BALANCE OF ALKALINE AND ACIDIC POLLUTION LOADS IN THE AREA AFFECTED BY OIL SHALE COMBUSTION

M. KAASIK*

University of Tartu,
Institute of Environmental Physics
4 Tähe St., Tartu
51010 Estonia

Ü. SÕUKAND

Tartu Environmental Research Ltd.
4 Akadeemia St., Tartu
51004 Estonia

Field measurements of concentrations of SO_2 and NO_2 in the air and deposition of Ca^{2+}, Mg^{2+}, K^+, Na^+, SO_4^{2-}, NO_3^- and Cl^- in northeastern Estonia were carried out in the end of winter 1998/99. Concentrations in the air were measured by passive sampling method (Palmes tubes); snow samples were used to quantify the deposition loads. The measurement domain covered entire Ida-Viru County, eastern part of Lääne-Viru County and a few sites in Jõgeva County. These measurements and comparison with earlier investigations show that in wintertime most of sulfate over the area affected by oil-shale industrial complex appears to be deposited with fly ash particles. The regression formulae for wintertime sulfate and calcium deposition loads for oil-shale region are derived. The inhomogenous chemical composition of fly ash and influence of other (domestic, traffic) emissions are suggested as possible factors affecting the ratio of sulfate and calcium deposition loads.

Introduction

Atmospheric emissions from the industrial complex in the North-East of Estonia consist mainly of (1) alkaline particles (fly ash and cement dust [1, 2]) and (2) sulfur dioxide. Although considerably decreased during recent two decades [3], both emissions remain still dominant in the total air pollution from Estonia. Nitrogen dioxide emissions are also remarkable. Due to high stacks and location near the state border the pollutants from Narva Estonian and Baltic power plants (PP) contribute seriously to the transboundary pollution transport.

---

* E-mail: *marko@apollo.aai.ee*

Alkaline and sulfur deposition remains still relatively high near Narva power plants [4]. Conditions are unfavourable for *Sphagnum* species and for the bog ecosystem as whole, but after the decrease in alkaline loads some revival processes are observed on some bogs located at the Kurtna Landscape Reserve [5].

The fly ash and sulfur dioxide emissions from Narva PP are too high considering the regulation of the Minister of environment (No. 60 from October 20, 1998, valid for existing power plants beginning from 2003). To meet the requirements, an extensive reconstruction of power plants is planned for a few forthcoming years. It foresees to decrease the present level of fly ash emissions 10–12 times. This has been achieved experimentally using the new purification system at one section of Estonian Power Plant. Reconstruction of combustion technology enables reduction of sulfur dioxide emissions as well [6].

This paper is aimed to quantify the present air pollution levels. The synopsis is based mainly on the original field measurement data collected during the late winter of 1999. Some former measurements and theoretical constructions are used to clarify relationships between different air pollution factors.

Experimental Methods

Sulfur dioxide concentrations in the air were measured using passive samplers from Swedish Environmental Institute (IVL) [7]. Nitrogen dioxide concentrations were measured using the Palmes tubes from *Tartu Environmental Research* Ltd. [8]. Both producers performed chemical analyses of their samplers. SO_2 was measured at eighteen and NO_2 at nine sites (Table 1). Two parallel samples were taken for NO_2 in each site. For SO_2 parallels were used only in four sites (to check the random error as recommended by IVL). The samplers were installed in natural or semi-natural landscape, typically in the tree at 1–2 m height. Samplers were installed on February 6–10, 1999 and collected on February 20 – March 1 (NO_2) and February 27 – March 13 (SO_2). So the samplers for NO_2 were in operation for nearly two weeks and samplers for SO_2 nearly one month as recommended by their producers.

Deposition fluxes of fly ash were estimated from snow samples. The method has been developed and tested earlier [4]. Snow samples (41 sites in Ida-Viru and Lääne-Viru counties) were collected from February 25 to March 13 (two background samples from Jõgeva County on March 20). Considering that permanent snow cover accumulated since the second week of January, the average snow cover duration before sampling was 58 days. Snow was 40–70 cm thick, the average water equivalent was 90 l/m^2 (Table 2).

Table 1. **Positions, Sampling Times, and Concentrations of Sulfur Dioxide and Nitrogen Dioxide in Northeastern Estonia, February – March 1999 (Site Numbering is Unified with Snow Samples (Table 2))**

Nr.	Site	Latitude (N)			Longitude (E)			Begin date	End date (SO$_2$)	End date (NO$_2$)	SO$_2$, $\mu g/m^3$	NO$_2$, $\mu g/m^3$
		°	'	''	°	'	''					
3	Kulgu	59	19	25	27	56	15	10-Feb	8-Mar	25-Feb	4.9	4
5	Lemmaku	59	1	10	27	8	28	6-Feb	27-Feb	–	4.2	–
6	Metsküla	59	7	59	27	12	37	6-Feb	27-Feb	–	4.6	–
10	Soonuka	59	8	54	26	37	49	11-Feb	13-Mar	1-Mar	4.2	4
11	Agusalu	59	5	17	27	37	31	7-Feb	6-Mar	–	4.5	–
12	Gorodenko	59	8	36	27	48	37	7-Feb	6-Mar	20-Feb	2.4	3
13	Jaama	59	1	40	27	40	14	7-Feb	6-Mar	–	3.7	–
16	Pootsiku	59	4	6	27	24	40	7-Feb	7-Mar	20-Feb	3.7	3
21	Puhatu mv.	59	11	0	27	38	39	7-Feb	6-Mar	20-Feb	4.3	5
25	Martiska	59	15	50	27	34	12	7-Feb	8-Mar	–	4.2	–
26	Oru-Kurtna	59	19	21	27	33	28	7-Feb	8-Mar	20-Feb	4.3	5
27	Sirgala	59	19	50	27	48	4	10-Feb	8-Mar	–	5.5	–
30	Estonian PP	59	15	44	27	54	46	10-Feb	8-Mar	25-Feb	3.5	3
31	Baltic PP	59	20	39	28	7	56	10-Feb	8-Mar	–	4.7	–
32	Riigiküla	59	25	26	28	6	38	10-Feb	8-Mar	–	7.7	–
33	Ontika	59	25	44	27	17	12	10-Feb	8-Mar	25-Feb	9.3	8
34	Kiikla	59	16	55	27	16	42	6-Feb	8-Mar	20-Feb	5.1	4

All sulfur dioxide and nitrogen dioxide measurements were accompanied by snow sampling at the same site. Snow samples were taken in the end of passive air probe sampling; therefore the air probe sampling covered nearly the second half of snow accumulation period. Ca^{2+}, Mg^{2+}, Na^+, K^+, SO_4^{2+}, NO_3^- and Cl^- ions were analysed in the snow water by ion chromatographic method [9] and NH_4^+ and NO_2 nitrogen by flow analysis (CFA) and spectrum detection (ISO 11732:1997) at *Tartu Environmental Research* Ltd. Also pH of snow water was measured.

The sampling network was irregular, but optimized to cover the territory. The sites were chosen slightly closer to each other near the major pollution sources (Narva PP and *Kunda Nordic Cement* Ltd.) to cover representatively the expected highest pollution levels. Geographical co-ordinates of sites were determined using GPS. The kriging algorithm was used to interpolate the pollution levels to a regular grid (for mapping). The schematic map with sampling sites is presented in Fig. 1. Wind blew predominantly from southern and western directions as usual for Estonian winters.

The described field study was the most extensive one since 1985 [10, 11] (then snow was sampled from 80 sites in Ida-Viru and Lääne-Viru counties and from near-border areas of Russia). These data are used below as well as snow pollution measurements by M. Kaasik from 1996 [4] and 1994 (partially published in [12]).

Table 2. Positions, Sampling Times and Deposition Fluxes to the Snow of Anions and Cations in Northeastern Estonia, 1999

Number and site name	Northern latitude			Eastern longitude			Water equivalent, l/m²	Begin date	End date	pH	Deposition fluxes, mg/m² per day								
	°	'	"	°	'	"					NH_4^+	NO_2^-	NO_3^-	Cl^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Na^+	K^+
1. Ranna-Pungerja	58	59	20	27	10	12	75	7 Jan.	25 Febr.	5.7	0.11	0.05	1.42	1.44	1.0	3.5	0.44	2.60	0.32
2. Jõuga-Kuremäe	59	9	30	27	24	45	84	"	"	6.1	0.24	0.03	2.28	1.36	4.5	5.3	0.50	2.06	0.29
3. Kulgu	59	19	25	27	56	15	85	"	"	7.9	0.20	0.03	2.16	3.48	19.1	17.4	1.27	1.69	0.64
4. Mäetaguse	59	14	26	27	15	48	88	"	"	6.1	0.25	0.02	2.30	1.06	4.5	5.2	0.41	1.79	0.52
5. Lemmaku	59	1	10	27	8	28	91	"	"	7.1	0.21	0.02	2.53	2.15	3.0	4.8	1.09	2.68	0.30
6. Metsküla	59	7	59	27	12	37	80	"	"	5.2	0.16	0.01	1.67	0.80	1.9	2.4	0.28	2.20	0.19
7. Varessaare	59	10	10	27	6	44	101	"	1 March	5.3	0.20	0.01	2.76	2.54	3.7	4.1	0.43	3.32	0.16
9. Lepassaare	59	8	19	26	53	28	104	"	"	7.0	0.23	0.01	2.86	2.15	3.5	6.8	0.94	2.93	0.18
10. Soonuka	59	8	54	26	37	49	75	"	"	6.1	0.11	0.01	1.95	1.19	1.6	2.8	0.35	2.27	0.11
11. Agusalu	59	5	17	27	37	31	50	5 Febr.	"	5.9	0.51	0.02	2.48	5.18	2.9	1.8	0.33	0.56	0.33
12. Gorodenko	59	8	36	27	48	37	95	7 Jan.	"	6.6	0.25	0.01	1.99	0.59	1.8	2.5	0.31	0.41	1.10
13. Jaama	59	1	40	27	40	14	157	"	"	6.2	0.50	0.02	3.02	0.83	2.4	3.3	0.23	0.59	1.84
14. Alajõe	59	1	23	27	23	14	104	"	"	5.7	0.25	0.02	2.00	0.39	1.4	3.5	0.19	0.29	0.14
15. Imatu	59	6	8,2	27	31	0,5	58	"	"	5.3	0.25	0.01	1.21	0.59	1.1	1.4	0.10	0.21	0.21
16. Pootsiku	59	4	5,7	27	24	40	102	"	"	5.9	0.35	0.01	2.04	0.56	2.1	2.1	0.19	0.38	0.21
21. Puhatu	59	11	0	27	38	39	115	"	6 March	6.4	0.33	0.01	3.51	1.50	4.7	3.4	0.57	1.01	0.28
22. Puhatu	59	9	26	27	40	56	71	"	7 March	6.6	0.26	0.01	2.14	1.57	2.1	2.1	0.33	1.21	0.25
23. Dobrina	59	8	24	27	43	51	111	"	"	6.3	0.24	0.02	2.83	1.28	2.8	3.8	0.62	0.79	0.41
24. Puhatu	59	10	41	27	43	19	113	"	"	6.6	0.20	0.02	2.21	1.02	2.9	3.8	0.58	0.73	0.27
25. Martiska	59	15	50	27	34	12	75	"	8 March	7.2	0.24	0.02	1.83	1.11	4.3	8.3	0.55	0.59	0.23
26. Oru-Kurtna	59	19	21	27	33	28	117	"	"	7.5	0.33	0.06	2.50	1.59	8.4	8.8	0.91	0.80	0.31
27. Sirgala	59	19	50	27	48	3,5	123	"	"	7.3	0.26	0.02	2.35	1.21	6.7	16.6	1.21	0.69	0.16

Table 2. Positions, Sampling Times and Deposition Fluxes to the Snow of Anions and Cations in Northeastern Estonia, 1999 (ending)

| Number and site name	Northern latitude			Eastern longitude			Water equivalent, l/m²	Begin date	End date	pH	Deposition fluxes, mg/m² per day								
	°	'	"	°	'	"					NH_4^+	NO_2^-	NO_3^-	Cl^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Na^+	K^+
28. Mustjõe	59	16	8	27	49	21	100	7 Jan.	8 March	7.4	0.34	0.02	1.85	1.27	6.7	8.3	0.43	0.62	0.30
29. Narva jõgi	59	13	35	27	53	53	82	"	"	7.2	0.19	0.02	1.88	0.96	6.6	6.4	0.45	0.33	0.22
30. Estonian PP	59	15	44	27	54	46	114	"	"	6.9	0.24	0.02	1.69	0.76	3.8	5.9	0.23	0.55	0.13
31. Baltic PP	59	20	39	28	7	56	55	"	"	7.8	0.36	0.01	2.10	2.01	8.9	8.1	1.00	0.45	0.58
32. Riigiküla	59	25	26	28	6	38	77	"	"	8.4	0.23	0.03	1.59	2.18	16.7	15.4	1.14	0.28	0.62
33. Ontika	59	25	44	27	17	12	67	"	"	6.4	0.43	0.01	1.38	1.67	2.2	2.4	0.33	0.39	0.14
34. Kiikla	59	16	55	27	16	42	101	"	"	7.0	1.24	0.02	2.39	1.67	2.9	4.6	0.69	1.00	0.78
35. Kalmaküla	58	54	15	26	56	35	77	"	13 March	4.0	0.21	0.06	1.21	0.25	0.7	1.2	0.22	0.28	0.12
36. Soonuka	59	8	54	26	37	49	13	"	"	4.8	0.04	0.00	0.22	0.08	0.2	0.2	0.02	0.05	0.05
37. Ubja	59	23	37	26	27	12	102	"	"	5.4	0.77	0.03	1.46	0.61	0.9	1.5	0.20	0.39	0.16
38. Kunda-Aru	59	28	33	26	28	20	99	"	"	8.1	0.17	0.03	1.42	0.62	1.8	5.9	0.30	0.29	0.26
39. Kunda	59	30	9,3	26	30	44	99	"	"	10.2	0.27	0.05	2.09	1.67	16.7	25.8	1.22	0.65	1.67
40. Viru-Nigula	59	28	4,1	26	39	33	105	"	"	4.8	0.27	0.02	1.72	1.04	1.6	2.6	0.24	0.70	0.31
41. Uljaste	59	22	21	26	46	36	98	"	"	5.5	0.25	0.01	1.60	0.95	2.4	2.7	0.23	0.74	0.29
42. Kiviõli	59	21	31	26	56	31	49	"	"	9.2	0.07	0.02	0.81	0.76	9.1	7.3	0.84	0.23	0.22
43. Lüganuse	59	23	21	27	0	27	47	"	"	6.8	0.14	0.01	0.90	0.55	1.2	1.8	0.17	0.30	0.20
44. Aa	59	24	15	27	10	19	98	"	"	6.7	0.31	0.01	1.80	0.88	2.9	3.5	0.24	0.45	0.18
45. Peeri	59	22	30	27	19	50	89	"	"	6.8	0.23	0.01	1.28	0.70	2.7	3.4	0.26	0.34	0.33
46. Toila	59	24	7	27	30	18	108	"	"	7.5	0.24	0.02	1.85	0.75	5.8	7.0	0.52	1.05	0.25
47. Atsalama	59	13	35	27	26	9,5	118	"	"	6.7	0.42	0.03	2.17	0.80	3.1	4.7	0.44	0.44	0.25
49. Saare	58	42	3,8	26	45	16	93	"	"	6.7	0.08	0.06	1.48	1.55	1.2	1.7	0.25	0.97	0.37
50. Saduküla	58	38	36	26	22	2,7	96	"	20 March	6.7	0.15	0.02	1.42	0.39	0.7	1.0	0.15	0.29	0.24
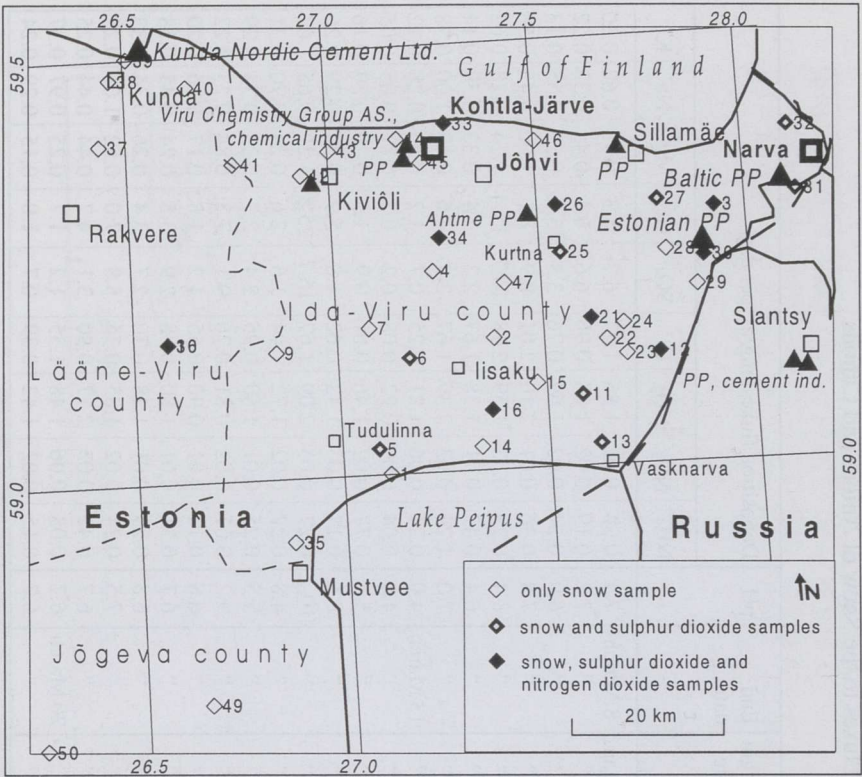
Fig. 1. Schematic map of research area with sampling site numbers (See Tables 1 and 2). Main pollution sources are marked with black triangles, geographical co-ordinates (latitude – longitude in degrees) are used

Results

Measured sulfur dioxide concentrations in the air (Table 1) are low in the southern part of Ida-Viru County and slightly enhanced in the northern part, especially at Ontika and Riigiküla. Nitrogen dioxide concentrations are slightly enhanced at Ontika, which is 2–3 km north-east from Kohtla-Järve (55,000 inhabitants, local power plant, chemical industry). The SO_2 concentrations at Riigiküla (about 10 km north from Baltic Power Plant and 20 km NE from Estonian PP) are probably enhanced due to emissions from Narva PP (Fig. 2). The NO_2 concentrations at all sites except Ontika are at the usual background level in Estonia (about 3 $\mu g/m^3$).

The results of snow water analyses are given in Table 2. The loads of calcium (Fig. 3) and sulfur (Fig. 4) are definitely higher near Narva PP, Kiviõli and Kunda (the site named Kunda is located 1 km west and Kunda-Aru 4 km south-west from the cement factory). Loads in most remote sites (e.g. Saduküla, Jõgeva County) are 10–20 times lower. The Ca^{2+} and SO_4^{2-} loads at the most polluted sites have decreased about 5–10 times since the middle of eighties [10].
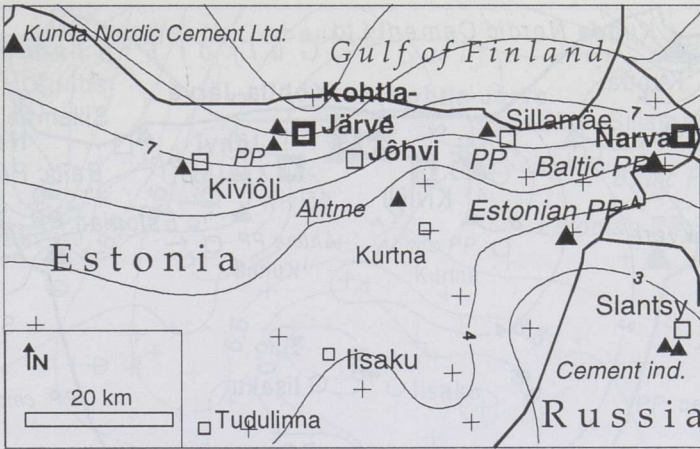
Fig. 2. Average sulfur dioxide concentrations in northeastern Estonia, February – March 1999, µg/m³ (crosses – sampling sites, triangles – main pollution sources)

Fig. 3. Average calcium deposition loads in northeastern Estonia, January – March 1999, mg/m² per day (crosses – sampling sites, triangles – main pollution sources)
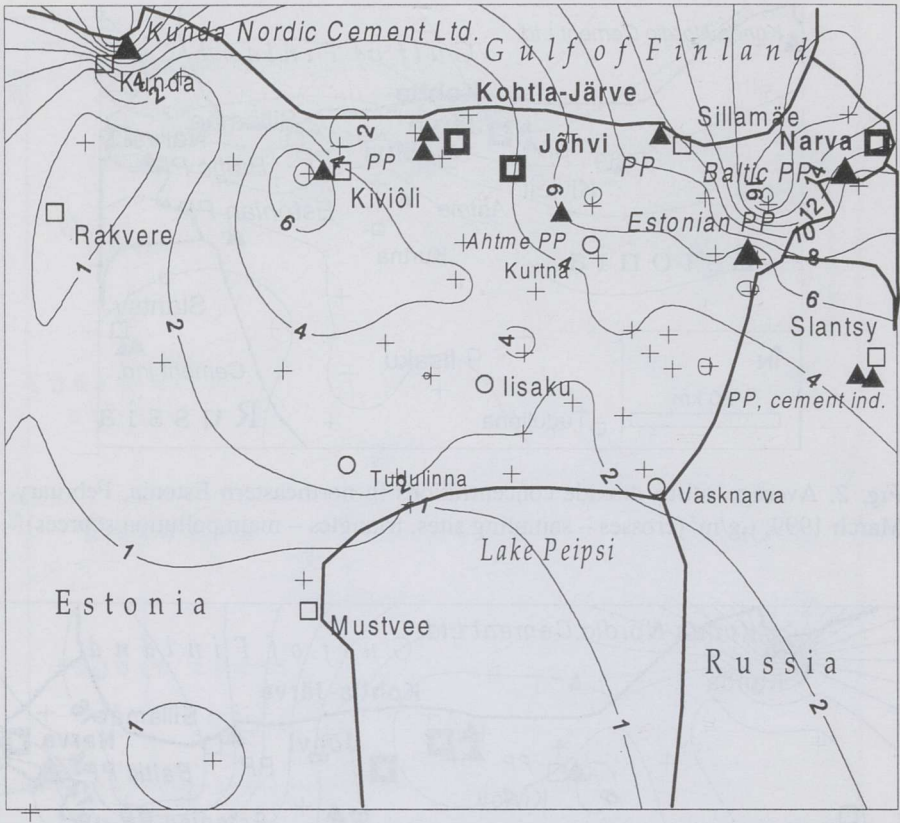
Fig. 4. Average sulfate deposition loads in northeastern Estonia, January – March 1999, mg/m² per day (crosses – sampling sites, triangles – main pollution sources)

A remarkable part of magnesium, chlorine and nitrate loads seems to be related to the oil-shale complex, but the differences from remote areas are less than those for calcium and sulfate. The Na^+, K^+, NO_2^- and NH^{4+} loads seem to originate mainly from other sources like domestic heating, agricultural activities and long-distance transport. The alkaline character of industrial pollution is still obvious despite the decrease in pollution loads. The value of pH (Fig. 5) in the most polluted areas is 7–9 *versus* 4–6 in remote areas (nearly the same as during the winter 1984/85 [10]). This is not surprising, because the proportions of alkaline Ca^{2+} and Mg^{2+} and acidic SO_4^{2-} and Cl^- loads are not very much changed. The alkalinity of precipitation is considerably decreased in Kunda: the recent pH was 8–10 *versus* 10–12 during 1984/85 [11].

All statistically significant correlations (at the 95 % confidence level) between deposition loads of studied components are presented in Fig. 6. Calcium, sulfate and magnesium are related most closely with each other. Other components, especially nitrite and ammonium have much weaker connections.
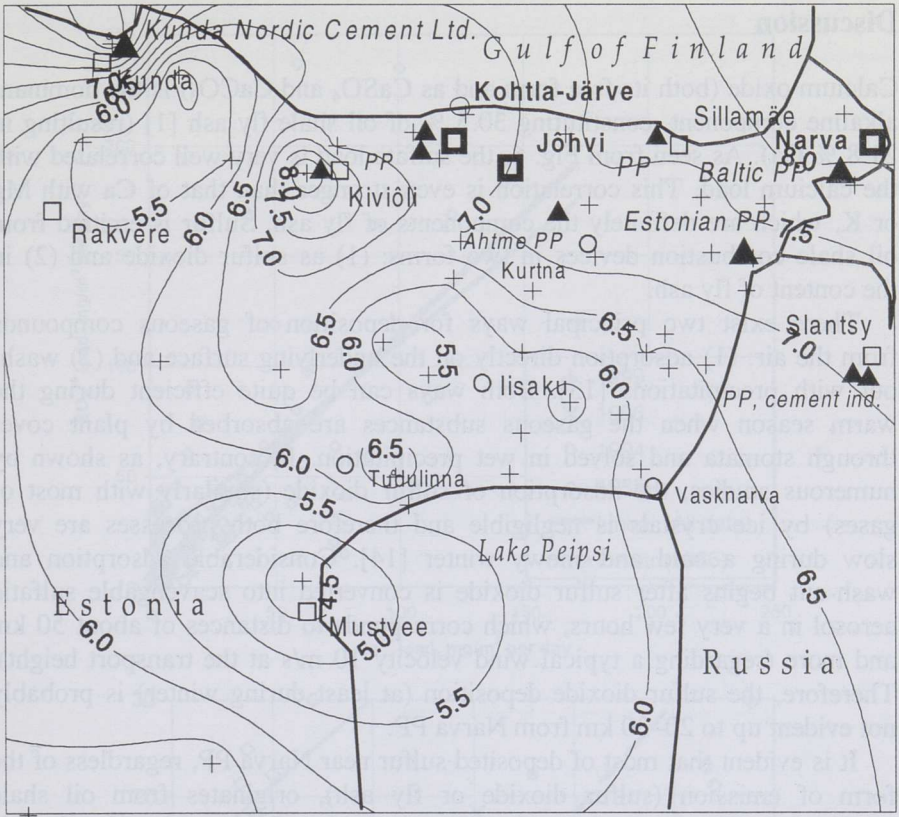
Fig. 5. Snow melt water pH in northeastern Estonia, January – March 1999 (crosses – sampling sites, triangles – main pollution sources)
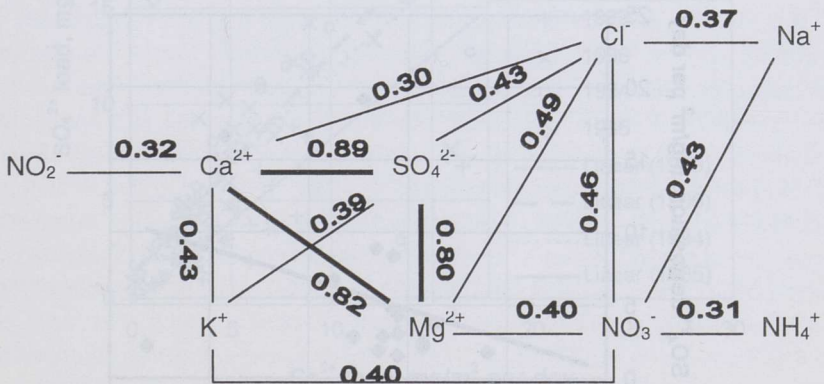
Fig. 6. Correlation graph of loads of snow melt water components, January – March 1999, northeastern Estonia

Discussion

Calcium oxide (both its free form and as $CaSO_4$ and $CaCO_3$) is the dominant alkaline component, constituting 30.5 % of oil shale fly ash [1] (resulting in 21.8 % Ca). As seen from Fig. 6, the sulfate load is very well correlated with the calcium load. This correlation is even stronger than that of Ca with Mg or K, which are definitely the components of fly ash. Sulfur is emitted from oil shale combustion devices in two forms: (1) as sulfur dioxide and (2) in the content of fly ash.

There exist two principal ways for deposition of gaseous compounds from the air: (1) adsorption directly on the underlying surface and (2) wash-out with precipitations [13]. Both ways can be quite efficient during the warm season when the gaseous substances are absorbed by plant cover through stomata and solved in wet precipitation. In contrary, as shown by numerous studies, the adsorption of sulfur dioxide (similarly with most of gases) by ice crystals is negligible and therefore both processes are very slow during a cold and snowy winter [14]. Considerable adsorption and wash-out begins after sulfur dioxide is converted into scavengable sulfatic aerosol in a very few hours, which corresponds to distances of about 50 km and more (regarding a typical wind velocity 10 m/s at the transport height). Therefore, the sulfur dioxide deposition (at least during winter) is probably not evident up to 20–30 km from Narva PP.

It is evident that most of deposited sulfur near Narva PP, regardless of the form of emission (sulfur dioxide or fly ash), originates from oil shale combustion. The comparison of sulfate deposition fluxes and sulfur dioxide concentrations at the same sites gives a positive correlation, but not a strong one (correlation coefficient +0.30). The scatter of data points is quite large (Fig. 7).
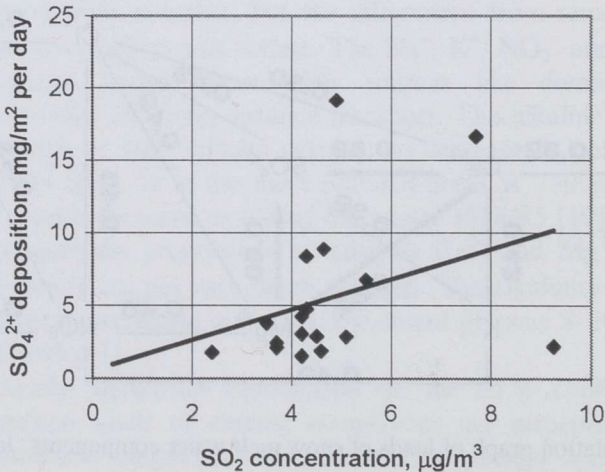

Fig. 7. Sulfate deposition loads *versus* sulfur dioxide concentrations, January – March 1999, northeastern Estonia
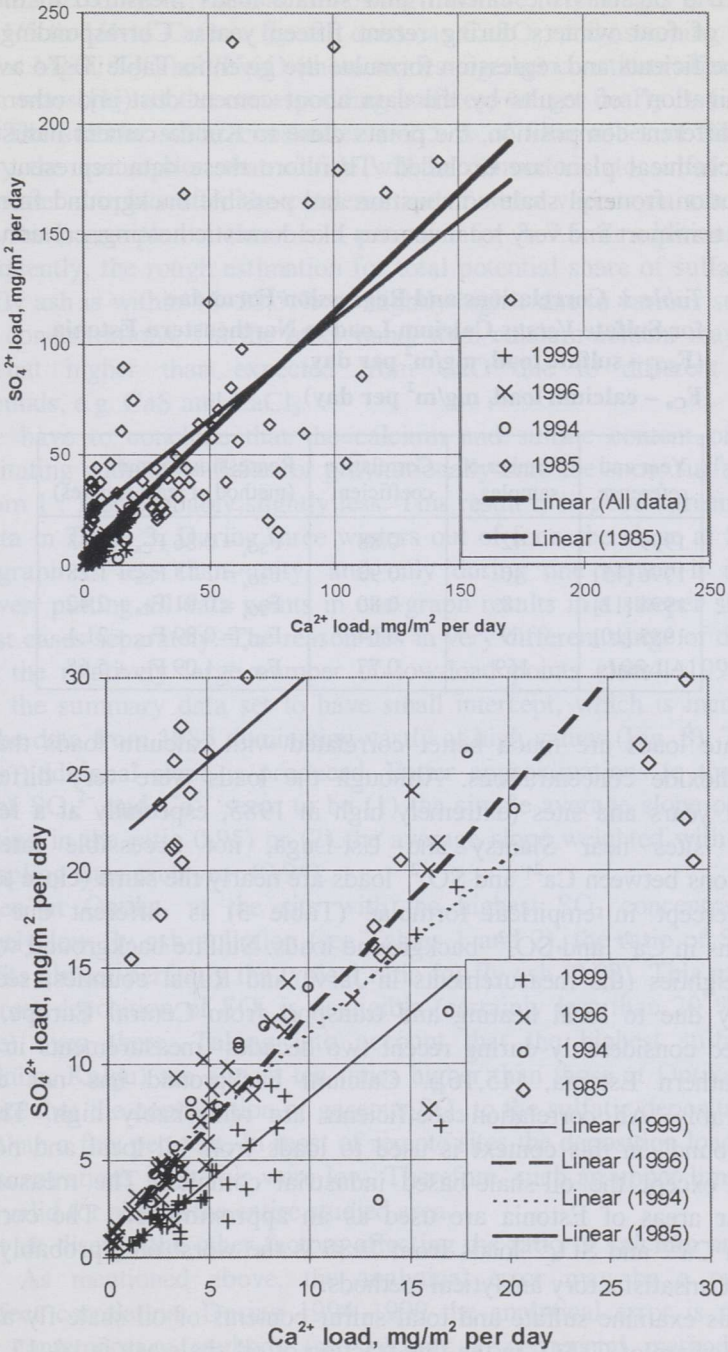
Fig. 8. Calcium *versus* sulfate loads: full data set (above) and small loads in detail (below, all subsets except 1985 entirely)

Figure 8 presents the calcium and sulfate loads measured in the snow samples of four winters during recent fifteen years. Corresponding correlation coefficients and regression formulae are given in Table 3. To avoid the "contamination" of results by the data about cement dust and other wastes having different composition, the points close to Kunda cement industry and Kiviõli chemical plant are excluded. Therefore these data represent mainly the pollution from oil shale combustion and possible background from long-distance transport and very local sources like domestic heating, erosion, etc.

Table 3. Correlations and Regression Formulae
for Sulfate Versus Calcium Load in Northeastern Estonia
(F_{SO_4} – sulfate load, mg/m^2 per day,
F_{Ca} – calcium load, mg/m^2 per day)

Year and reference	Number of samples	Correlation coefficient	Regression formula (method of least squeres)
1999	42	0.88	$F_{SO_4} = 0.86\,F_{Ca} - 0.33$
1996 [15]	40	0.93	$F_{SO_4} = 1.13\,F_{Ca} + 1.28$
1994 [12]	18	0.80	$F_{SO_4} = 0.91\,F_{Ca} + 2.42$
1985 [10]	69	0.64	$F_{SO_4} = 0.89\,F_{Ca} + 21.1$
All years	169	0.77	$F_{SO_4} = 1.09\,F_{Ca} + 5.68$

Sulfate loads are much better correlated with calcium loads than with sulfur dioxide concentrations. Although the loads were very different in different years and sites (extremely high in 1985, especially at a few very polluted sites near Slantsy and Ust-Luga, not accessible later), the proportions between Ca^{2+} and SO_4^{2-} loads are nearly the same (close to 1 : 1). The intercept in empirical formulae (Table 3) is different due to the variations in Ca^{2+} and SO_4^{2-} background loads. Sulfate background was high in the eighties (the measurements in Järva and Rapla counties, see [10]), probably due to local heating and transport from Central Europe, and it decreased considerably during recent two decades (measurements in central and southern Estonia, [15,16]). Calcium background has not changed considerably. All correlation coefficients are remarkably high. The term "background" in this context is used to loads from all local and non-local sources except the oil-shale-based industrial complex. The measurements from far areas of Estonia are used as an approximation. The correlation between Ca^{2+} and SO_4^{2-} loads from 1985 is the worst one, probably due to the most unsatisfactory analytical methods.

Let us examine sulfate and total sulfur contents of oil shale fly ash. The reported share of $CaSO_4$ in the fine fraction of oil shale ash is 14–17 % [17], which constitutes 10–12 % SO_4^{2-}. This is in fair agreement with 8.8 % sulfate content of electrostatic precipitator ash, considering the trend towards higher sulfate content in finer fly ash fractions [18]. Unfortunately, no direct data on the content of other sulfates ($MgSO_4$, K_2SO_4, Na_2SO_4) in the fly ash

are available. Considering that (following from the percentages given above) about 1/5 to 1/4 of CaO in fly ash exists as $CaSO_4$, and assuming the same rates for MgO, K_2O and Na_2O (these oxides together constitute about 9 % of fly ash mass [1]) as the corresponding sulfates, we get nearly 3–4 % SO_4^{2-} more. The sulfidic sulfur constitutes 1–2.5 % of filter ashes of Baltic TPP [1]. By the assumption that sulfide will be converted into sulfate form in small water droplets after the condensation of water vapour on ash particles in the stack gas plume, there is a potential for 3–7.5 % additional SO_4^{2-}. Consequently, the rough estimation for total potential share of sulfate in oil-shale fly ash is within 16–23.5 % or slightly higher due to various sulfates of minor concentrations. On the other hand, total calcium content may be also somewhat higher than expected from CaO due to different calcium compounds, e.g. CaS and $CaCl_2$.

We have to conclude that the calcium and sulfate content of fly ash precipitating with snow flakes or gravitationally onto the snow surface is not far from 1 : 1 or probably slightly less. This result is in good agreement with the data in Table 3. During three winters out of four, the slope at SO_4^{2-} vs. Ca^{2+} graph is less than unity, and only during one winter it is larger. However, putting all data points in one-graph results in a steeper slope than in most cases separately. The reason lies in very different range of deposition loads: the relatively large number of low-load points (1994, 1996, 1999) forces the summary data set to have small intercept, which is incompatible with the data from 1985 dominating vastly at high values (Fig. 8). Therefore a false additional slope is produced. Better approximations to the average ratio of SO_4^{2-} and Ca^{2+} seem to be (1) the simple average slope over years (resulting in the ratio 0.95) or (2) the average slope weighted with numbers of sampling sites each year (0.94).

Even at Ontika, at the site with the highest SO_2 concentration and relatively low fly ash pollution (see Tables 1 and 2), the ratio of SO_4^{2-} and Ca^{2+} fits almost perfectly the typical ratio for fly ash (0.92). This means that the direct deposition of SO_2 is negligible (certainly less than 20 % of total sulfate) even there. Taking into account that the highest sulfate loads (Riigiküla, Kulgu) are almost ten times higher than those at Ontika, we can estimate that the contribution of gaseous SO_2 to the sulfatic depositions is no more than a few per cent. In most of remote sites the deposition loads as well as concentrations in the air were low. Therefore, such an upper limit is most likely valid for almost the entire studied area.

Let us discuss the other factors affecting the ratio of calcium and sulfate loads. As mentioned above, the analytical error may be a reason for imperfect correlation. During 1994–1999 the analytical error is minimized using contemporary methods (see section: Experimental methods). As a result, the correlation coefficient has risen higher than 0.8. The highest correlation (0.93) was achieved in 1996, when all samples were collected from large forest or bog areas, far from inhabited sites and considerable traffic roads. Therefore, the local (domestic, traffic) emissions appear to

have a certain contribution. As the ratio of sulfate and calcium loads was highest (1 : 1.13) in 1996, it seems that local emissions tend to diminish the ratio, i.e. their calcium emissions are higher than sulfur emissions (e.g. road and soil erosion, wood burning). Another possible reason for the variations of sulfate – calcium ratio is the inhomogenous composition of fly ash itself: the chemical composition of particles depends on their size [7]. Large particles are deposited more easily (gravitational sedimentation and wash-out).

The sulfate loads near Kunda are remarkably high, but the proportion of sulfate and calcium loads is different (about 1 : 3 to 2 : 3). As the ashes of oil shale combustion are used for cement production, various fly ash components are also represented in the cement dust, but due to different ash fractions and other mineral components in the cement the proportions can deviate considerably. Another site with remarkably high loads but different ratio $SO_4^{2-} : Ca^{2+}$ (1 : 2.5) is Sirgala, where the effect of explosion dust from openpit mines (6–10 km to south and west) is expected.

Conclusions

In wintertime (cold and snowy season) a large majority of deposited sulfatic pollution from oil-shale-fired power plants appears to be carried with fly ash. The ratio of sulfate and calcium loads nearly 1 : 1 (variations in the range of 10–15 %) is typical for the composition of oil shale fly ash (combustion technology used in Narva PP). Both calcium and sulfate ions constitute about 1/5 of fly ash. During the warm season the share of gaseous sulfur dioxide may be larger due to its solubility in liquid water and stomatal transpiration of plants.

The regression formulae for wintertime sulfate and calcium deposition loads for oil shale region are derived. The inhomogenous chemical composition of fly ash and influence of other (domestic, traffic) emissions are suggested as possible factors affecting the ratio of sulfate and calcium deposition loads.

Acknowledgements

REFERENCES

1. *Pets, L. I., Vaganov, P. A., Knoth, I., Haldna, Ü., Schwenke, H., Schnier C., Juga, R.* Microelements in oil shale ash of the Baltic Thermoelectric Power Plant // Oil Shale. 1985. V. 2, No. 4. P. 379–390 [in Russian with English Summary].

2. *Mandre, M.* Air pollution and growth conditions of forest trees // Dust Pollution and Forest Ecosystems / M. Mandre (Ed.), Publ. Inst. Ecol. Acad. Sci. 1995. P. 18–22.

3. *Punning, J.-M., Liblik, V., Alliksaar, T.* History of fly ash emission and paleorecords of atmospheric deposition in the oil shale combustion area // Oil Shale. 1997. V. 14, No. 3. P. 347–362.

4. *Kaasik, M., Liblik, V., Kaasik, H.* Long-term deposition patterns of airborne wastes in the North-East of Estonia // Oil Shale. 1999. V. 16, No. 4. P. 315–330.

5. *Karofeld, E.* The effects of alkaline fly ash precipitation on the *Sphagnum* mosses in Niinsaare bog, NE Estonia // Suo. 1996. V. 47, No. 4. P. 105–114.

6. Environmental Report. Eesti Energia. 1999.

7. *Ferm, M.* A sensitive diffusional sampler / Swedish Environmental Institute. – Göteborg, 1991.

8. *Koskentalo, T.*, Passiivikeräys ulkoilman typpidioksidin määrityksessä. YTV. – Helsinki, 1992.

9. Chemical analysis // EMEP manual for sampling and chemical analysis, EMEP/CCC-Report 1/95 / Norwegian Institute for Air Research, 1996. P. 4-1 – 4-7.

10. *Voll, M., Trapido, M., Luiga, P., Haldna, Ü., Palvadre, R., Johannes, I.* Spread of atmospheric wastes from power equipments and oil shale processing enterprises // Natural State and Development of the Kurtna Lakeland / M. Ilmomets (Ed.). – Tallinn, Valgus, 1989. P. 29–42 [in Estonian].

11. *Tuulmets, L.* Chemical composition of precipitations // Dust pollution and forest ecosystems / M. Mandre (Ed.), Institute of Ecology, publication 3/1995. Tallinn, 1995 P. 23–32.

12. 12.*Kaasik, M.* Atmospheric transport and deposition of technogenic calcium: model estimation and field measurement // Proc. Estonian Acad. Sci. Ecol. 1996. V. 6, No.1/2. P. 41–51.

13. *McMahon, T. A., Denison, P. J.* Empirical atmospheric deposition parameters – a survey // Atmospheric Environment. 1979. V. 13. P. 571–585.

14. George, W, Slinn, N., Precipitation scavenging // Atmospheric Science and Power Production / D. Randerson (Ed.), U.S. Dept. of Energy, Oak Ridge, 1984. P. 466–524.

15. *Kaasik, M., Rõõm, R., Røyset, O, Vadset, M., Sõukand, Ü, Tõugu, K, Kaasik, H.* Elemental and base anions deposition in the snow cover of North-Eastern Estonia. The impact of industrial Emissions // Water, Air and Soil Pollution (in print).

16. *Roots, O., Talkop, R.* (Ed.) Keskkonnaseire 1995 / Informational and Techno-logical Center of Estonian Ministry of Environment, 1996.

17. *Kikas, V. H., Hain, A. A., Reispere, H. J.* Physico-chemical parameters and binding properties of the oil-shale fly ash fraction // Proc. Tallinn Polytechnical Institute, Series A 1968. No. 272. P. 29–47 [in Russian].

18. *Kuusik, R., Kaljuvee, T., Veskimäe, H., Roundigin, Yu., Keltman, A.* Reactivity of oil shale ashes towards sulfur dioxide. 3. Recurrent use of ash for flue gas purification // Oil shale. 1999. V. 16, No. 4. P. 315–330.