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APPLICATION OF SPHERICAL FLY-ASH PARTICLES TO STUDY SPATIAL DEPOSITION OF ATMOSPHERIC POLLUTANTS IN NORTH-EASTERN ESTONIA

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Spherical fly-ash particles, emitted to the atmosphere in the high-temperature combustion process of fossil fuels, were found in considerable amounts in analysed snow samples of north-eastern Estonia. Spatial deposition of particles in snow cover is compared with the results of surface sediment samples of lakes. The results from snow characterise well the distribution of pollution sources and the distance from the main power plants in north-eastern Estonia. Variations in particle deposition of closely situated snow samples were found to be negligible. Fly-ash particle influxes in snow samples correlate well with modelled maximum concentration fields of fly-ash in the near-surface air layer.

Introduction

The development of industrialisation brings about a rapid increase in human impact on the environment. Emissions into the atmosphere, especially fossil-fuel combustion, have an essential impact on the environment and are one of the most important anthropogenic sources of several gaseous and solid pollutants affecting ecosystems. Most of the compounds emitted to the atmosphere and then deposited on the land are chemically mobile and do not leave good record in environment. This is particularly important when annual average or long-term distribution and deposition of pollutants is studied.

Due to the landscape patchiness the deposition of particulates on the land surface is very variable for the short time interval. Therefore palaeo-geographical approach enables to look at that process in time. Spherical fly-ash particles formed during the combustion of fossil fuels are due to their composition chemically more resistant and preserve well in both terrestrial and aquatic environments for centuries [1]. Being a part of fly-ash these particles can be used cursorily as general indicators to study atmospheric deposition of particulate pollutants from combustion.

Fly-ash emitted to the atmosphere during the combustion of fossil fuels consists of several components. Their proportion and composition can vary

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in a quite large scale depending on the type of fuel and the characteristics of thermal process. In case of high temperature in the furnace, there can be found two types of spherical particles in fly-ash [2–4]. First, so-called carbonaceous particles formed during incomplete combustion of the organic part of fuel, which are composed mainly of elemental carbon [5]. And second, inorganic ash spheres formed by the fusing of inorganic minerals within the fuel, which consist mainly of aluminosilicate glassy material [6–7]. The former particle type is dominating in fly-ash of liquid fuels like heavy and light fuel oils. The latter type of particles is most often represented in fly-ash of solid fuels (e.g. coal, oil shale, brown coal and peat). In coal and oil shale fly-ash versicolorous inorganic ash spheres, whose colour depends on the iron content of particles, are observed [8–9].

Since the middle of the 20th century, studies of fly-ash particles were connected with their physical characteristics (size distribution, morphology) chemical composition and problems of emission reduction [10–11]. In environmental and palaeogeographical studies these particles have attracted interest since the end of the 1970s and the beginning of the 1980s [12–13]. At present attention is more and more concentrated on the spatio-temporal distribution of spherical fly-ash particles [1, 14–15] and their usefulness as carriers of information about historical as well as contemporary deposition of atmospheric pollutants.

In order to study spread and deposition of airborne pollutants current work concentrates on north-eastern Estonia. This area has been and still is one of the biggest air polluters in the Baltic Sea region. Numerous thermal power plants using oil shale emitted annually about 70 thousand tonnes of fly-ash into the atmosphere in 1995–1998 [16]. During the highest energy production period in the 1970s, this number exceeded 250 thousand tonnes per year [17]. Due to the installation of purification systems to the power plants (PP) since the middle of the 1970s (1976–77 Ahtme PP; 1988–89 Kohtla-Järve PP) and reduction in electricity generation at the beginning of the 1990s, emissions of alkaline oxides and various trace metals affecting forest and bog ecosystems [18–19] have decreased.

North-eastern Estonia was chosen as study area as in this region there are well-defined pollution sources and fuels consumption statistics is well documented. Deposition of atmospheric impurities was earlier studied here in lake sediments and in mosses [8–9, 17, 20] and was found to be quite variable for study sites only few kilometres apart from each other. To find out whether these differences are connected with variations in deposition, it is necessary to know the deposition pathways and regularities of particulate emissions. In order to evaluate spatial deposition of fly-ash particles in north-eastern Estonia, in the current work particles present in snow samples are analysed and these results are compared with fly-ash particle concentration data obtained earlier from lake surface sediments [20] covering the last 3-5 years.

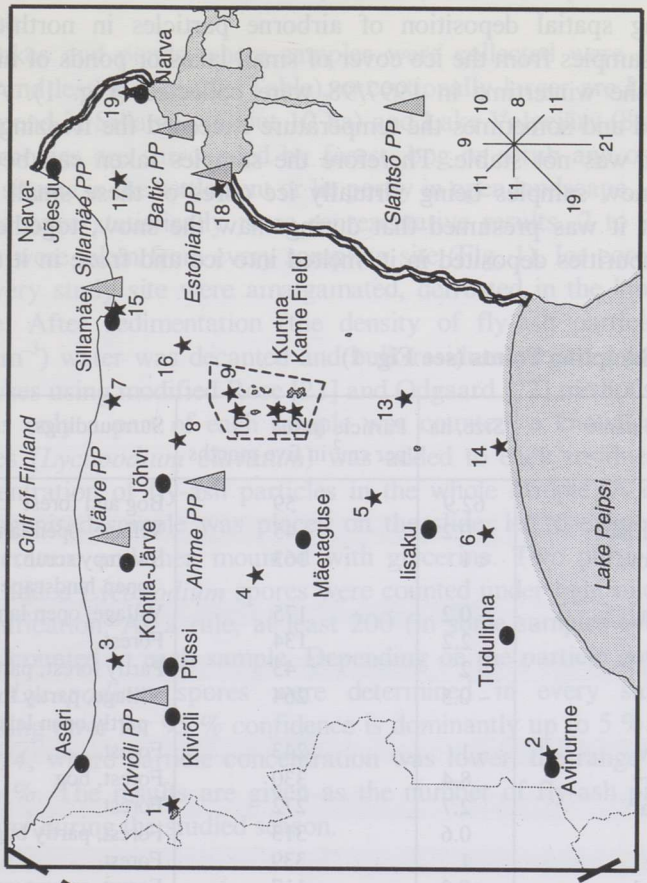

Fig. 1. Location of sampling points (★, numbers as in the Table) and pollution sources (Δ) in north-eastern Estonia, long-term average (1958–1991) wind direction in Jõhvi Meteorological Station

Material and Methods

For determining spatial deposition of airborne particles in north-eastern Estonia, snow samples from the ice cover of small lakes or ponds of nineteen sites covering the wintertime in 1997/98 were collected (Fig. 1). As this winter was mild and sometimes the temperature exceeded the freezing point, the snow cover was not stable. Therefore the samples taken can be called provisionally snow samples being virtually ice cores of these small waterbodies, whereat it was presumed that during thaw the snow, together with atmospheric impurities deposited in it, melted into ice and froze in it at cold weather.

Description of Sampling Points (see Fig. 1)

Site number and name	Size, ha	Particle influx per cm^2 in five months	Surroundings
1. Lake Uljaste	62.9	59	Bog and forest
2. Pond in Avinurme	~ 0.2	45	Village, open landscape
3. Pond in Moldova	< 1	163	Swampy scrub, open landscape
4. Pond in Kiikla	~ 0.2	175	Village, open landscape
5. Lake Jõuga	2.2	134	Forest
6. Lake Võhma	~ 2	43	Partly forest, partly bog
7. Pond in Voka	~ 0.5	264	Village, partly forest, partly open landscape
8. Lake Isandjärv	~ 1	243	Forest
9. Lake Valgejärv	8.4	330	Forest, bog
10. Lake Martiska	2.7	272	Forest
11. Lake Potri	0.6	313	Forest, partly bog
12. Lake Linajärv	1	339	Forest
13. Pond in Agusalu	< 0.2	117	Forest, swampy scrub
14. Pond in Remniku	< 0.5	112	Swampy scrub, partly forest
15. Pond in Sillamäe	~ 10	221	Town, scrub, open landscape
16. Pond in *Viivikonna* quarry	< 0.5	218	Partly scrub, partly forest
17. Pond in Laagna	~ 2	637	Scrub, open landscape
18. Pond near Estonian PP	< 0.5	1775	Scrub
19. Pond in Narva	~ 1	1320	Town, scrub, open landscape

The studied period in 1997–1998 embraced approximately five months, from permanent ice cover on the waterbodies since the end of October in 1997 until the collection of samples on March 25, 1998. According to the data of Institute of Meteorology and Hydrology in Estonia, days with average temperature below zero as well as snow cover were observed since October 22, 1997 in north-eastern Estonia. This was followed by warmer period in the middle of November, when snow cover melted but the ice

cover still remained on the small lakes. Another melting period was registered at the end of February continued with temperatures below zero in March.

Lakes and ponds where samples were collected were dominantly about 2 ha and less in size (the Table), exceptionally larger are Lake Uljaste (62.9 ha), pond in Sillamäe (about 10 ha) and Lake Valgejärv (8.4 ha). Mostly the waterbodies are surrounded by forest, bog or scrub and only few sampling sites situate in the settlement or lie partly in open landscape.

To have statistically more representative results, 2 to 3 total-length ice cores were taken from every sampling site (Fig. 1). Ice cores (143 cm^2 each) of every study site were amalgamated, defrosted in the lab and then left to settle. After sedimentation (the density of fly-ash particles is more than 1 $g\ cm^{-3}$) water was decanted and bulk residues prepared for fly-ash particle analyses using modified Rose [21] and Odgaard [22] methods.

As only a part of each sample was counted, a known amount of exotic spores (*Lycopodium clavatum*) was added to each residue to calculate the concentration of fly-ash particles in the whole sample. A drop of carefully homogenised sample was placed on the slide, let to evaporate at the room temperature and then mounted with glycerine. Two particle types together with added *Lycopodium* spores were counted under light microscope at 400× magnification. As a rule, at least 200 (in some samples even 400) particles were counted in each sample. Depending on the particle concentration up to 250 *Lycopodium* spores were determined in every sample. Statistical counting error for 95 % confidence is dominantly up to 5 %. For sites *1*, *2*, *6* and *14*, where particle concentration was lower, the range of uncertainty is ±7-9 %. The results are given as the number of fly-ash particles deposited per cm^2 during the studied season.

Results

Black-coloured inorganic ash spheres (IAS) as well as spherical carbonaceous particles (SCP) were counted in all snow samples. In addition to that almost colourless glassy IAS were found in considerable amounts in analysed snow samples.

Examination of ash from electrical precipitators of several oil shale operating power plants in north-eastern Estonia showed a great variety of spherical particles in it [8]. In all fly-ashes IAS with smooth and metallic shiny surface were represented. The colour of IAS-type particles varied from black and orange to colourless depending on the Fe content of the particle [9]. Colourless glassy IAS were found to be very abundant in the fly-ash of two power plants – Estonian and Baltic PP. There were also some porous SCP in fly-ash of Ahtme PP [8].

All particle types found in the samples were counted in analysed snow samples. Current work looks only at the distribution of black-coloured IAS and SCP.

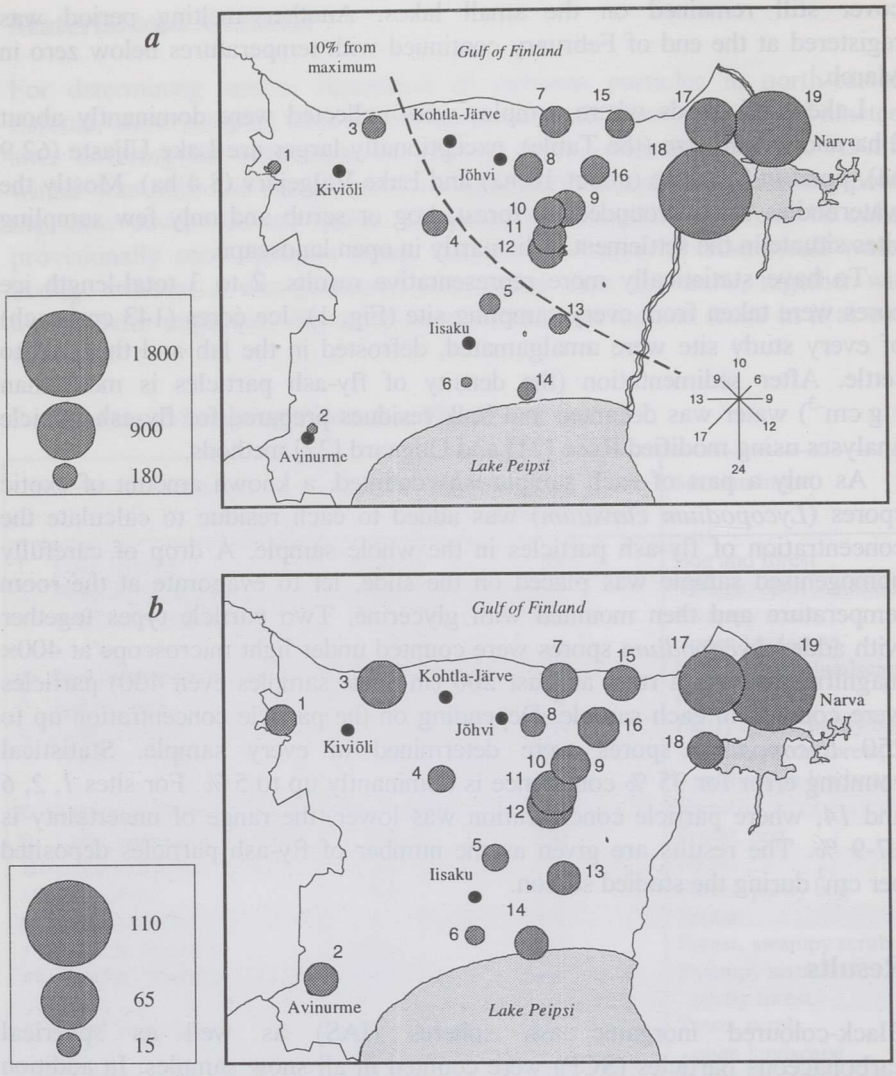

Fig. 2. Total fly-ash particles (sum of IAS and SCP) (*a*) and SCP (*b*) influx (number per cm^{-2} in 5 months) in 19 snow samples of north-eastern Estonia in 1997/98 (study sites numbered as in the Table). Wind rose for the studied period (November 1997 – March 1998) is also given

The influx values of black-coloured IAS as well as the sum of IAS and SCP per surface area show similar trends with the highest values in the north-easternmost area of Estonia and decreasing towards west and south-west (Fig. 2,*a*). The similarity of these two distributions is due to the fact that the overwhelming majority of totally deposited particles in snow samples are IAS. The share of SCP varies in different samples being less than 40 % in the westernmost samples and 10–20 % in most of the samples

east from the town of Kohtla-Järve. Some samples in the nearest vicinity to Estonian and Baltic PP have less than 5 % SCP in the entire amount of particles deposited.

In analysed snow samples the highest total influx of particles per surface area is in the north-easternmost area of Estonia, being more than 1000 particles per cm^{-2} in five months (Fig. 2,*a*). The smallest deposition values (around 50 particles per cm^{-2} in 5 months) were recorded in the case of sampling sites *1*, *2* and *6*.

The influx of SCP in snow samples varies dominantly between 15 and 40 particles per cm^{-2} in five months, only in the case of sites *17* and *19* it is higher, 68 and 109 SCP per cm^{-2} in five months, respectively (Fig. 2,*b*).

Discussion

The total particle influx per surface area in analysed snow samples follows most accurately the location of air-pollution sources in north-eastern Estonia, having the highest values in the very North-East of Estonia and decreasing towards west and south-west (Fig. 2,*a*). The main fly-ash polluters are schematically given in Fig. 1. Since the middle of the 1990s the majority of emissions (more than 90 %) are coming from two large power plants near the town of Narva – Baltic and Estonian PP. Also the chimneys of these power plants are the highest (150–250 m), which favour better spread of pollutants. The other fly-ash emitting sources in north-eastern Estonia (Ahtme PP, Järve PP, Kiviõli PP, Sillamäe PP and smaller heating plants of municipalities, mines and quarries) are of minor importance compared with atmospheric emissions of two above-mentioned plants. One former huge fly-ash polluter – Slantsy PP in Russia – is consuming natural gas since 1992 [23].

Although the prevailing wind direction in Estonia is from south and south-west (long-term average frequency 21 and 26 % respectively, measured in Jõhvi Meteorological Station; Fig. 1) [24], which carries atmospheric emissions north and north-east to Finland and Russia, the study area still has quite a high fly-ash deposition [23, 25]. Meteorological conditions were examined in detail also for the period under study in 1997/98. The recurrence of wind directions for this winter in north-eastern Estonia is quite variable within months, but the five-month average (Fig. 2,*a*) is approximately the same as the long-term annual observation results for this area (Fig. 1). According to the data of Jõhvi Meteorological Station (average for years 1958–1991), the wind has been blowing predominantly from south and south-west during autumns and winters (September-February), whereas at springs and summers different directions are distributed more evenly [24].

Although almost all the snow-sampling points are located upwind from the main emission sources (Estonian and Baltic PP), the fly-ash particle influx values (sum of IAS and SCP) in the samples are decreasing with an

increase in the distance from the closest of these two power plants to the sampling site (Fig. 3).

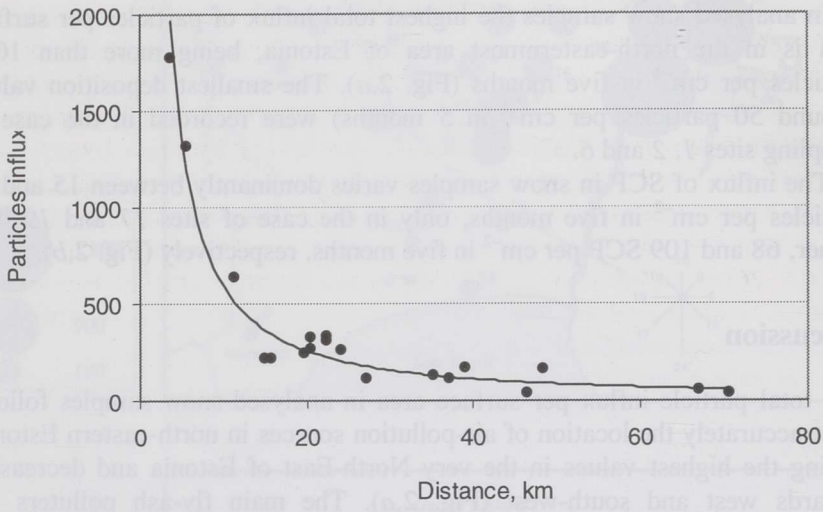

Fig. 3. Total fly-ash particle influxes (number cm^{-2} per 5 months) in nineteen snow samples compared with the distance (km) from the two main power plants of north-eastern Estonia

The impact of smaller emission sources in north-eastern Estonia and also transboundary pollution cannot be ignored, but their share is much less than the emissions from Estonian and Baltic PP. The deposition from the last-mentioned power plants is superimposed on the top of the background values and the impact of smaller sources. The highest influx values (site *18* and *19*) are probably due to the substantial role of dry deposition as well as snowfalls, which increase the deposition load close to the source. Similar rapid growth in the deposition rate of particles within 10 km from the power plants has been observed by other researchers, too (e.g., [1, 26]). Beyond about 10–15 km from the power plants the decrease in deposition declines rapidly, but still remains dependent on the distance from pollution sources.

As it has been conclusively proven, the washout of particles by snow is much more efficient than by rain [27]. Also the emissions are maximal during wintertime, as the fuel consumption is then 20–30 % (in small boilerhouses even 40–60 %) larger than in summer or as is annual average [16]. Therefore the daily deposition of fly-ash particles in snow should be higher than yearly average and especially around the pollution sources where snowfalls cause higher deposition load. If we compare fly-ash particle influx values in snow samples with computed fly-ash concentration fields for the near-surface air layer, then it is necessary to take into account calculated maximum pollution fields. According to Liblik *et al.* [16], these maximum

concentrations describe better the situation in winter when power plants work at higher load and when emission intensity of pollutants is maximal.

Fly-ash particle distribution in snow and fly-ash maximum concentration fields in 1997 [16] show similar trends. Higher values are recorded near Baltic and Estonian PP decreasing towards south and south-west. The isoline with 10 % from the maximum (counted or modelled) value is given in Fig. 2,*a*. There is quite a good correlation between fly-ash particle deposition in snow and calculated maximum near-surface concentration of fly-ash (R^2 = = 0.8; Fig. 4), although we should look at trends rather than quantitative relation. Generally the deposition pattern of fly-ash particles in snow samples in 1997/98 is similar to snow geochemical mappings carried out earlier [26, 28–29], only influx load of airborne particles has rapidly decreased since the 1980s.

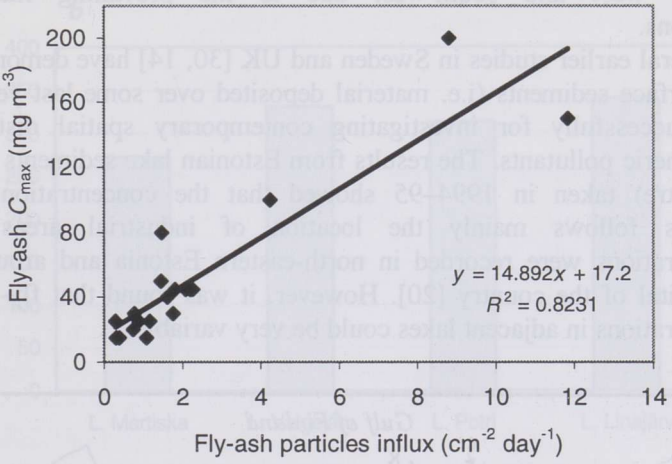

Fig. 4. The comparison of fly-ash particle influx values in the 19 snow samples of north-eastern Estonia in 1997/98 and modelled fly-ash maximum concentrations (C_{max}) in the overground air layer in 1997 [16]

The ratio of black-coloured IAS to SCP is greater than 1.0 for all snow cover sampling points. This ratio shows the relationship between solid and liquid fuels as IAS-type fly-ash particles are emitted mostly from solid fuels. Combustion of oil shale produces mainly IAS and only smaller and less effective power plants (like Ahtme PP) emit also some SCP. The main sources of SCP in north-eastern Estonia are several small municipal boilerhouses and Kohtla-Järve PP (the height of chimney 150 m), which consume also fuel oil during full load in winter time. Long-distance transport may also be one of the sources of SCP. The deposition of SCP in snow cover in 1997/98 was found to be quite even (Fig. 2,*b*), only in some sampling points in the northern part of north-eastern Estonia (Nos. *3*, *17* and *19*),

where majority of industry and population are located, a little bit higher influx of SCP was recorded.

As it was shown by study of lake surface sediments [20], there are only three areas in Estonia, where the IAS : SCP ratio is more than 1.0. The most extensive of these is north-eastern Estonia, where the above-mentioned ratio exceeds even 11.0 [20]. According to the snow samples, IAS : SCP ratio was found to be more than 5.0 for all sampling points east from the town of Kohtla-Järve (Fig. 5), and the maximum values (up to 70.0) were recorded in the nearest vicinity to Estonian PP. Compared with the highest values the ratio was only between 1.0 and 2.0 in the westernmost sampling sites (Nos. *1* and *2*; Fig. 5). The results of snow samples show that, just like the sediment surface samples [20], the influence of oil-shale-using power plants is very restricted to the north-easternmost part of the country and decreases quickly towards west and south-west due to the prevailing meteorological conditions.

Several earlier studies in Sweden and UK [30, 14] have demonstrated that lake surface sediments (i.e. material deposited over some last years) can be used successfully for investigating contemporary spatial distribution of atmospheric pollutants. The results from Estonian lake sediments (top half of centimetre) taken in 1994–95 showed that the concentration of fly-ash particles follows mainly the location of industrial areas – higher concentrations were recorded in north-eastern Estonia and around Tallinn, the capital of the country [20]. However, it was found that fly-ash particle concentrations in adjacent lakes could be very variable.

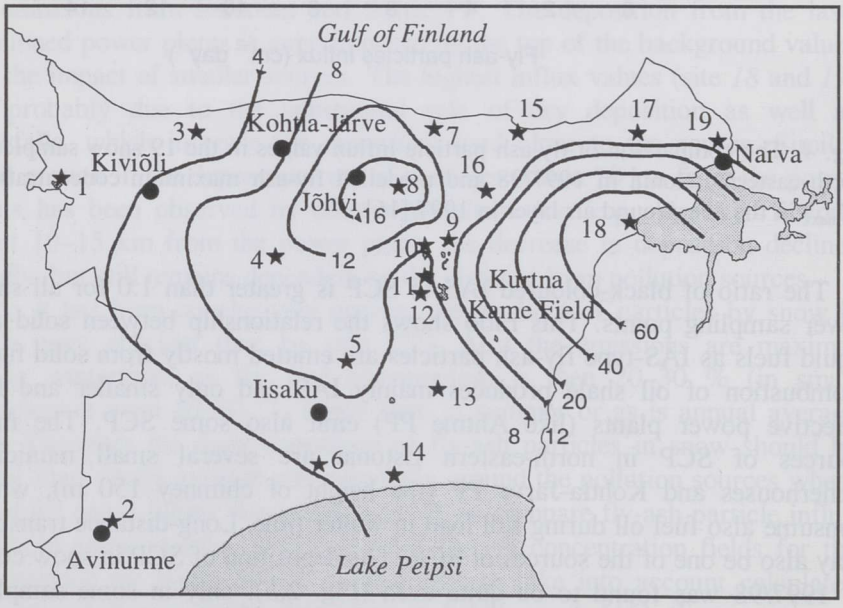

Fig. 5. IAS : SCP influx ratio in the 19 snow sampling points of North-East Estonia

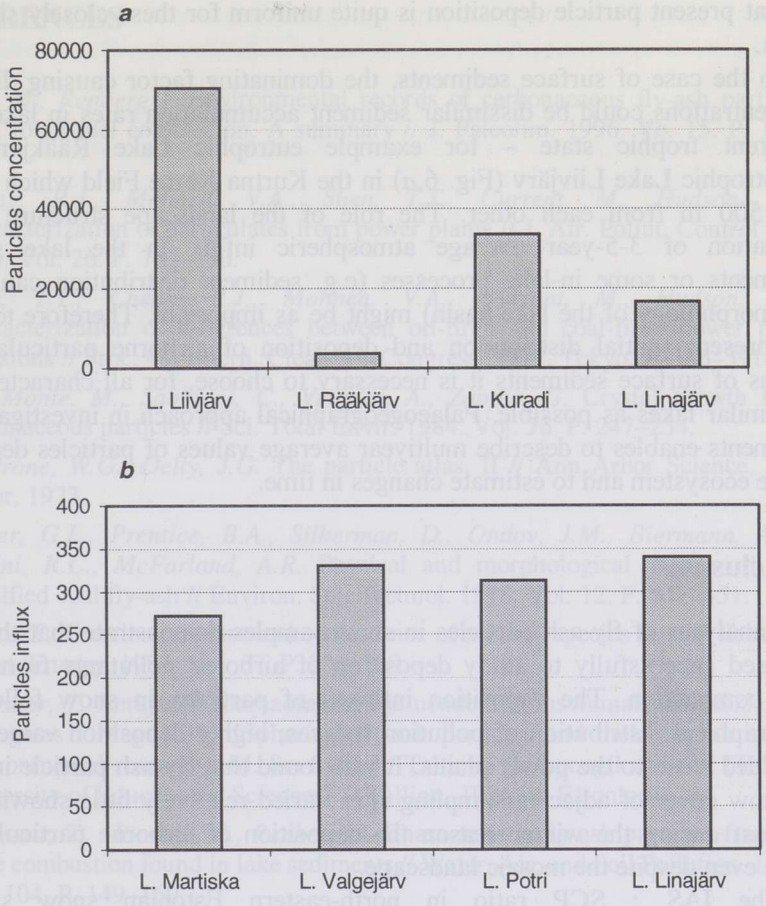

Fig. 6. Fly-ash particle concentration (number per gDM) in lake surface sediments (*a*) and influx (number per cm^{-2} in 5 months) in snow cover (*b*) of adjacent sampling sites in north-eastern Estonia

In north-eastern Estonia, where in the Kurtna Kame Field forty lakes lie on approximately 30 km^2 (see Fig. 1), the concentration of fly-ash particles in the uppermost sediment sample of four lakes just 6–8 km from each other had 5 to 20-fold differences (Fig. 6,*a*). At the same time fly-ash particle influx in snow samples of study sites in the same area some 5-6 km apart (points *9–12* on Fig. 1) showed that variations in the particle deposition per surface unit are quite small – 270–330 particles per cm^{-2} in five months (Fig. 6,*b*). Even though deposition fluxes of atmospheric pollutants are highly dependent on weather conditions and the landscape structure (the openness, topography, the surface roughness, etc.), in present occasion the variations in particle deposition in snow cover of these adjacent sampling sites are negligible. Whether this is the case during the winter season only is unclear, but according to the results obtained from snow samples it seems

that at present particle deposition is quite uniform for these closely situating lakes.

In the case of surface sediments, the dominating factor causing different concentrations could be dissimilar sediment accumulation rates in lakes with different trophic state – for example eutrophic Lake Rääkjärv and oligotrophic Lake Liivjärv (Fig. 6,*a*) in the Kurtna Kame Field which situate just 500 m from each other. The role of the landscape structure in the formation of 3-5-year average atmospheric influx in the lake surface sediments or some in-lake processes (e.g. sediment distribution caused by the morphology of the lake-basin) might be as important. Therefore to study the present spatial distribution and deposition of airborne particulates by means of surface sediments it is necessary to choose, for all characteristics, as similar lakes as possible. Palaeogeographical approach in investigation of sediments enables to describe multiyear average values of particles deposited in the ecosystem and to estimate changes in time.

Conclusions

The analyses of fly-ash particles in snow samples demonstrate that they can be used successfully to study deposition of airborne pollutants from fossil fuel combustion. The deposition influxes of particles in snow follow the geographical distribution of pollution sources; higher deposition values were recorded close to the power plants. It was found that fly-ash particle influxes in snow cover of adjacent sampling sites varied relatively little showing that at least during the winter season the deposition of airborne particulates is quite even despite the mosaic landscape.

The IAS : SCP ratio in north-eastern Estonian snow samples demonstrates that the deposition of IAS-type particles is very high here, which indicates the overwhelming share of local emission sources in the total influx of airborne pollutants. Due to the prevailing wind directions, the deposition of atmospheric particulates from oil-shale-using power plants is very restricted to the north-easternmost part of the country and decrease quickly towards west and south-west.

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