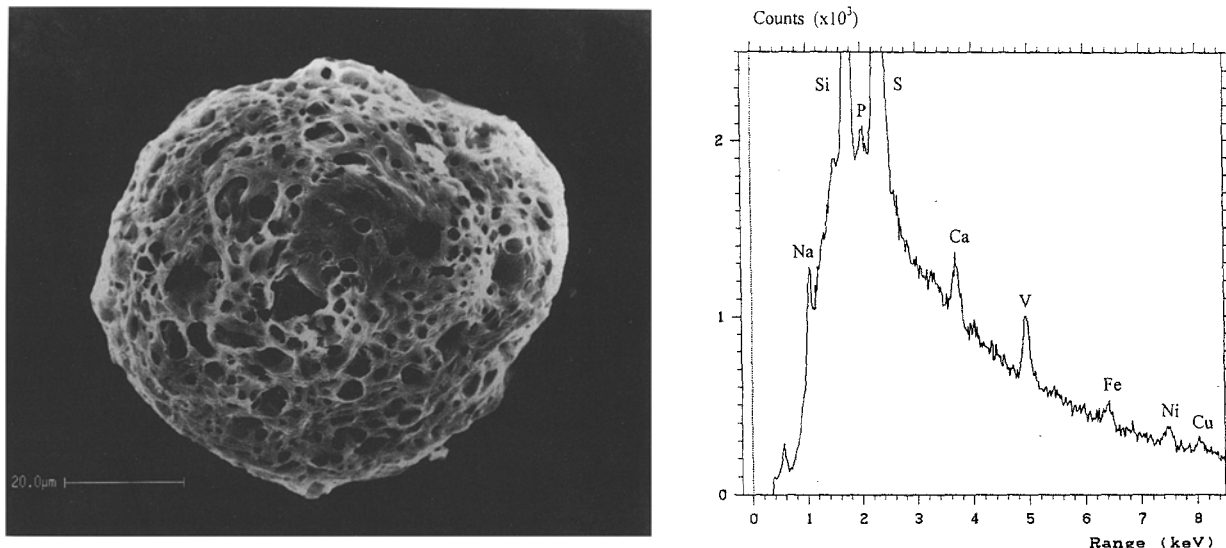


Fig. 1. SEM-photograph of a spheroidal carbonaceous particle derived from oil combustion (left) and a spectrum of energy dispersive X-ray analysis showing the presence of some pollutants from the source-fuel dispersed in the carbon matrix of this fly-ash particle (right).

ical analysis of recent environmental changes, close-interval sub-sampling is often desired, and it is also advantageous if a single core can be used for several different analyses including SCP, metals, diatoms, and dating. Enough sediment for the infrared method can, therefore, not be obtained using, for example, a freeze corer or a gravity tube corer. 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 anthropogenic carbon signal may be blurred.

We developed a robust method for enumeration of SCP that only needed small amounts of sediment, was reasonably fast and simple, and did not require expensive or sophisticated instruments (Renberg & Wik, 1985). The method includes the following major steps: oxidation of sediment with hydrogen peroxide, washing with water, homogenization of the suspension, and pouring of aliquots into glass Petri dishes. The water is allowed to evaporate slowly, and then the SCP are counted under a stereomicroscope at $\times 50$ magnification. SCP larger than 5–10 μm can be identified, although the detection limit is slightly variable, depending on the origin of the sedimentary material. For some sediments, and particularly for soils, high mineral grain concentration and large concentrations of dark minerals reduce the ability to identify the smaller spheres (5 μm). Hydrogen fluoride has been used occasionally to dissolve mineral matter. Under the stere-

omicroscope the SCP are black with a shiny lustre and break when touched with a fine-tipped pointer. Other black particles with an appearance similar to SCP occur, but these are much more difficult to disintegrate.

Rose (1990a, 1994) has developed a third method for carbonaceous particle analysis. His method, which digests not only the organic material but also most of the mineral matter, uses a chemical treatment similar to that of the method presented by Griffin & Goldberg (1975). Sub-samples of the residue are then allowed to evaporate onto coverslips and the particles counted at $\times 400$ using a light microscope. With this technique, using $\times 1000$ magnification, it is possible to count particles as small as 1 μm and slides are easily stored.

Historical trends of atmospheric deposition

In the western industrialised countries, the use of fossil fuels has increased markedly 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 early 1900's coal was the major fossil fuel in Europe, but over the last fifty years the use of oil has increased tremendously. Whether oil has become to be the major fuel in any nation 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 (Fig. 2).

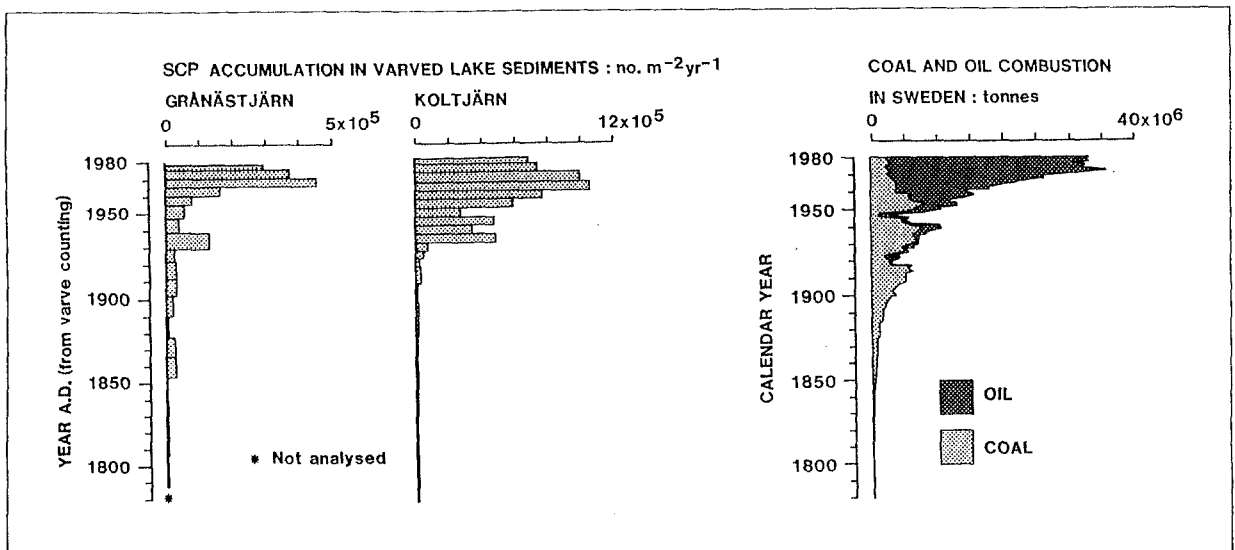


Fig. 2. Diagrams showing the annual accumulation rates of spheroidal carbonaceous particles in sediment cores from two Swedish lakes with varved sediments (left) and coal and oil combustion in Sweden (right). Modified from Renberg & Wik (1985b).

Most of the analyses of carbonaceous fly-ash particles in lake sediments have been done in the USA, Sweden, Great Britain, Norway, Finland, Denmark, and Estonia. A common feature is the close resemblance between the carbonaceous particle pattern in sediment cores and the history of fossil-fuel consumption in each region.

In the USA, cores have been analysed from Lake Whitney (Bertine & Mendeck, 1978), L. Michigan (Goldberg *et al.*, 1981; Griffin & Goldberg, 1981, 1983), Green Lake N.Y. (Kothari & Wahlen, 1984), and more recently from PIRLA-lakes (Charles *et al.*, 1990; Davis *et al.*, 1990). These studies demonstrated an increasing black carbon content in the most recent sediments, reflecting the increased use of fossil fuels during the 20th century. In High Arctic Canada, local pollution of spherical black carbon particles have been recorded (Doubleday *et al.*, 1995).

The first Swedish sediment profile analysed for SCP was from Lake Gårdsjön, situated in southwestern Sweden, where there was an obvious stratigraphic correlation between the diatom-inferred pH trend and the SCP pattern; the increase in SCP concentration was contemporaneous with the onset of severe acidification (Renberg, 1984; Renberg & Wallin, 1985). Since then several Swedish lakes with non-varved as well as varved sediments have been analysed (Fig. 3).

With varved sediments, an absolute chronology can be established. When quantitative sub-sampling is performed (known number of years and a known area of

the lake bottom; Renberg, 1981), reliable estimates of the annual accumulation of SCP can be calculated (number of particles m⁻² yr⁻¹). SCP have been analysed in three Swedish lakes with varved sediments; Grånästjärn, Koltjärn and Buvatten. The latter core was only analysed back to sediments dating to 1953 when varve formation began, while the analyses from the other two lakes extend back to the latter part of the 18th century. The SCP diagrams from the varved lakes display several interesting features. The SCP fluxes to the sediments show a remarkable correspondence with the Swedish consumption of oil and coal (Fig. 2). 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 1930s, 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 peaked around 1970, before the so-called 'oil crisis' (Fig. 2).

When comparing fuel consumption statistics and the sedimentary SCP record, it is important to remember that the amounts and distribution of particles emit-

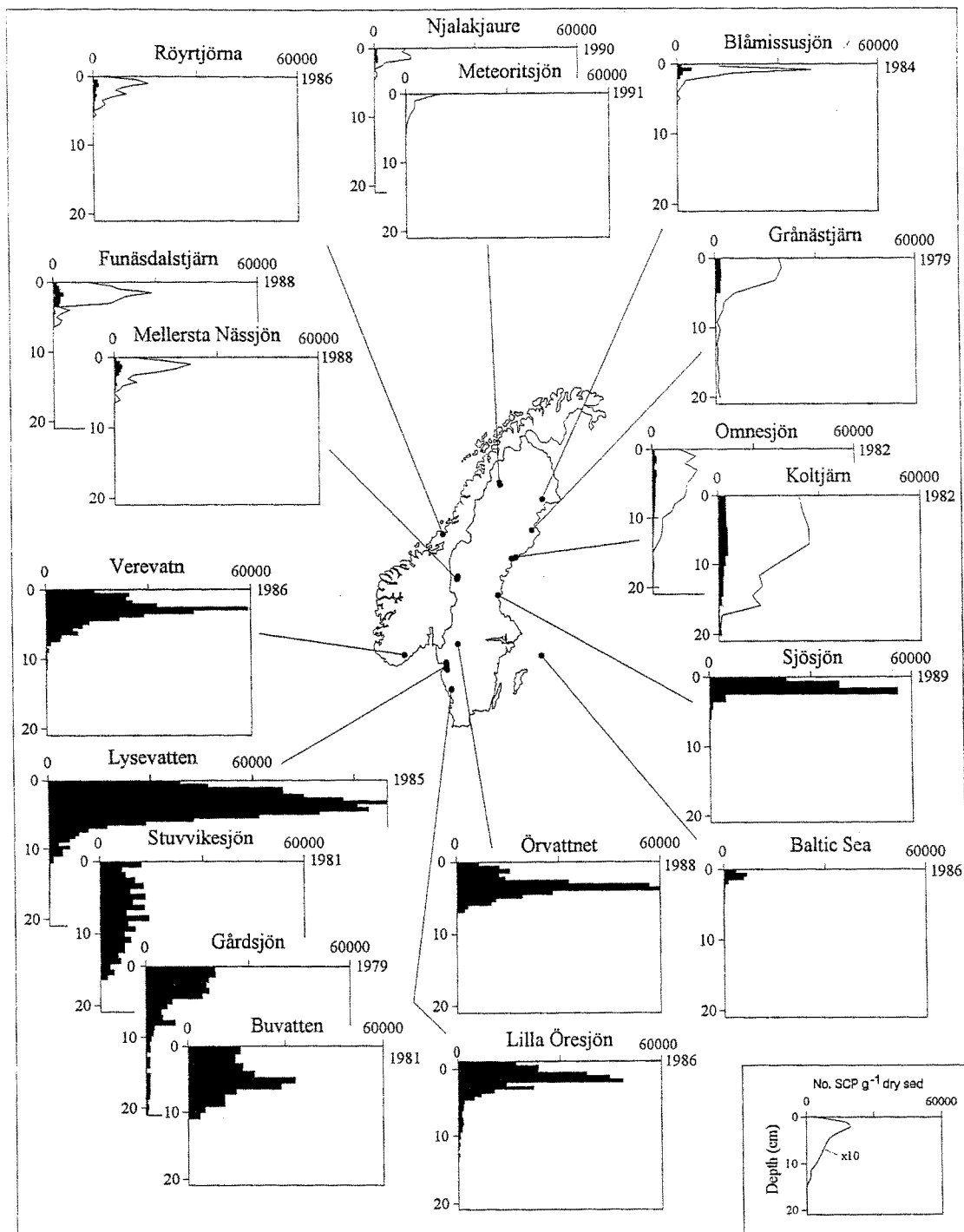


Fig. 3. Spheroidal carbonaceous particle concentrations in sediment cores from fifteen Swedish and two Norwegian lakes, and one core from the Baltic Sea (from Wik, 1992).

ted from point sources have changed through time; also combustion techniques and emission controls have improved. 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.

Non-varved sediments are, to various degrees, affected by mixing. Despite this loss of resolution, the profiles from Lysevatten, Lilla Öresjön, Örvatnet, Sjösjön, Funäsdalstjärn, Mellersta Nässjön, Blåmissusjön and Njalakjaure display features characteristic of the SCP pattern in the varved lakes (Fig. 3). However, there are lakes where bioturbation, high sediment accumulation rates, or variations in sediment accumulation result in indistinct patterns. 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 (Fig. 3). Meteoritsjön is a high mountain lake with a very low sediment accumulation rate.

When comparing SCP profiles from the different lakes, it should be noted that the cores have been taken in different years (Fig. 3). There is a 12 year difference between the first lakes sampled, Gårdsjön and Grånästjärn, cored in 1979 and the latest, Meteoritsjön, cored in 1991. 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 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 (Darley, 1985, see Wik *et al.*, 1986) 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 and some Irish lakes have been studied (Battarbee *et al.*, 1988; Wik & Natkanski, 1990; Rose, 1991; Jones *et al.*, 1993; Flower *et al.*, 1994; Rose & Juggins, 1994). As with Swedish sites, on the British Isles the SCP record follows the history of fossil-fuel combustion (Darley, 1985; Rose, 1990a; Wik & Natkanski, 1990). Some particles are present in sediment older than 1900, a sharp increase in concentration occurs at about 1940 and continues towards the sediment surface. However, there have been a slight reduction in surface concentrations (Wik & Natkanski, 1990; Rose, 1991).

The SCP profiles from Verevatn and Röyrtjørna were the first results published for Norway (Wik & Natkanski, 1990). Lake Verevatn is situated in S. Norway in an area of high sulphur deposition, whereas Röyrtjørna 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 is about 35 times higher than in the northern lake (Fig. 3). Cores from two lakes from southwestern Norway have been analysed by Birks *et al.* (1990). Both had high SCP concentrations.

Analyses of SCP in sediment profiles from Finland have been published by Lampi *et al.* (1992), Tolonen *et al.* (1992) and Sandman *et al.* (1990). Tolonen *et al.* (1992) report agreement between historically known consumption of coal and oil and the SCP stratigraphy in varved lake sediments. Also in Danish lakes, SCP records follow the general trend of increasing concentrations after World War II, maximum values around 1970 and thereafter decreasing values (Odgaard, 1993). SCP are also present in lakes on the Kola Peninsula, Svalbard, and in remote mountain lakes in Europe and Asia (Rose, 1995).

Geographic surveys of recent atmospheric deposition

Surface sediments

The differences in SCP concentration between sediment profiles from different parts of Sweden suggested investigating 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 map of SCP concentrations clearly showed how emissions from Gothenburg are distributed over a large area. However, local back-

ground concentrations about 50 km from the city were still very high compared to other parts of Sweden (Renberg & Wik, 1985b).

The above results initiated a large survey of recent SCP deposition covering all of Sweden (Wik & Renberg, 1991a). The objective was to map the SCP distribution and test if 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 yrs) were collected from 114 lakes distributed all over Sweden. The lakes were small, relatively deep, headwater lakes with forested catchments and situated away from local SCP emitting sources. There was 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 (Fig. 4). The SCP distribution was similar to the deposition pattern of lead derived from a moss survey by Å. Rühling (Statens Naturvårdsverk, 1987) and of sulphate from the Swedish air pollution monitoring network (Granat, 1989) (Fig. 4). 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 local SO_2 emissions. Therefore, it is not possible to determine to what extent the SCP distribution is influenced by regional and foreign sources respectively. Rose & Juggins (1994) also showed a relationship between measured SCP surface-sediment fluxes and sulphur deposition in Scotland. Fly-ash particle analysis of surface sediments can contribute important information complementary to air monitoring programs. While air monitoring is momentary and for economic reasons normally restricted to a limited number of sites, numerous surface sediment samples give an integrated picture of the deposition and increase the spatial coverage and resolution (Wik & Renberg, 1991a).

Soils

We evaluated SCP deposition in soils of the northern Swedish province of Västerbotten (55 430 km²) (Wik & Renberg, 1987). 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. The SCP mainly accumulate in the thin organic horizon (horizons L–F according to Bridges, 1986, also 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. SCP are resistant to degradation and the biological activity of Boreal forest soils in general is low, and the soil has a long physical turnover time. It is likely that the total amount of SCP in soil (number of particles m⁻²) reflects the cumulative deposition since industrialisation began. However, the overwhelming amount of particles have been deposited since the Second World War.

The study area comprises 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 within 3–4 km of towns and industries had elevated values. More than 15×10^6 particles m⁻² occurred in the industrialized coastal areas. In the remote mountain area particle numbers were $>0.2 \times 10^6$ particles m⁻² (Fig. 5). The distribution of SCP in soil in the province agrees well with the distribution of industry, population, and prevailing wind conditions. However, the main SCP distribution pattern 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 (Ross & Granat, 1986). Even though we believe that the SCP distribution reflects primarily the fall-out from local and regional emissions, distant sources likely contribute to the concentrations.

This investigation by Wik & Renberg (1987) demonstrated that soil samples are useful tools in determining regional SCP deposition. The sampling technique is very simple and can be undertaken by inexperienced field assistants. Sampling sites are innumerable in natural forest regions, 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 integrated historical deposition can be studied.

Snow

Contemporaneous atmospheric deposition can be surveyed using sampling of precipitation. We have collected snow from various places in northern Sweden, including very remote areas. SCP are ubiquitous. Provided that there has been no extensive snow melt, the accumulated SCP deposition over weeks or months can be estimated using quantitative sampling of the

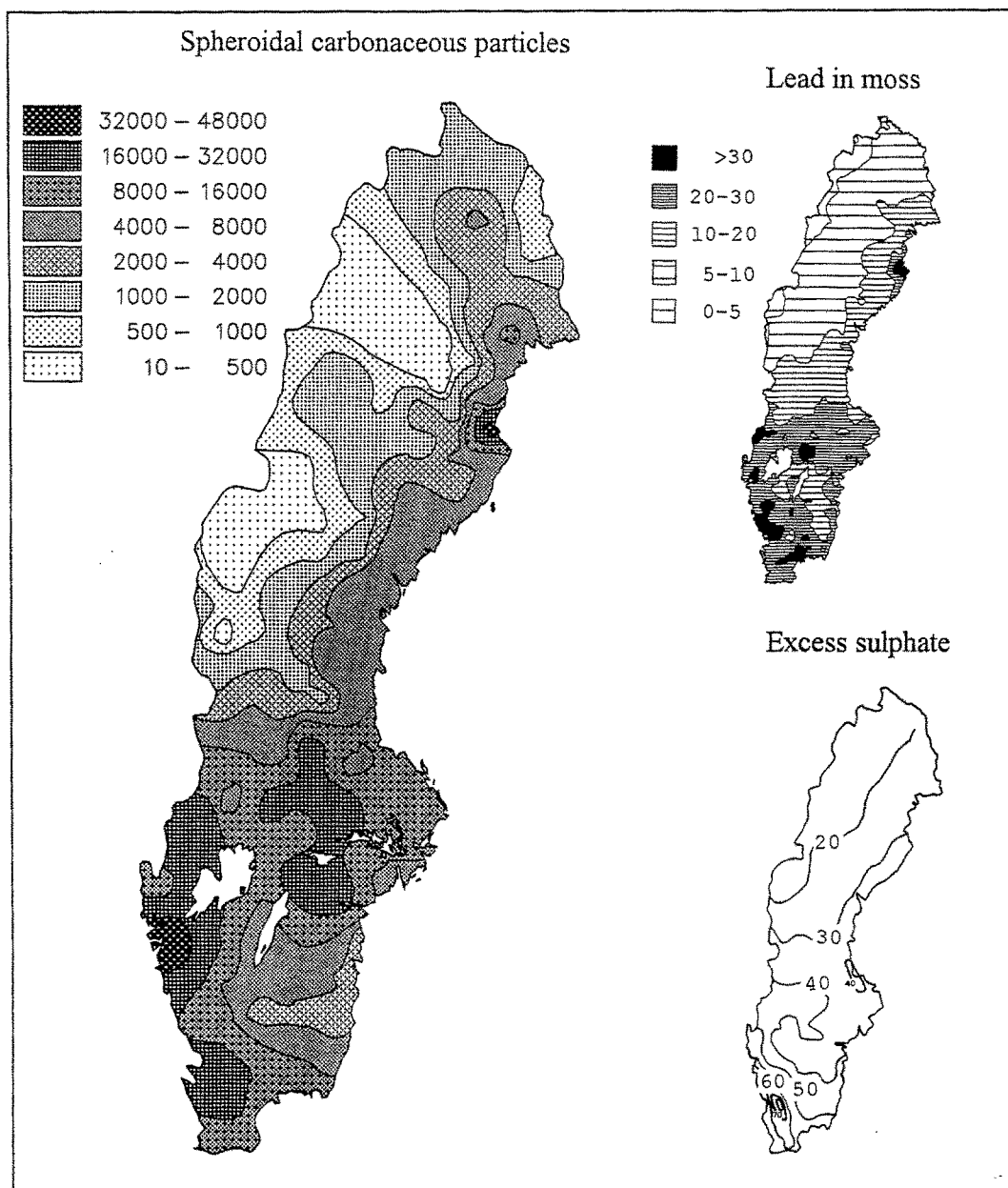


Fig. 4. Spheroidal carbonaceous particle concentrations in surface sediments (0–1 cm) of Swedish lakes (number g^{-1} dry sediment). The map is based on analyses of 114 lakes (re-drawn from colour map in Wik & Renberg, 1991a). To the right are two independent analyses of deposition of airborne pollutants for comparison; (above) is lead in moss in 1985 ($\mu\text{g g}^{-1}$ dry mass) and this map is based on samples from more than 800 sites (redrawn from Statens Naturvårdsverk 1987); (below) is annual excess sulphate wet deposition 1983–1987 ($\text{meq m}^{-2} \text{yr}^{-1}$) from the Swedish monitoring network (redrawn from Granat, 1989).

snow on the ground. For example we conducted a snow survey along a transect from a small central heating plant situated in Lycksele (9300 inhabitants) (Fig. 6). The snow represented all of January and February. The influence on SCP deposition by the heating plant, which used about 700 m^3 oil during the two

months, is clear. However, beyond about 10 km from the town, a constant value of about 10000 particles per m^2 occurred. This flux probably represented the 'background' fall-out level for this region at that time, with influence both from local and distant sources.

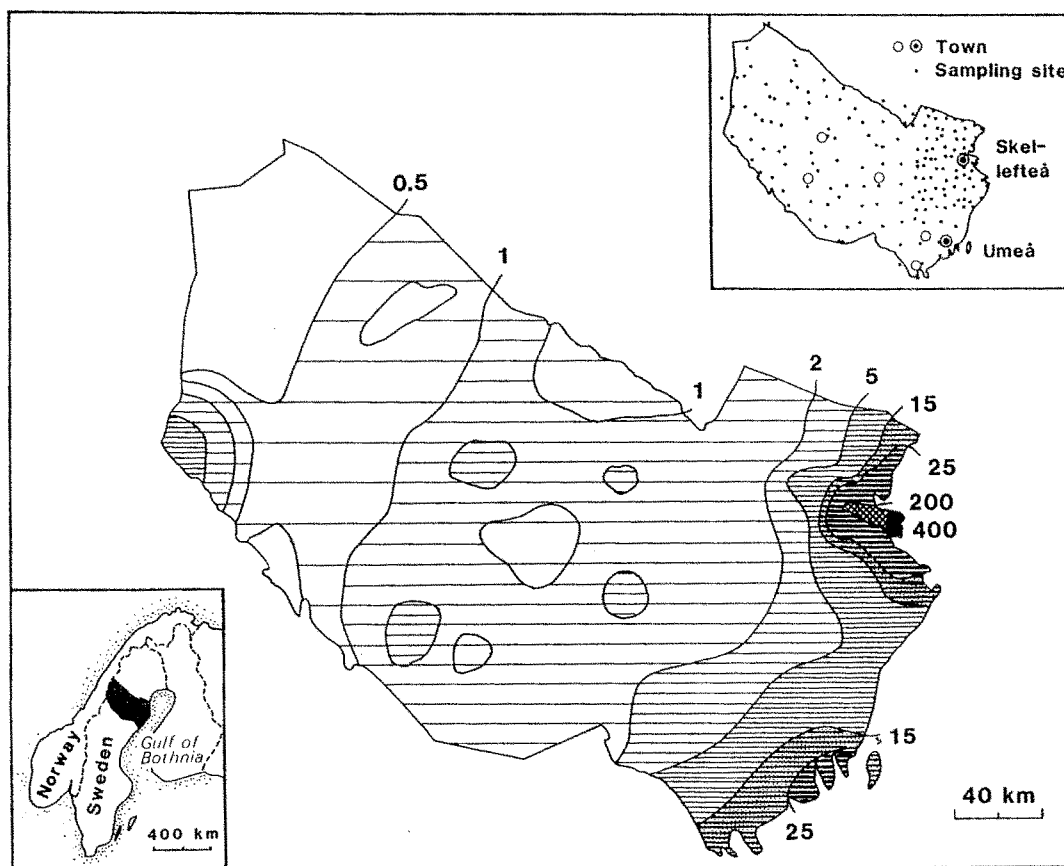


Fig. 5. Contour map showing the content of spheroidal carbonaceous particles (diam. $>10\mu\text{m}$) in L-F horizon of pine forest soil in Västerbotten province, N. Sweden. Results are expressed as number of particles $\times 10^6 \text{ m}^{-2}$ ground surface (from Wik & Renberg, 1987).

Dating of sediments

The SCP content of sediment profiles can be used as an indirect dating method for non-varved sediments. A prerequisite for SCP-dating is a profile previously dated by independent dating methods or by comparison with emission statistics. This model for SCP-dating is based on the identification of characteristic changes in the SCP concentration profiles, e.g. distinct increases or peaks (Renberg & Wik, 1984, 1985a). In Sweden, potential dating points are the slight increase in the middle of the 19th century, a peak during the 1930's, an increase about 1950 and the peak about 1970. The latter two changes are most characteristic and can be identified even when the sediment records are slightly mixed. A second model for SCP-dating, which in theory makes it possible to derive continuous dates, is based on SCP deposition fluxes (Renberg & Wik, 1984). 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 percent of the total SCP deposition during all times. These values must then be compared to a calibration curve 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 from a SCP-sediment profile dated by an independent dating method (varve counting or ^{210}Pb). Indirect SCP-dating has been used in several investigations (Renberg & Hellberg, 1982; Renberg & Wik, 1984, 1985a; Birks *et al.*, 1990; Tolonen *et al.*, 1992; Odgaard, 1993). Additionally, the SCP pattern may be used for correlation between cores from the same lake (Renberg & Hultberg, 1992).

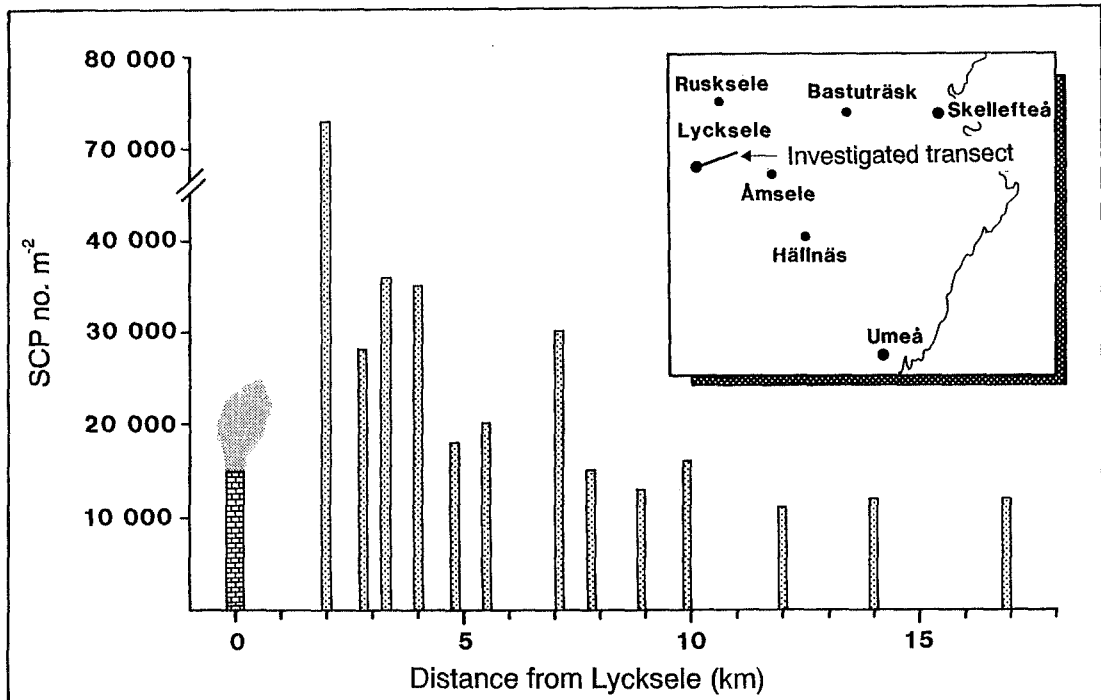


Fig. 6. Accumulation of spheroidal carbonaceous particles in the snow cover along a transect starting from the small town Lycksele. This snow was deposited 1 Jan–17 Febr 1985. Samples were taken with a wide plastic tube (diam. 8 cm; 7 samples for each site) that was pushed down into the snow to a distinct hard snow layer formed at Christmas time. The snow was melted, water was filtered through a 10 μm Nucleopore filter, the filter with residue was oxidized in hydrogen peroxide, the sample filtered again, and particles retained on this filter were counted (from Renberg, 1986).

Sediment distribution

With the intention of making a sediment budget for the post-war period for Gårdsjön (acidified in the 1950s; Renberg & Hellberg, 1982) using the SCP as a marker for the sediment distribution, a total of 55 sediment cores were collected in 1982 (Wik & Renberg, 1991b). Each core was long enough to cover the industrial period. We hypothesized that there should be a relationship between the SCP accumulation and the sediment accumulation. Field observations of a clear gradation in the thickness of the total lake-sediment deposit, from shallow to deeper water, demonstrated that sediment focusing had occurred during the post-glacial period. We expected, therefore, to find high total accumulation values of SCP (particles m^{-2}) in deep basins and lower values in shallower areas. There was, however, no correlation between SCP accumulation and water depth in the three transects or in the total core collection (Fig. 7b). The particles were more or less evenly distributed over the lake bottom ($61 \pm 6 \times 10^6$ particles m^{-2}). In the pine and spruce forest soil close to the lake about 40% more particles were found ($88 \pm 13 \times 10^6$

particles m^{-2} , $n = 18$). This is probably due to effective scavenging of airborne particulates by the conifers.

In order to test whether the hypothesis that SCP could be used as a sediment-accumulation indicator was false, or if acidification had changed the sedimentation patterns as suggested by Andersson (1985), SCP distribution was studied in two non-acidified lakes (Koltjärn and Stora Galten) and in Gårdsjön after liming.

In both Koltjärn (Fig. 7a) and Stora Galten (not shown) there was a statistically significant correlation between total SCP accumulation and water depth. These results suggest that SCP and other fine sedimentary components had accumulated in the deep areas in accordance with sediment focusing (Likens & Davis 1975). Laboratory experiments supported the assumption that SCP settle in a similar manner to other fine inorganic and organic sediment components (Wik & Renberg, 1991b).

In 1985, three years after the first liming of Gårdsjön, 30 new cores were sampled along the same transects as in 1982 (Wik & Renberg, 1991b). This time a significant correlation between SCP accumu-

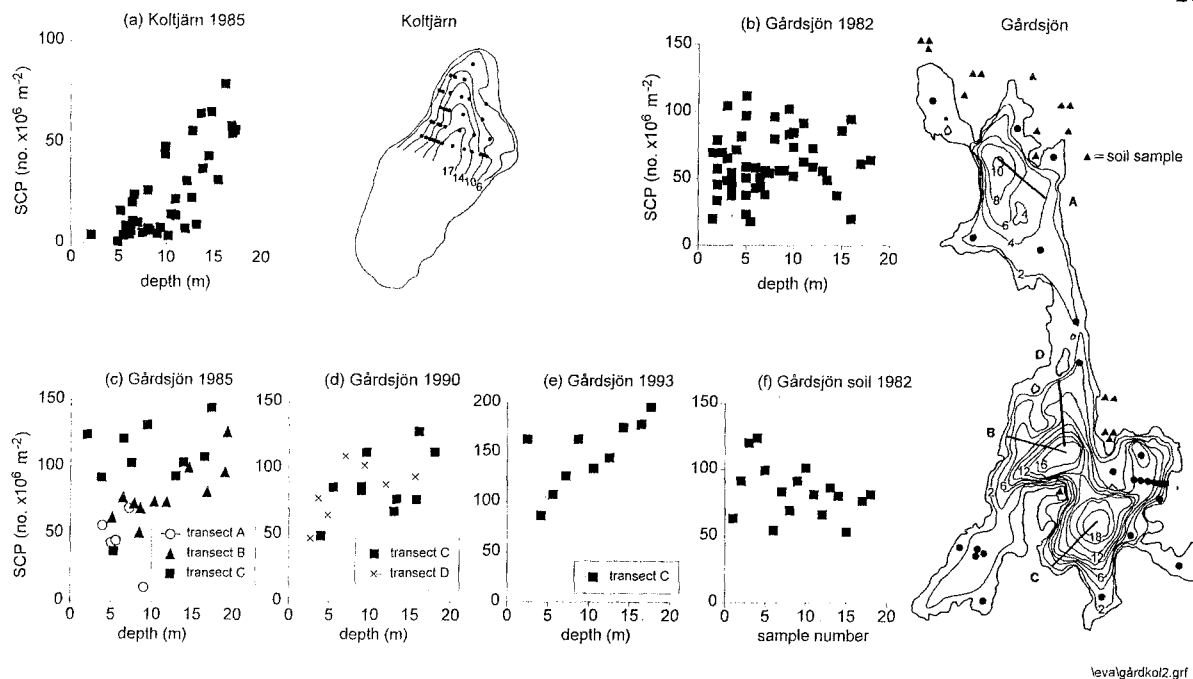


Fig. 7. Spheroidal carbonaceous particle accumulation (number of particles m^{-2} deposited during the industrial period) plotted against water depth from (a) a non-acidified lake (Koltjärn) and (b) an acidified, (c,d,e) later limed lake (Gårdsjön). Cores were sampled along transects (Koltjärn), and transects and dispersed sampling points (Gårdsjön), as indicated on the bathymetric maps. For details about the lakes and sampling see Wik & Renberg (1991b). The cores from Gårdsjön were sampled in 1982 (prior to liming), 1985, 1990 and 1993. Gårdsjön was limed in 1982, 1985, 1986, 1989 and 1992. The samples from 1993 were counted by E.-M. Diehl using a stereomicroscope with better optics, which may explain why total accumulation values this time were generally slightly higher. (f) shows the content of spheroidal carbonaceous particles in forest soil collected near the shore of Gårdsjön (number m^{-2} in horizons L–F). Partly from Wik & Renberg (1991b).

lation and depth was found for one of three profiles (Fig. 7c). In a second profile, some change towards increasing SCP accumulation with depth was observed. The results indicate that normal sedimentation processes had begun to work again. This was confirmed by a new investigation in 1990, after the lake had been treated with lime four times; now cores from two transects were used and both showed a clear correlation between SCP accumulation and water depth (Fig. 7d). These results were re-confirmed by analyses of cores taken in 1993 (Fig. 7e).

The results from Koltjärn, Stora Galten and Gårdsjön demonstrate that SCP can be used as a marker to study recent sediment distribution. The contrasting sediment distribution in the acidified lake Gårdsjön (in 1982 prior to liming) is probably caused by the trapping, incorporation and stabilisation of material by the mat of filamentous algae and *Sphagnum* spp., a feature typical for severely acidified lakes in Sweden (Lazarek, 1982; Grahn, 1985). The liming in 1982 and the following four re-limings (1985, 1986, 1989 and 1992) severely reduced the abundance of *Sphagnum* spp., and filamentous algae, and the dead material started to

decompose. This phenomenon of changed sedimentation patterns in acid lakes may have important implications for lake chemistry and biology as well as for the interpretation of palaeolimnological data (Anderson & Renberg, 1992).

Concluding remarks

Research in several countries over the last two decades has demonstrated that fly-ash particles can be recovered from environmental archives, identified, and used to study past and present deposition of airborne pollutants from fossil fuel combustion. In addition to coarse spheroidal carbonaceous particles discussed in this paper, aluminosilicate microspheres in lake sediments have also been studied (Rose, 1990b). Recent sediments of lakes from polluted areas, such as southern Sweden, leave a rather black residue after treatment with hydrogen peroxide. This black colour is not always correlated to the concentration of SCP. It is very likely caused primarily by fine black carbonaceous particles (soot). In winter, this black material is also often

visible on lake surfaces, when there is a water layer on the ice itself, or in snow (Davies *et al.*, 1984). Clearly, there is a challenge to develop methods to quantify these particles in sediments too.

Another challenge is to develop methods to identify particles from different fuels and combustion processes. The separation based only on particle morphology (Griffin & Goldberg, 1981) is too crude for detailed analyses. Development of a technique based on chemical characterisation using scanning electron microscopy and energy dispersive X-ray spectroscopy is in progress (Rose *et al.*, 1994; Alliksaar *et al.*, in prep). Such a method could help answer the question to what extent SCP distribution is influenced by local or long distance sources.

So far, most work has focused on carbonaceous particles as an indicator for the deposition of airborne pollutants derived from the combustion of fossil-fuels. However, SCP also deserve attention because they are carriers of metals, sulphur (Cheng *et al.*, 1976; Bacci *et al.*, 1983), 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 for chemical reactions, and in the atmosphere the catalytic oxidation of SO₂ to SO₄²⁻ is of special importance (Chang & Novakov, 1983). Carbonaceous particles are also strong adsorbents of PAH, and PAH adsorbed on carbonaceous particles are stabilised against 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 & Vittori, 1985). The possibility of carbonaceous particles interfering with natural weathering processes in soils is also worth considering.

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References

- Alliksaar, T., P. Hörstedt & I. Renberg, in prep. Characteristic fly-ash particles from oil-shale combustion found in lake sediments.
- Anderson, N. J. & I. Renberg, 1992. A palaeolimnological assessment of diatom production responses to lake acidification. *Environ. Pollut.* 78: 113–119.
- 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., M. Del Monte, A. Longhetto, A. Piano, F. Prodi, P. Redaelli, C. Sabbioni & A. Ventura, 1983. Characterization of the particulate emission by a large oil fired power plant *J. Aerosol. Sci.* 14: 557–572.
- Battarbee, R. W., N. J. Anderson, P. G. Appleby, R. J. Flower, S. C. Fritz, E. Y. Haworth, S. Higgitt, V. J. Jones, A. Kreiser, M. A. R. Munro, J. Natkanski, F. Oldfield, S. T. Patrick, N. G. Richardson, B. Rippey & A. C. Stevenson, 1988. Lake acidification in the United Kingdom 1800–1986 ENSIS, London, 66 pp.
- Bertine, K. K. & M. F. Mendek, 1978. Industrialization of New Haven, Conn., as recorded in reservoir sediments. *Environ. Sci. Technol.* 12: 201–207.
- Birks, H. J. B., F. Berge, J. F. Boyle & B. F. Cumming, 1990. A palaeoecological test of the land-use hypothesis for recent lake acidification in south-west Norway using hilltop lakes. *J. Paleolim.* 4: 69–85.
- Bridges, E. M. 1986. *World soils*. Cambridge University Press, New York, 128 pp.
- Broman, D., C. Näf, M. Wik & I. Renberg, 1990. The importance of spheroidal carbonaceous particles (SCPs) for the distribution of particulate polycyclic aromatic hydrocarbons (PAHs) in an estuarine-like urban coastal water area. *Chemosphere* 21: 69–77.
- Chang, S.-G. & T. Novakov, 1983. Role of carbon particles in atmospheric chemistry. In S. E. Schwartz (ed), *Trace Atmospheric Constituents: Properties, Transformations & Fates*. J. Wiley & Sons, New York: 191–219.
- Charles, D. F., M. W. Binford, E. T. Furlong, R. A. Hites, M. J. Mitchell, S. A. Norton, F. Oldfield, M. J. Paterson, J. Smol, A. J. Uutala, J. R. White, D. R. Whitehead & R. J. Wise, 1990. Paleocological investigation of recent lake acidification in the Adirondack Mountains, N.Y. *J. Paleolim.* 3: 195–241.
- Cheng, R. J., V. A. Mohnen, T. T. Shen, M. Current & J. B. Hudson, 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., D. S. Anderson, M. C. Whiting, J. P. Smol & S. S. Dixit, 1990. Alkalinity and pH of three lakes in northern New England, USA, over the past 300 years. *Phil. Trans. r. Soc., Lond. B* 327: 413–421.
- Davies, T. D., P. W. Abrahams, M. Tranter, I. Blackwood, P. Brimblecombe & C. E. Vincent, 1984. Black acidic snow in the remote Scottish Highlands. *Nature* 312: 58–61.
- Del Monte, M. & C. Sabbioni, 1984. Morphology and mineralogy of fly ash from a coal-fueled power plant. *Arch. Met. Biocl. B* 35: 93–104.
- Del Monte, M. & O. Vittori, 1985. Air pollution and stone decay: the case of Venice. *Endeavour* 9: 117–122.
- Del Monte, M., C. Sabbioni, A. Ventura & G. Zappia, 1984. Crystal growth from carbonaceous particles. *Sci. Tot. Envir.* 36: 247–254.

- Doubleday, N. C., M. S. V. Douglas & J. P. Smol. 1995. Paleoenvironmental studies of black carbon deposition in the High Arctic: a case study from Northern Ellesmere Island. *Sci. Tot. Environ.* 161: 661–668.
- Dunstan, T. D. J., R. F. Mauldin, Z. Jinxian, A. D. Hipps, E. L. Wehry & G. Mamantov, 1989. Adsorption and photodegradation of pyrene on magnetic, carbonaceous, and mineral subfractions of coal stack ash. *Envir. Sci. Technol.* 23: 303–308.
- Energy Statistics Yearbook 1989. United Nations, New York.
- Fisher, G. L., B. A. Prentice, D. Silberman, J. M. Ondov, A. H. Biermann, R. C. Ragaini & A. R. McFarland, 1978. Physical and morphological studies of size-classified coal fly ash. *Envir. Sci. Technol.* 12: 447–451.
- Flower, R. J., B. Rippey, N. I. Rose, P. G. Appleby & R. W. Battarbee, 1995. Palaeolimnological evidence for the acidification and contamination of lakes by atmospheric pollution in western Ireland. *J. Ecol.* 82: 581–596.
- Gay, A. J., R. F. Littlejohn & P. J. van Duin, 1984. Studies of carbonaceous cenospheres from fluidised-bed combustors. *Sci. Tot. Envir.* 36: 239–246.
- Goldberg, E. D., 1985. Black carbon in the environment. J. Wiley & Sons, New York, 198 pp.
- Goldberg, E. D., V. F. Hodge, J. J. Griffin, M. Koide & D. N. Edgington, 1981. Impact of fossil fuel combustion on the sediments of Lake Michigan. *Envir. 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 nederbördskemiska stationsnätet inom PMK, rapport från verksamheten 1988. Statens Naturvårdsverk SNV PM 3649, Solna, 64 pp. (in Swedish).
- Griest, W. H. & L. A. Harris, 1985. Microscopic identification of carbonaceous particles in stack ash from pulverized-coal combustion. *Fuel* 64: 821–826.
- Griffin, J. J. & E. D. Goldberg, 1975. The fluxes of elemental carbon in coastal marine sediments. *Limnol. Oceanogr.* 20: 256–263.
- Griffin, J. J. & E. D. Goldberg, 1979. Morphologies and origin of elemental carbon. *Science* 206: 563–565.
- Griffin, J. J. & E. D. Goldberg, 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. & E. D. Goldberg, 1983. Impact of fossil fuel combustion on sediments of Lake Michigan: A reprise. *Envir. Sci. Technol.* 17: 244–245.
- Jones, V., R. J. Flower, P. G. Appleby, J. Natkanski, N. Richardson, B. Rippey, A. C. Stevenson & R. W. Battarbee, 1993. Palaeolimnological evidence for the acidification and atmospheric contamination of lochs in the Cairngorm and Lochnagar areas of Scotland. *J. Ecol.* 81: 3–24.
- Kothari, B. J. & M. Wahlen, 1984. Concentration and surface morphology of charcoal particles in sediments of Green Lake, N.Y.: Implications regarding the use of energy in the past. *Northeast. Envir. Sci.* 3: 24–29.
- Lampi, P., K. Tolonen, T. Vartiainen & J. Tuomisto, 1992. Chlorophenols in lake bottom sediments: a retrospective study of drinking water contamination. *Chemosphere* 24: 1805–1824.
- Lazarek, S., 1982. Structure and function of a cyanophyten mat community in an acidified lake. *Can. J. Bot.* 60: 2235–2240.
- Likens, G. E. & M. B. Davis, 1975. Post-glacial history of Mirror Lake and its watershed in New Hampshire, USA: An initial report. *Verh. int. Ver. Limnol.* 19: 982–993.
- Medalia, A. I. & D. Rivin, 1982. Particulate carbon and other components of soot and carbon black. *Carbon* 20: 481–492.
- McCrone, W. G. & J. G. Delly, 1973. The Particle Atlas, II. Ann Arbor Science, Ann Arbor, 267 pp.
- Odgaard, B. V., 1993. The sedimentary record of spheroidal carbonaceous fly-ash particles in shallow Danish lakes. *J. Paleolim.* 8: 171–187.
- Peterson, K. F., 1972. Stoffbildning vid oljeeldning. Ph.D. thesis, The Royal Institute of Technology, 229 pp. (in Swedish).
- Raask, E., 1980. Quartz, sulphates and trace elements in p.f. 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., M. Demuyne, W. Dorrine & F. Adams, 1988. Characterization of oil fly ash particles by electron probe microanalysis. *Int. J. envir. 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., 1986. Kartläggning av deposition av kolhaltiga partiklar från olje- och kolförbränning. In Förbränningsteknisk Projektexposé – Proceedings. Energieforskningsnämnden Efn:UTR 1986: 1, Stockholm, 316–325 (in Swedish).
- Renberg, I. & T. Hellberg, 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. & H. Hultberg, 1992. A paleolimnological assessment of acidification and liming effects on diatom assemblages in a Swedish lake. *Can. J. Fish. Aquat. Sci.* 49: 65–72.
- Renberg, I. & J.-E. Wallin, 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. & M. Wik, 1984. Dating recent lake sediments by soot particle counting. *Verh. int. Ver. Limnol.* 22: 712–718.
- Renberg, I. & M. Wik, 1985a. Soot particle counting in recent lake sediments: An indirect dating method. *Ecol. Bull.* 37: 53–57.
- Renberg, I. & M. Wik, 1985b. Carbonaceous particles in lake sediments – pollutants from fossil fuel combustion. *Ambio* 14: 161–163.
- 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.* 4: 61–67.
- Rose, N. L., 1991. Fly-ash particles in lake sediments: Extraction, characterisation and distribution. Unpublished PhD thesis. University of London.
- Rose, N. L., 1994. A note on further refinements to a procedure for the extraction of carbonaceous fly-ash particles from sediments. *J. Paleolim.* 11: 201–204.
- Rose, N. L., 1995. Carbonaceous particle record in lake sediments from Arctic and other remote areas of the northern Hemisphere. *Sci. Tot. Envir.* 161: 487–496.
- Rose, N. & S. Juggins, 1994. A spatial relationship between carbonaceous particles in lake sediments and sulphur deposition. *Atmos. Env.* 28: 177–183.
- Rose, N., S. Juggins, J. Watt & R. Battarbee, 1994. Fuel-type characterization of spheroidal carbonaceous particles using surface chemistry. *Ambio* 23: 296–299.
- Ross, H. B. & L. Granat, 1986. Deposition of atmospheric trace metals in northern Sweden as measured in the snowpack. *Tellus* 38B: 27–43.

- Sandman, O., K. Eskonen & A. Liehu, 1990. The eutrophication history of Lake Särkinen, Finland and the effects of lake aeration. *Hydrobiologia* 214: 191–199.
- Shen, T. T., R. J. Cheng, V. A. Mohnen, M. Current & J. B. Hudson, 1977. Characterization of differences between oil-fired and coal-fired power plant emissions. *International Clean Air Congress*, 4. Tokyo: 386–391.
- Smith, D. M., J. J. Griffin & E. D. Goldberg, 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, 182 pp. (in Swedish).
- Tolonen, K., R. Haapalahti & J. Suksi, 1992. Comparison of varve dated soot ball chronology and lead-210 dating in Finland. In M. Saarnisto & A. Kahra (eds), *Laminated sediments, proceedings of the Workshop at Lammi Biological Station*. Geological Survey of Finland, Special Paper 14: 65–75.
- Wik, M., 1992. Environmental records of carbonaceous fly-ash particles from fossil-fuel combustion. PhD thesis. Department of Ecological Botany, University of Umeå, Sweden.
- Wik, M., I. Renberg & J. Darley, 1986. Sedimentary records of carbonaceous particles from fossil fuel combustion. *Hydrobiologia* 143: 387–394.
- Wik, M. & J. Natkanski, 1990. British and Scandinavian lake sediment records of carbonaceous particles from fossil-fuel combustion. *Phil. Trans. r. Soc., Lond. B* 327: 319–323.
- Wik, M. & I. Renberg, 1987. Distribution in forest soils of carbonaceous particles from fossil fuel combustion. *Water Air Soil Pollut.* 33: 125–129.
- Wik, M. & I. Renberg, 1991a. Recent atmospheric deposition in Sweden of carbonaceous particles from fossil-fuel combustion surveyed using lake sediments. *Ambio* 20: 289–292.
- Wik, M. & I. Renberg, 1991b. Spheroidal carbonaceous particles as a marker for recent sediment distribution. *Hydrobiologia* 214: 85–90.