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HEAVY METALS IN ROADSIDE: CHEMICAL ANALYSIS OF SNOW AND SOIL AND THE DEPENDENCE OF THE PROPERTIES OF HEAVY METALS ON LOCAL CONDITIONS

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Abstract. The behaviour of lead, copper, zinc, manganese, and cadmium was investigated in roadside by chemical analysis of snow and soil. Traffic of over 1000 vehicles per day was found to increase the concentration of heavy metals in roadside within a distance of up to 100 m from the road. The concentration of cadmium was not correlated with traffic density. The main factor influencing the solubility and mobility of heavy metals was the pH of meltwater and soil. Alkalinity is rising with growing traffic and the metals become less soluble. No effect of chloride, which is used for deicing roads, on the solubility could be detected by correlation analysis. Principal component method was used to reveal connections between pH, chloride, distance from road, soluble and total concentrations of metals, and the location of sampling.

Key words: heavy metals, snow, soil, traffic.

Traffic is known as a source of emission of heavy metals [1]. Emissions from vehicles are often the only anthropogenic source of pollution with heavy metals in rural areas. Areas in the vicinity of roads and highways are almost always contaminated with heavy metals. Tetraethyl lead in petrol has for a long time been the main source of lead pollution [2]. During the last ten years its use has been remarkably reduced the world over, including Estonia. European countries introduced Pb-free petrol over the period 1986–89. Within the European Union, the maximum permissible content of lead in petrol was fixed as 0.15 g/L [1]. Diesel oil is a source of cadmium, copper, nickel, vanadium; tire attrition of zinc and cadmium; steel parts attrition of nickel, chromium, manganese, vanadium, tungsten, and molybdenium; the wear of bearings and electric contacts results in the emission of copper. The emitted pollutants settle down on the roadside ground as wet and dry deposits within hundreds of meters from the road. The further fate of heavy metals depends to a large extent on their fixation in the dry matter [3]. Consequently, the ecological risk of heavy metal pollution cannot be predicted only on the basis of the total metal content in the soil. Soil properties determining the solubility and mobility of compounds of metals have to be taken into account. It should be mentioned that the fate of heavy metals in roadside areas depends to a large extent on meteorological and other local conditions such as use of deicing salts in winter [4].

Both snow and rainwater collected in the roadside can be used for the determination of the atmospheric load of heavy metals. Snow has several advantages over rain:

– heavy metals in snow-pack represent the fallout accumulation of the whole snowing period;
– thanks to its bigger specific area snow is normally more efficient in catching particles from the air;
– snow can be collected during a long period, revealing thus integrated atmospheric pollution;
– sampling of snow is an inexpensive, simple, and convenient way of collecting atmospheric depositions, and can be done practically everywhere where a snow cover exists.

The deposits and behaviour of heavy metals (Pb, Cd, Cu, Zn, Mn) were investigated at different distances from roads of different density of traffic. The main analytical method used for the determination of the concentration of heavy metals was atomic absorption spectrometry. Meltwater as well as the particulate matter of snow were analysed. The soluble parts of elements in the dry matter were determined by the extraction with different solutions capable of dissolving certain groups of metallic compounds. The importance of acidity and alkalinity and of the concentration of chloride in snow and soil in the accumulation of heavy metals was studied.

EXPERIMENTAL PART

Sampling sites

A* Rural area in South Estonia near Otepää, less than 1000 vehicles per day (Otepää–Piiri and Arula–Sihva roads)

B* Pärnu highway (10 km from Tallinn) and Narva highway (80 km from Tallinn), 6000 vehicles per day

C** City of Tallinn, 500 000 inhabitants (Narva Road, Kadaka Road), 10 000 vehicles per day

D** Suburb of Tallinn (Laagri), less than 1000 vehicles per day

* Snow was collected by the research group of the Department of Transportation of Tallinn Technical University from 13 February to 20 March 1987.

** Snow was collected by the research group of analytical chemistry of Tallinn Technical University on 2 February 1993.

Collection of samples

1. Snow

Roadside snow samples were collected before the final melting of snow. A vertical column of snow was taken using a plastic tube with an inner cross-section of 50×50 cm^2. The tube was thrust through the snow cover and the snow inside the tube was transferred into a plastic container.

2. Soil

Roadside soil was collected in the sampling sites C and D from areas of 10×10 cm. All samples were taken at two depths: a surface sample at a depth of 0–5 or 0–10 cm and the remaining part of the sample at 5–10 or 10–20 cm. Soil was sampled in spring after snow had melted. Samples were transferred into plastic bags and closed air-tight.

Preparation and analysis of samples

1. Snow

Heavy metals. Snow was allowed to melt at room temperature and the volume of meltwater was measured with a graduated glass cylinder. The melt-water was filtered through a plankton net with a hole diameter of 90 nm and the dry residue on the net was thrown away. The filtrate was passed through filter paper (d. = 5 nm) and the residue on the paper (d. = 5–90 nm) was dried at 105 °C and weighed. The particulate matter of snow was dissolved in concentrated nitric acid in a closed Teflon bomb at 140 °C. An aliquot of 400 ml of the filtrated meltwater was acidified with 1 ml of concentrated nitric acid and evaporated to 20 ml. The concentrated solutions were diluted with distilled water to 25 ml in a graduated flask. The dissolved particulate matter and the concentrated snow-melt were analysed for the total concentration of Pb, Cd, Cu, Zn, and Mn by conventional flame atomic absorption spectrometry (AAS). For the speciation analysis of particulate matter of snow an additional snow sample was melted and the dry residue was produced similarly. The dry particulate matter of snow was treated sequentially [5] with four extractants with regulated pH: (1) ammonium acetate 1 M, pH 4.8 (regulated by acetic acid); (2) hydroxylamine chloride 1 M, pH 2.4 (regulated by HCl); (3) ammonium oxalate 0.2 M, pH 3.0 (regulated by oxalic acid); (4) hydrogen peroxide 15%, pH 1.3 (regulated by nitric acid). The extracts were analysed by AAS. Soil samples were treated in the similar way to carry out the extraction analysis.

pH. The pH value was determined by the potentiometric method using a snow sample taken for this purpose from the surface horizon (5 cm depth) on the same day as snow samples were taken for heavy metal analysis. pH was measured immediately after snow had melted in the laboratory at room temperature.

Chloride. Chloride was titrated amperometrically in an aliquot of meltwater used for the determination of heavy metals. The meltwater was acidified with nitric acid and chloride was titrated with silver nitrate using a rotating platinumwire electrode. As the reference electrode, a mercury sulphate–mercury electrode was used [6].

2. Soil

Soil was dried at room temperature and sieved through the net with a hole diameter of 1 mm. A mean sample was taken (d.<1 mm) and ground in agate mortar. The analysis of the total concentration of heavy metals and the sequential analysis were carried out as described for the particulate matter of snow.

AAS instrumentation

An SP9 700 Pye Unicam AA-spectrometer (UK) was used for the determination of the concentration of heavy metals. The conditions of analysis are presented in Table 1. An acetylene-air flame system was used. To avoid the scattering effect of light, a deuterium-lamp background was used.

Table 1

The conditions of AAS analysis

Element	Wave-length, nm	Lamp current, mA	Determination limit, mg/L*	Optimal concentration range, mg/L
Pb	217.0	5	0.1	0.5–10
Cu	324.6	5	0.04	0.1–10
Zn	213.9	10	0.01	0.1–2.0
Mn	279.5	10	0.03	0.1–5.0
Cd	228.8	5	0.01	0.1–5.0

* Error 6%.

The instrumental standard error on the treatment solution with nominal concentration of 2.00 mg/L ($n = 5$) was 0.02 mg/L for all elements except lead (0.065 mg/L). To check the matrix influence on the absorption signal, the sample solutions were diluted and the analysis was repeated.

Data processing

Computing and statistical data processing were carried out with the program STATGRAPHICS [7].

RESULTS AND DISCUSSION

Heavy metals in the roadside snow in rural areas

Samples A and B from both sides of the roads were collected at distances of 10, 25, 50, and 100 m from the roads. The traffic density as well as the general ecological situation of the sampling sites were different. Sampling sites of group A were in South Estonia where the industrial and urban pollution as well as traffic density are low. The sampling sites in North Estonia (B) were chosen near highways. One of them, on the Tallinn–Pärnu highway, was 10 km from the capital Tallinn. The other was on the Tallinn–Narva highway 80 km from Tallinn near Viitna. Characteristics of five sampling sites are presented in Table 2. The depth of the snow-pack formed during a two-month snowing period on both sides of the road was mostly in the range of 30 to 50 cm.

Table 2

Conditions of snow sampling; volume, pH, and the content of chloride of melt-water; and the content of dry matter in snow sample

Location*	No. of sample**	Distance from road, m	Depth of snow-pack, cm	Volume of meltwater, L	pH	Chloride, mg/L	Dry matter, g
Otepää–Piiri, 1a	1_1	10	47	4.48	6.48	3.1	0.1513
	1_2	25	38	2.82	6.45	1.4	10.4802
	1_3	50	39	2.95	5.90	1.7	0.0385
	1_4	100	37	2.96	5.52	2.2	0.0752
Otepää–Piiri, 1b	1_5	10	33	2.39	6.95	2.4	16.1613
	1_6	25	39	3.46	7.00	0.8	0.5857
	1_7	50	42	3.09	6.87	2.1	0.184
	1_8	100	32	2.65	6.76	1.0	10.9362
Arula–Sihva, 2a	2_1	10	46	2.26	5.71	0.8	0.1340
	2_2	25	53	3.42	4.42	0.6	0.0417
	2_3	50	51	3.24	6.46	0.9	0.2571
	2_4	100	56	3.66	5.65	0.4	0.1685
Arula–Sihva, 2b	2_5	10	53	3.28	4.53	1.0	0.2136
	2_6	25	37	2.60	6.77	1.6	0.8376
	2_7	50	51	2.82	3.98	1.0	0.5206
	2_8	85	55	2.66	3.23	0.2	0.1691
Tallinn–Pärnu, 3a	3_1	10	43	3.88	7.15	61.6	2.4465
	3_2	25	27	2.30	6.72	55.8	0.1618
	3_3	50	30	2.87	6.07	24.6	8.6981
	3_4	100	25	2.30	6.49	5.2	2.3545
Tallinn–Pärnu, 3b	3_5	10	26	2.07	6.72	69.5	0.8625
	3_6	25	28	2.28	6.42	18.6	0.1195
	3_7	50	26	2.10	6.55	8.8	29.1000
	3_8	100	37	3.20	6.48	5.2	11.9600
Tallinn–Pärnu behind a hedge, 4	4_1	10	28	3.26	6.76	25.1	1.2173
	4_2	25	33	3.38	7.15	6.1	3.6937
	4_3	50	36	3.70	6.68	2.6	1.4344
	4_4	100	33	3.10	6.39	2.1	3.9551
Tallinn–Narva, 5	5_1	10	25	2.38	7.50	29.0	0.5912
	5_2	25	58	3.83	7.75	10.5	0.9895
	5_3	50	39	2.80	7.11	2.9	2.1165
	5_4	100	44	4.14	7.18	1.6	7.8013

* a and b denote the two opposite sides of a road; ** numbers of sample mark the dots of locations in Fig. 1.

Table 3

Heavy metals in roadside snow calculated per volume of meltwater (subscript t) and the percentage of the soluble part of metals calculated per total concentration of metals of snow (subscript s)

Snow sample*	Distance, m	Pb_t, µg/L	Pb_s, %	Cu_t, µg/L	Cu_s, %	Cd_t, µg/L	Cd_s, %	Zn_t, µg/L	Zn_s, %	Mn_t, µg/L	Mn_s, %
1a	10	18	44.9	13	60.3	0.4	69.2	54.2	69.1	4.9	20.5
	25	47	20.2	34	2.7	2.3	16.7	210	12.4	159	4.1
	50	5	94.4	2	92.2	0.5	72.1	24.0	90.8	2.9	26.1
	100	8	67.1	2	21.3	1.5	29.7	34.6	74.6	9.3	64.5
1b	10	27	21.0	21	11.1	0.7	42.5	119	8.4	779	0.1
	25	16	38.3	3	84.6	0.3	88.9	10.6	65.8	25.8	2.9
	50	4	65.9	7	33.1	0.4	60.8	32.5	56.2	34.7	2.2
	100	16	15.9	7	25.7	4.5	6.7	101	5.9	583	0.2
$\bar{x}$ ± SD**		20±19		11±11		1.3±1.5		73.2±67.0		200±306	
2a	10	9	51.5	3	32.0	0.3	37.2	43.0	69.2	16.6	60.3
	25	11	86.7	6	74.0	0.2	22.3	95.1	89.9	8.6	78.8
	50	10	67.1	3	44.4	0.6	67.6	28.0	40.4	21.3	23.4
	100	16	77.4	3	41.6	0.8	83.1	28.6	62.9	15.5	37.2
2b	10	9	79.6	3	42.6	0.8	80.8	72.4	87.4	15.0	75.2
	25	12	72.5	3	15.4	0.5	85.3	70.7	40.3	33.7	17.8
	50	52	19.3	4	37.7	2.1	3.8	53.1	81.9	67.5	89.3
	85	9	89.1	4	72.3	0.9	79.7	50.2	86.6	44.3	94.9
$\bar{x}$ ±SD**		15±15		3.6±1.1		0.8±0.6		55.1±23.2		27.8±19.8	
3a	10	27	3.6	9	37.1	0.9	65.1	630	1.9	92.2	2.2
	25	2	93.6	5	49.8	0.3	98.0	40.8	47.8	26.2	45.8
	50	46	3.8	18	13.8	0.6	69.0	202	6.9	1214	0.2
	100	22	7.9	6	43.2	0.7	55.0	68.8	17.9	761	0.1
3b	10	15	15.3	5	30.5	0.7	54.2	41.2	22.6	137	7.8
	25	2	95.0	3	46.1	0.6	78.6	65.8	22.0	237	4.6
	50	25	5.0	41	4.9	1.5	18.3	358	2.9	1886	0.1
	100	41	2.4	24	8.3	0.9	48.9	216	3.6	1092	0.1
$\bar{x}$ ±SD**		22.5±16.1		13.9±13.1		0.8 ±0.3		203±206		681±674	
4	10	26	6.8	10	38.5	0.8	83.6	57.8	35.4	56.7	7.1
	25	22	4.6	6	29.1	0.9	76.2	86.8	8.1	385	0.2
	50	12	8.7	5	43.0	0.8	90.3	37.2	14.7	142	1.8
	100	18	9.5	5	30.3	1.0	68.1	89.3	12.9	333	1.1
5	10	20	32.8	8	31.2	2.0	83.5	59.7	21.8	125	4.5
	25	15	36.5	6	27.3	1.9	89.0	41.2	26.7	152	5.7
	50	12	31.5	10	42.0	1.8	70.8	48.6	25.3	254	1.6
	100	12	28.0	6	17.3	2.1	76.6	56.4	34.9	324	1.0

* See Table 2 for sampling locations; ** the arithmetic mean ($\bar{x}$) and standard deviation (SD) of total concentration for the locations 1, 2, and 3.

The concentration of chloride in the meltwater of the snow collected from the roadside of Tallinn–Pärnu and Tallinn–Narva highways was high but diminished with the distance from the road. The hedge on the Tallinn–Pärnu highway reduced the chloride concentration in meltwater nearly twice at a distance of 10 m from the highway. In South Estonia the concentration of chloride was low and at a distance of 10 m from the road did not exceed 2–3 mg/L of meltwater. Some differences occurred in the pH values of meltwater. The alkalinity of meltwater was the highest near Viitna and acidity on the Arula–Sihva road.

Table 3 presents total concentrations of heavy metals in snow, calculated per 1 L of meltwater. The soluble part found in meltwater was calculated as percentage of the total concentration of the metal in snow. Some statistically significant ($\alpha = 0.1$) differences were found, using arithmetic mean ± standard deviation, in the snow from the Arula–Sihva and Tallinn–Pärnu highways in the concentrations of lead, zinc, and manganese. The lowest concentration of these elements was found in the snow near the Arula–Sihva road. No significant differences were found in the concentration of copper and cadmium. The highest concentration of cadmium in snow was found near Viitna (sample 5, Table 3). No correlation was detected there between the cadmium content and the distance from the road.

To find the possible relationship between the concentrations of metals in snow, the pH value and the chloride content of meltwater, and the distance from the road, correlation analysis was performed. The results of the correlation analysis of the variables in snow (see Tables 2 and 3) are given in Table 4.

Table 4

Correlation between the total concentration (subscript t) and soluble fractions (subscript s) of heavy metals, pH and chloride in meltwater (Cl) and the distance from the road (T) ($\alpha = 0.05$)

pH										
Cl	0.29									
T		–0.39								
Pb_t										
Pb_s	–0.44			–0.57						
Cu_t				0.63	–0.42					
Cu_s	–0.35			–0.48	0.51	–0.56				
Zn_t		0.38		0.43	–0.41	0.54	–0.35			
Zn_s	–0.69	–0.31		–0.37	0.71	–0.50	0.66	–0.48		
Mn_t				0.24	–0.48	0.70	–0.47	0.40	–0.55	
Mn_s	–0.89				0.57	–0.36	0.39	0.26	0.82	–0.39

A significant negative correlation between the pH value of meltwater and the soluble part of elements indicates the higher solubility of heavy metals in a more acidic medium. The soluble fractions of elements are correlated positively with each other. Also the total concentrations of metals are correlated with each other. The chloride concentration is diminishing with the distance from the road. Only total zinc appears to be positively correlated with chloride. Cadmium has no significant correlation with the other elements and was therefore omitted from the table.

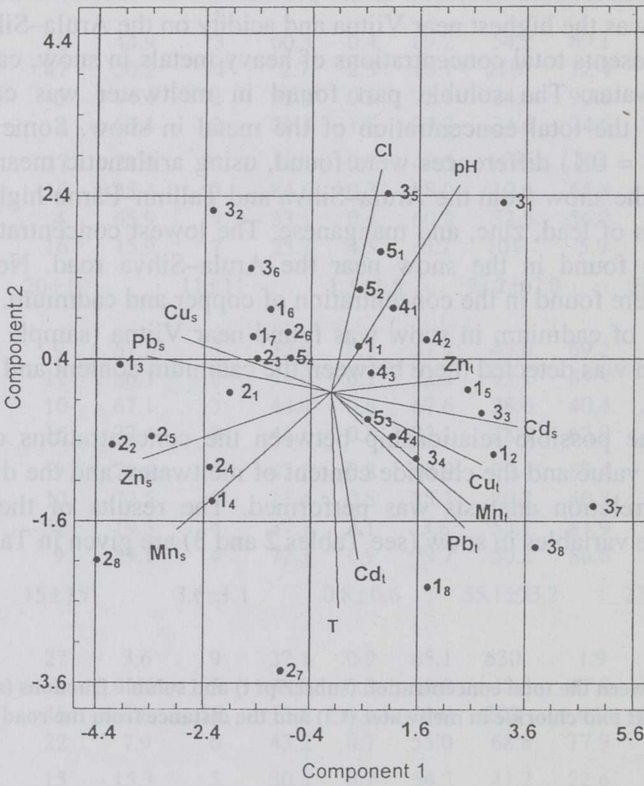

Fig. 1. Heavy metals in roadside snow: biplot for two principal components characterizing the variables and snow samples. Vectors reflect relationships between pH, chloride, distance from the road (T), total concentration of metals (subscript t), and soluble fractions (subscript s) of metals. Dots represent the snow samples listed in Table 2.

As an alternative approach to the previously discussed correlation analysis of the data, principal component analysis [8] was applied. A new set of variables, termed components, were calculated on the basis of the correlation matrix of initial data. The first component explains as much as possible of the variance of the original data, the second component explains a maximum of the remaining variance, and so on. For the principal component analysis of the data in this work two first components were used. These two components were used to draw a biplot (Fig. 1) that reflects the relationship between the variables as well as between the variables and snow samples. It must be taken into account that the variance explained by these two components was less than usually needed (<80%). However, the results were meaningful enough for our purposes. The pH value and chloride content were closely correlated with each other (small angle between the vectors) and negatively correlated with the distance from the road. The total concentrations and soluble fractions form separate groups of vectors in opposite directions in the plot.

The dots representing the snow samples are clustered according to their location with the Arula–Sihva road in the lower left corner, the Otepää–Piiri road in the centre, and the Tallinn–Pärnu road in the upper corner of the plot. The soluble fractions of metals coincide on the plot with the Arula–Sihva cluster of snow samples. The pH value and chloride content coincide with the snow samples from the Tallinn–Pärnu road.

Heavy metals in urban and suburban snow

Snow was gathered in Tallinn, in late winter 1993 after a twenty-four days period of snow cover. The samples were taken from two lawns about 25 m from the street. One sampling site was located near Narva Road with heavy bus, car, and tram traffic. The other site was located in a suburb of Tallinn (Laagri) where the traffic was light. Tables 5 and 6 present the sampling conditions and characteristics of the snow samples.

Table 5

Urban snow: sampling conditions, pH, content of chloride and particulate matter

Location	Distance from road, m	Height of snow-pack, cm	Volume of meltwater, L	pH	Chloride, mg/L	Particulate matter, mg/L
Narva Road, lawn	25	7	4.26	7.8	7.4	134.7
Laagri, lawn in kindergarten	25	12	5.15	4.9	5.4	14.4

The snow samples from the city (Narva Road) and the suburb (Laagri) differ in all variables. The low pH of snow in Laagri may be due to deposition of smoke emitted by the local heating centre. Snow is alkaline near Narva Road. The chloride content of meltwater did not differ significantly between the two sites. The quantity of particulate matter in the snow cover in the city was about ten times as high as in the suburb.

Table 6

Urban snow: total concentration (subscript t) and soluble part (subscript s) of heavy metals

Location	Pb_t, µg/L	Pb_s, %	Cu_t, µg/L	Cu_s, %	Zn_t, µg/L	Zn_s, %	Mn_t, µg/L	Mn_s, %
Narva Road	230	11.2	120	24.9	380	70.4	89	57.2
Laagri	30	93.5	20	83.3	290	83.3	31	89.5

There is a clear difference between the concentration of heavy metals in the city snow and the suburban snow. The total concentration of metals is significantly higher in the city snow than in the suburban snow. At the same time the soluble fraction in snowmelt is higher in the suburban snow than in the urban snow (Table 6). The same effect could be detected earlier by comparing the concentration of heavy metals and their solubilities in the snow at Otepää and in the roadside of the highways in North Estonia (Table 3). To facilitate interpretation of the data on the solubility of heavy metals, the dry residue in snow was analysed by the extraction (speciation) method. Similar treatment was used also for the soil samples collected near Narva Road. Extraction was applied in a four-step system. The results of speciation for the snow and soil (0–5 cm) samples from Narva Road are presented as bar graphs in Fig. 2.

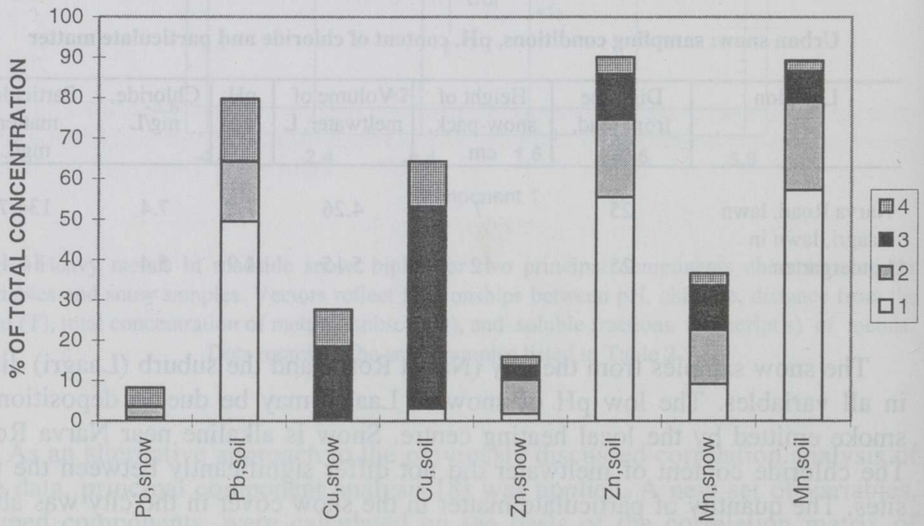

Fig. 2. Distribution (%) of lead, copper, zinc, and manganese among four extraction steps (1–4) of speciation analysis of snow particulate matter and soil horizon (0–5 cm) under snow.

The total solubility of the compounds of Pb, Cu, Zn, and Mn in the four-step extraction system was considerably lower for the dry residue of snow (8–40%) than for the soil (65–90%). Zinc and manganese had similar distribution patterns between the extraction steps. The most soluble fraction of copper belonged to the oxalate buffer (step 3) where usually soluble iron compounds and minerals can be met. It is possible that copper is combined with the compounds of iron. Step 3 was missing for lead, whose oxalate is practically insoluble. The main soluble fraction of the soil sample belongs to the moderately acidic (step 2, pH 4.8) acetic buffer with an exception for copper.

As traffic is the most important source of the input of heavy metals into the roadside soil we studied the possible extention of soil pollution. Soil was analysed in the place of sampling snow near Narva and Kadaka roads situated in different areas of Tallinn. The traffic intensity was nearly the same in both sites. Soil was investigated at distances of 1, 10, and 25 m from the road in the horizons of 0–5, 0–10, and 10–20 cm. To characterize the horizons of soil the pH_{KCl} value, the content of chloride, the redox potential (E_h), and the content of humus (loss of weight on heating at 450 °C) were determined (Table 7).

Table 7

Soil characteristics in the sampling sites of Tallinn

Location	Distance from road, m	Horizon, cm	pH_{KCl}	Chloride, mg/kg	E_h, mV	Loss of weight on heating, %
Narva Road*	25	0–5	7.4	200	–	13
		5–10	7.6	175	–	12
Kadaka Road	1	0–10	7.6	16.2	15	10
	1	10–20	7.8	11.2	25	5
	10	0–10	7.7	12.1	25	5
	10	10–20	7.8	15.3	15	5
	25	0–10	7.1	11.4	20	20
	25	10–20	6.7	9.6	30	16

* Collected on the place of snow sampling.

Table 8 presents the content of heavy metals in the soil of Narva and Kadaka roads and in the particulate matter in snow collected near Narva Road. The content of lead, copper, and zinc in the particulate matter of snow near Narva Road is 2–4 times higher than in the corresponding soil. At the same time the solubility of compounds of metals is much poorer in snow. The effect of traffic on the concentration of metals in the roadside soil is still remarkable at a distance of 25 m from the road and at a depth of 20 cm on Kadaka Road.

Table 8

Heavy metals in particulate matter of snow and in soil in the city of Tallinn

Location	Distance from road, m	Horizon, cm	Pb_t, mg/kg	Pb_s, %	Cu_t, mg/kg	Cu_s, %	Zn_t, mg/kg	Zn_s, %	Mn_t, mg/kg	Mn_s, %
Snow from Narva Road, dry matter	25	–	569	8.3	182	19.5	644	15.9	225	36.6
Soil from Narva Road*	25	0–5	116	79.8	45	64.3	266	90.1	240	89.2
Soil from Kadaka Road	1	0–10	70	64.6	41	86.9	123	52.7	447	76.9
	1	10–20	50	68.6	30	77.4	146	38.1	230	84.2
	10	0–10	99	30.0	35	93.8	131	43.1	251	89.5
	10	10–20	70	56.9	27	86.8	59	33.8	317	87.8
	25	0–10	113	63.1	28	82.3	100	63.5	609	89.0
	25	10–20	97	52.1	18	63.7	68	35.7	427	93.2

* Collected on the place of snow sampling.

The investigation of the snow samples from different locations showed that the load of heavy metals in roadside depends on traffic density. The place with the lowest density of traffic, the Arula–Sihva road near Otepää, had also the lowest load of heavy metals in snow. The load of heavy metals was also low near the Otepää–Sihva road. Moderate concentrations of heavy metals were found in roadsides of both North Estonian highways studied. High contents of lead, copper, and zinc were found in the snow of the city of Tallinn on Narva Road where the traffic density is over 10 000 vehicles per day. The concentration of lead in snow 25 m from the road was about 7 times as high in the city of Tallinn as in the suburb of Laagri. The content of copper was 6 times, manganese 3 times, and zinc 1.3 times higher in the city than in the suburb. The mean concentrations of lead, copper, and zinc were in the suburb of Tallinn 1.5–2 times higher than in the roadside of rural areas. Cadmium had background values in all sampling sites and its content was the highest in the roadside near Viitna on the Tallinn–Narva highway.

The maximum values of elements occurred at different distances from the road. Also the ratio between the content of heavy metals found in meltwater and in dry residue of snow varied. The spread of pollutants depends on the geomorphologic character of the landscape and the roadside flora. The data in Table 3 indicate that a roadside hedge can change the distribution of elements on the roadside. The sampling places near the Tallinn–Pärnu highway were chosen without a hedge in roadside (site 3) and with a boardening hedge (site 4). The largest protective effect of a hedge against the distribution of pollutants was found for chloride and manganese. Also the content of lead at a distance of 100 m from the road was smaller in the case of a hedge.

One of the most important environmental problems is accumulation of heavy metals in the roadside soil. Accumulation occurs when metals are in insoluble form or forming insoluble forms with components of soil. Therefore, the ratio of the soluble and insoluble fractions of metals in snow is important. Correlation analysis showed the soluble forms of elements in meltwater to be negatively correlated with pH, which means that the solubility will grow with rising acidity. The mean solubility (%) of metals in four different ranges of pH values of snow-melt is shown in Fig. 3.

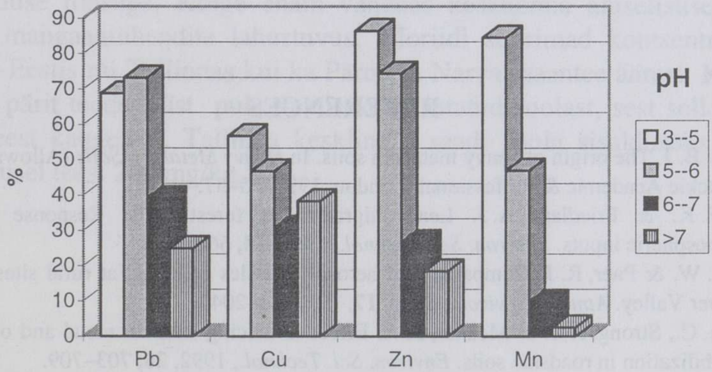

Fig. 3. Solubility of lead, copper, zinc, and manganese in snowmelt in different pH ranges.

The influence of pH on the solubility of zinc and manganese is the strongest. In an alkaline region (pH>7) the solubility of manganese compounds was in the range of 1–2% and in the acidic medium (pH 3–5) nearly 85%. The alkalinity of snow as well as of the soil increases in the roadside with heavy traffic (Tables 2 and 7). The increase of pH can be connected with the development of reducing conditions in roadsides polluted by traffic.

The fate and quantity of the heavy metals of snow deposited in the soil depend on the humus content of soil. In a sandy roadside of Kadaka Road where the humus content is small the metals are not tightly bound in the soil. The maximum concentration of metals in soil can be found at a distance of 25 m from the road in an area richer in humus than the vicinity of the road (Tables 7 and 8).

CONCLUSIONS

The results of this study confirm that

- traffic is a significant source of pollution of roadsides with heavy metals even at a distance of 100 m from the road;
- traffic seems to be a source of lead, copper, zinc, and manganese pollution but not of cadmium;
- traffic density under 1000 vehicles per day has only an insignificant effect on the content of heavy metals in roadside;
- the accumulation of heavy metals in the roadside soil depends on the degree of the solubility of the compounds of metals;
- the main factors found to regulate the accumulation of metals are the pH of the medium and the humus content of soil.

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RASKMETALLID TEEDE ÄÄRES: LUME JA PINNASE KEEMILINE ANALÜÜS NING RASKMETALLIDE OMADUSTE SÕLTUVUS KOHALIKEST OLUDEST

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On vaadeldud raskmetallide levikut linnadevaheliste eri liiklustihedusega maanteede ääres ja Tallinna kesk- ning äärelinna tänavate ääres lume ja pinnase keemilise uuringu abil. Lume analüüsimine võimaldas saada teavet atmosfääri kaudu pinnasele langevast raskmetallide kogusest. On selgitatud plii, vase, kaadmiumi, tsingi ja mangaani esinemist ning selle ligikaudseid seoseid liiklustihedusega. Liiklustiheduse puhul alla tuhande auto päevas ei leitud raskmetallide kontsentratsiooni märgatavat seost liiklusega. Kõrgeimad raskmetallide kontsentratsioonid saadi Tallinna kesklinnas. Kaadmiumi sisaldus lumes ei sõltunud liiklusest.

On uuritud mitmete tegurite mõju raskmetalliühendite lahustuvusele. Põhiliseks teguriks raskmetallide jaotumisel lahustuvaks ja vähelahustuvaks osutus keskkonna pH väärtus. Teedeäärse lume ja pinnase aluselisus kasvas liiklustiheduse tõusuga. Kõige enam vähenes keskkonna aluselisuse kasvuga tsingi- ja mangaaniühendite lahustuvus. Kloriidi suurimad kontsentratsioonid leiti Põhja-Eestis nii Tallinnas kui ka Pärnu ja Narva maantee äärest. Kloriid on nähtavasti pärit teede jääst puhastamiseks kasutatud soolast, sest selle sisaldus väheneb teest kaugemal. Tallinna kesklinnas saadi soola sisalduseks pinnases 25 m kaugusel teest 200 mg/kg.