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INVESTIGATION OF MICROCOMPONENTS IN THE SNOW COVER IN TALLINN

Abstract. Results of a research of microcomponents in snow deposits obtained in Tallinn are presented. Concentrations of Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, and Ca^{2+} ions, heavy metals, and polycyclic aromatic hydrocarbons (PAH) in snow melt have been determined. On this basis, the intensity of the deposition of the microcomponents is characterized in different districts of the city and in a background area (Vaskjala).

Key words: polycyclic aromatic hydrocarbons, heavy metals, anorganic ions, snow cover, pollution.

The estimation of air pollution is a very complicated problem because of a significant variability in the concentrations of pollutants due to meteorological conditions, season, time of the day, and many other factors. Representative data can be obtained only by means of long-term investigations.

Very important data on air pollution may be obtained by investigations of meteorological precipitation. Analyses of rain water contamination are widely used for air pollution estimations. However, in northern countries, investigations of snow cover are also very significant in air pollution monitoring (Василенко et al., 1985; Грей and Мейл, 1986). Harmful compounds are captured on the snow cover over a long period of time. Therefore, analysis of snow cover characterizes air pollution during the whole winter season. Atmospheric pollution by such compounds as sulphates, nitrates, ammonium, heavy metals, polycyclic aromatic hydrocarbons (PAH), oil, and other pollutants are characterized quite thoroughly by snow cover analyses (Василенко et al., 1985).

Snow cover sampling is very simple and quick and does not require any complicated equipment. In Estonia, snow cover stays in some years for 2—3 months without significant thaw, thereby enabling collection of data on the environmental state during a long period.

This paper presents the results of snow cover investigations carried out in Tallinn in the winters of 1986/87 and 1987/88. We were not able to collect data during the three following winters because of the lack of snow cover in northern Estonia, although lack of snow cover three years running is unusual.

Materials and Methods

As sampling locations various districts of the city (see Fig. 1), such as Mustamäe, Õismäe, Lasnamäe, Nõmme (residential), Maardu, Kopli, Lasnamäe (industrial), and Hirvepark (in the central part of the city), were chosen. This choice makes it possible to characterize air pollution in residential and industrial districts of the city, as well as in districts with

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different types of heating systems. We have also sampled snow cover in the Vaskjala water storage basin (out of the city) as a background area in order to compare the pollution levels. Sampling began 40 days (1987/88) and 90 days (1986/87) after the formation of snow cover. Therefore the data, which are presented in Table 1, are quite trustworthy.

Snow was collected with a 9.5 cm diameter corer; 7—10 samples from each point were united and analysed as a single sample (covering an area of about 100 m^2). There were three or four sampling points in each district (covering 0.5—1.0 m^2). The whole snow core down to the ground (or ice) was used for the following analysis. Snow was thawed at room temperature, stirred, and divided into four parts for different analyses. Altogether we analysed 55 samples.

PAHs were extracted by hexane from unfiltered snow melt and determined by high-pressure liquid chromatography (Брюханов et al., 1986; Trapido and Palm, 1991). Ions (Ca^{2+}, Na^{+}, NH_4^{+}, Cl^{-}, SO_4^{2-}, NO_3^{-}) were determined from filtered snow melt by ionchromatographic method (Еоров et al., 1986). For heavy metal analyses (Co, Cu, Cd, Zn, Pb) unfiltered snow melt was evaporated, treated by HNO_3, and analysed by atomic absorbtion method with flame atomization (Хавезов and Цалев, 1983).

Several fresh snow samples collected immediately after the snowfall were also analysed (see Table 2).

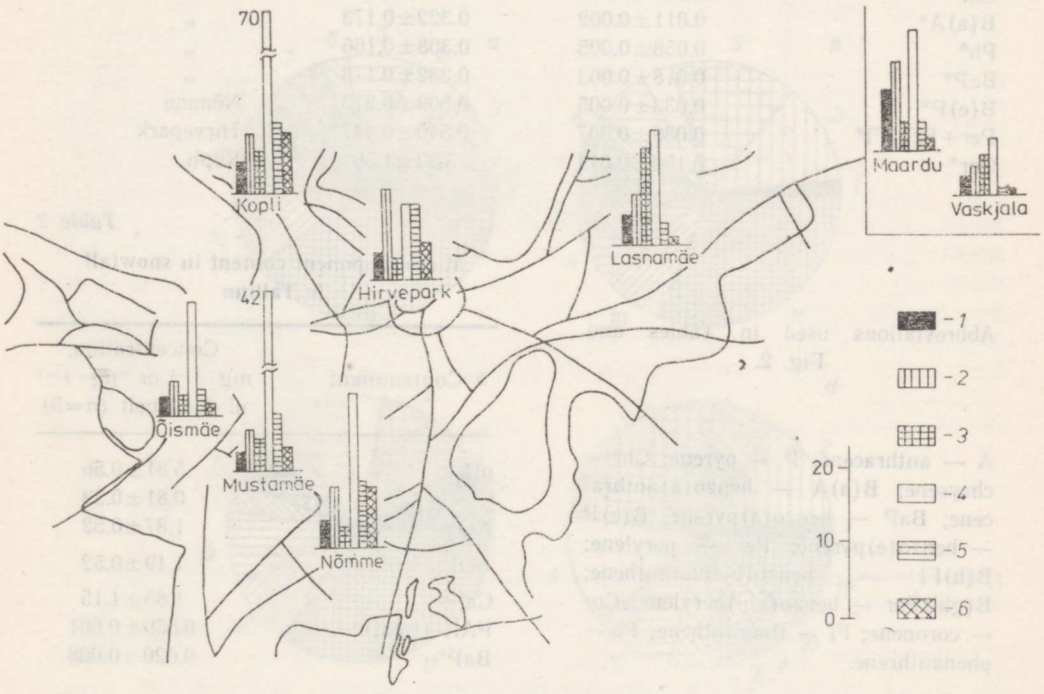

Fig. 1. Average intensities of the deposition of microcomponents in snow cover in Tallinn.

1 — NO_3^{-}, $mg \cdot m^{-2} \cdot day^{-1}$; *2* — SO_4^{2-}, $mg \cdot m^{-2} \cdot day^{-1}$; *3* — Ca^{2+}, $mg \cdot m^{-2} \cdot day^{-1}$; *4* — heavy metals, 10 $\mu g \cdot m^{-2} \cdot day^{-1}$; *5* — PAH, $\mu g \cdot m^{-2} \cdot day^{-1}$; *6* — BaP, 0.1 $\mu g \cdot m^{-2} \cdot day^{-1}$.

Table 1

Microcomponent content in snow melt

Contaminant	Concentration, mg · l^{-1} or *μg · l^{-1}		
	Vaskjala (n=8)	Tallinn (n=42)	Most heavily polluted district
pH	7.36±1.18	6.33±0.26	
Cl^-	2.75±0.96	6.47±2.29	Kopli
NO_3^-	4.60±2.21	4.58±2.73	Maardu
SO_4^{2-}	5.27±1.39	9.87±3.05	Hirvepark
Ca^{2+}	3.20±0.98	3.85±2.56	Lasnamäe
Na^+	0.25±0.03	1.03±0.63	Maardu
NH_4^+	0.37±0.04	1.52±1.09	Maardu
Pb*	9.60±0.90	28.9±9.4	Nõmme
Cu*	2.89±0.63	17.1±12.0	Mustamäe
Co*	2.09±1.00	2.22±1.26	Lasnamäe
Zn*	4.53±1.52	171±140	Kopli
Cd*	0.51±0.16	0.65±0.26	Nõmme
PAH (total)*	0.443±0.088	7.50±4.28	Kopli
A*	0.012±0.003	0.040±0.022	Hirvepark
Fl*	0.028±0.014	0.36±0.24	„
P*	0.086±0.016	0.69±0.37	„
Chr*	0.032±0.004	0.59±0.37	„
B(a)A*	0.011±0.002	0.322±0.173	„
Ph*	0.058±0.005	0.308±0.166	„
BaP*	0.018±0.003	0.332±0.173	„
B(e)P*	0.033±0.005	0.509±0.273	Nõmme
Per+B(b)Fl*	0.038±0.007	0.540±0.447	Hirvepark
Cor*	0.150±0.014	3.33±1.59	Kopli

Abbreviations used in Tables and Fig. 2.

A — anthracene; P — pyrene; Chr — chrysene; B(a)A — benzo(a)anthracene; BaP — benzo(a)pyrene; B(e)P — benzo(e)pyrene; Per — perylene; B(b)Fl — benzo(b)fluoranthene; B(ghi)Per — benzo(ghi)perylene; Cor — coronene; Fl — fluoranthene; Ph — phenanthrene.

Table 2

Microcomponent content in snowfall in Tallinn

Contaminant	Concentration, mg · l^{-1} or *μg · l^{-1} of snowmelt (n=5)
pH	5.81±0.56
Cl^-	0.81±0.33
NO_3^-	1.37±0.52
SO_4^{2-}	1.19±0.52
Ca^{2+}	1.85±1.15
PAH (total)*	0.559±0.061
BaP*	0.020±0.008

Results and Discussion

The districts most heavily polluted by SO_4^{2-} and NO_3^- were Hirvepark and Maardu, respectively. Mustamäe and Õismäe residential districts were comparatively pure. SO_4^{2-} deposition intensity in Vaskjala was two times lower than in the city (see Fig. 1), while that of NO_3^- was almost the same in Vaskjala and the residential districts of the city. This indicates a significant role of long-range transport of SO_4^{2-} and NO_3^-. SO_4^{2-} deposition intensity was in harmony with the location of emission sources; above all the heating systems as the main SO_4^{2-} polluters. The highest NO_3^- contamination zones were observed near the highways.

We determined 11 individual PAHs in the snow melt of both fresh snowfall and the existing snow cover (see Fig. 2). It is very important to know the concentration of PAHs in air because of their considerable carcinogenic effect. As epidemiological investigations in the USA have shown, when benzo(a)pyrene (BaP) content in ambient air rose by 1 $ng \cdot m^{-3}$, the lung cancer death-rate increased by 5% (Cederlöf et al., 1978).

High deposition intensity of PAH was observed at Kopli, Nõmme, and Hirvepark. These districts are polluted by vehicle exhausts, they all have many individual heating systems, and Kopli is also an industrial area with large enterprises that use combustion processes in their technologies.

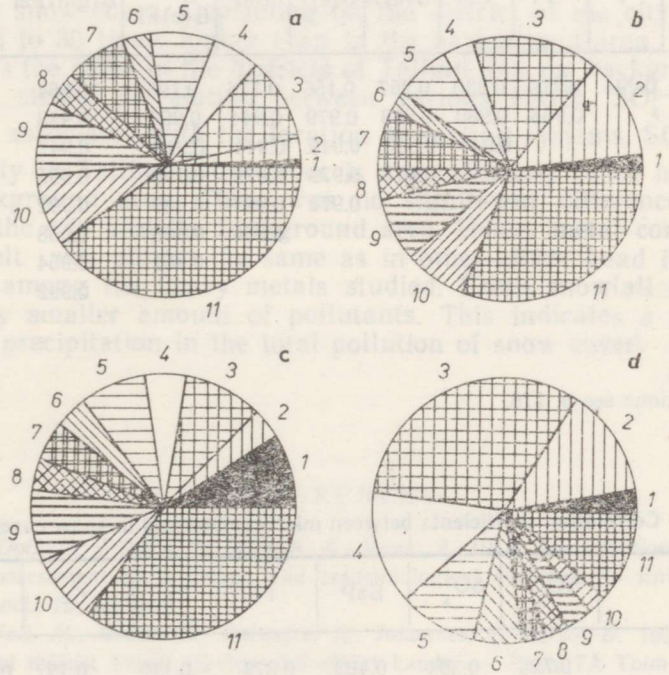

Fig. 2. Composition of PAHs in the snow cover in Hirvepark (*a*) (total PAH 14.1 $\mu g \cdot l^{-1}$ of snow melt), in Vaskjala (*b*) (total PAH 0.443 $\mu g \cdot l^{-1}$), in Mustamäe (*c*) (total PAH 7.59 $\mu g \cdot l^{-1}$), and in fresh snowfall in Mustamäe (*d*) (total PAH 0.498). *1* — A; *2* — Ph; *3* — P; *4* — Fl; *5* — Chr; *6* — B(a)A; *7* — B(e)P; *8* — BaP; *9* — Per + B(b)Fl; *10* — B(ghi)Per; *11* — Cor.

Our investigations showed that PAH composition was the same in different districts as well as at Vaskjala. The content of BaP, the best-known PAH, was 3.5—6.5% of the total PAH content. Coronene forms a significant part of the PAH content in the snow cover — 28—40% of the total PAHs. It is known that coronene emission is mainly connected with motor vehicles. The PAH composition in the fresh snowfall differs somewhat from that of the snow cover (see Fig. 2).

At Vaskjala the PAH content was one order of magnitude lower than in Tallinn. The average deposition intensity of PAH was 7.9 $\mu q \cdot m^{-2} \cdot day^{-1}$. Of that value, BaP accounted for 0.3 $\mu g \cdot m^{-2} \cdot day^{-1}$, which is almost ten times higher than that in northeastern Estonia (Paalme et al., 1990; Voll et al., 1989). The average deposition intensity of PAH in Vaskjala was 0.4 $\mu g \cdot m^{-2} \cdot day^{-1}$ and that of BaP made up 0.005 $\mu g \cdot m^{-2} \cdot day^{-1}$, which is lower than in all the other areas mentioned above. Deposition intensities of PAH are presented in Fig. 1.

Table 3

Correlation coefficients between PAHs in snow cover

	P	Fl	Chr	B(a)A	B(e)P	BaP	Per+B(b)Fl	B(ghi)Per	Cor	Ph
A	0.294	0.316	0.230	0.257	0.156	0.176	0.195	0.264	0.178	0.791
P		0.983	0.980	0.983	0.979	0.944	0.964	0.983	0.955	0.897
Fl			0.947	0.953	0.945	0.914	0.913	0.947	0.907	0.850
Chr				0.997	0.979	0.972	0.990	0.995	0.988	0.939
B(a)A					0.972	0.961	0.985	0.992	0.979	0.850
B(e)P						0.964	0.968	0.968	0.984	0.862
BaP							0.961	0.954	0.943	0.897
Per+B(b)Fl								0.992	0.983	0.810
B(ghi)Per									0.988	0.882
Cor										0.848

For abbreviations see p. 176.

Table 4

Correlation coefficients between microcomponents in snow cover

	NO_3^-	SO_4^{2-}	BaP	Pb	Cu	Co	Zn	Cd
Cl^-	0.725	0.394	0.403	0.374	−0.112	0.727	0.751	0.616
NO_3^-		0.869	0.649	0.495	−0.158	0.917	0.529	0.746
SO_4^{2-}			0.816	0.625	0.140	0.733	0.430	0.714
BaP				0.778	0.146	0.569	0.574	0.885
Pb					0.259	0.714	0.342	0.885
Cu						−0.189	0.338	0.022
Co							0.478	0.874
Zn								0.544

In the total amount of heavy metals determined Pb accounted for a large part. The content of Pb is mainly associated with ethyl petrol used by motor vehicles. The proportion of Pb in the total content of heavy metals varies among city districts. It is higher at Nõmme, Hirvepark, and Õismäe. Zn content is also high, especially at Kopli. Zn, Pb, and Cu contents in the city were significantly higher than in the background area (see Fig. 1).

So the microcomponents are distributed in the snow cover of the city quite unevenly.

All the data were statistically analysed by linear correlation method. The results are presented in Tables 3 and 4. They show a strong correlation between many contamination components of snow cover. A strong correlation appears between all PAHs, except anthracene. Therefore, it is possible to estimate PAH pollution on the basis of some easily measured PAH, for example BaP. There is strong correlation between SO_4^{2-} and NO_3^- ($r=0.869$), both of which are products of combustion. As to heavy metals, a strong correlation appears only between Pb and Cd ($r = 0.88$). Pb correlates also with BaP.

Summary and Conclusions

Complex investigations of snow cover in Tallinn yielded good results for estimating the state of the urban environment. Data on pollution by many toxic and carcinogenic compounds were obtained in different districts of the city. Heating systems and motor vehicles are the main polluters of snow cover. Depending on the district of the city, the PAH content is 5 to 30 times higher than in the background area. PAH composition was the same in the districts of Tallinn and the background area. There is a strong correlation between various PAHs. SO_4^{2-} pollution intensity is associated with the location of heating systems. SO_4^{2-} deposition intensity in Tallinn snow cover is approximately twice higher than in the background area. There was no significant difference in NO_3^- content in the city and the background area. Heavy metal concentration in snow melt was almost the same as in other cities. Lead is the most significant among the heavy metals studied. Fresh snowfall contains a considerably smaller amount of pollutants. This indicates a significant role of dry precipitation in the total pollution of snow cover.

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