

Heavy metals in roadside soils

Maire-Liis Hääl^{a*}, Helvi Hödrejärv^b, and Harri Rõuk^a

^a Department of Transportation, Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia

^b Department of Natural Sciences, Tallinn Pedagogical University, Narva mnt. 25, 10120 Tallinn, Estonia

Received 6 May 2004, in revised form 17 September 2004

Abstract. Strong correlations were found between traffic volume and heavy metals in the roadside soil, reflecting the vehicles as sources of Fe, Zn, Pb, and Cd and partly of Cr, Ni, and Co. In winter when de-icing salt is used an increased concentration of heavy metals, especially of Fe and Zn, in soil was observed. Zinc can be used as an indicator element to demonstrate the effect of traffic pollution in spring. In summer the mobility of Zn compounds rises due to better aeration and the lowering of the pH of soil.

Key words: soil contamination, heavy metals, chlorides, traffic, studded tires, road maintenance.

INTRODUCTION

Investigation of environmental contamination with heavy metals (HM) originating from motor vehicles started in Estonia in the late 1970s [1] when concentrations of HM in snow samples were determined. The rapid motorization during the last decades requires additional expenditure on road maintenance and environmental protection. Compared with the year 1991 by today the traffic of motor vehicles has grown in Estonia nearly two times and in Tallinn 2.5 times [2]. The growth of the traffic volume has stimulated taking care of roads and areas near the roads and strengthened environmental monitoring. According to the Estonian National Monitoring Programme such HM as mercury, cadmium, lead, copper, and zinc have a special place belonging into the list of most hazardous pollutants.

The European transportation policy up to the year 2010 puts special emphasis on environmental problems, especially on improving the quality of the air. The emphasis shifts from local pollutants to the ones creating a global threat. The most

* Corresponding author, liishaal@edu.ttu.ee

typical one of these – carbon dioxide, one of the causes of the greenhouse effect – is formed by burning fuel in an engine. Therefore it has been suggested that the speed of motor vehicles be decreased to reduce fuel consumption and that measures be taken to cut the distances driven by means of optimizing the routes. If the aim is to decrease total emissions from traffic, the generation of dust from the degradation of the road surfaces caused by traffic should be addressed alongside with vehicle exhaust emissions (CO, volatile organic compounds, NO_x, SO₂, soot, Pb) and the dust and wear particles of vehicle construction materials. The level of pollution also depends on the weather conditions and the amount of chlorides used. Studies show that during the winter period when the application of chlorides increases, also the proportions of other elements (Zn, Pb, polycyclic aromatic hydrocarbons, total hydrocarbons) in the stormwaters are increasing [3]. Motor-vehicle exhaust emissions due to tyre and brake wear, corrosion, etc., road and maintenance-related emissions due to wear of road surface, and the use of de-icing chemicals and herbicides, etc. can threaten the health of man and surrounding soils, water, and vegetation [4].

The wear of the components of motor vehicles introduces heavy metals into the adjacent environment. Alloys used in the modern vehicle industry correspond to the European standards [5]. For example, alloys used in brakes contain copper, iron, and nickel; dampers are covered with zinc; the occurrence of cadmium in the environment may be caused by the Cd–Ni batteries, vehicle tyres, and diesel fuels. Tyres consist of approximately 85% rubber mixture, 12% steel, and 3% textile. Tyres also loose about 10–20% of their weight during the period of use [4]. The bodies of the studs used in studded tyres are made of stainless steel, which includes iron, chromium, nickel, and manganese. The cores of the studs are prepared from an alloy that consists of a threatening metal – cobalt (3–30%) [5].

Many studies have been carried out on the problem of the lately introduced studded tyres [6–9]. It has been shown that the use of studded tyres results in a significant increase in the decay of pavement, which in addition produces dust, increases fuel consumption, and creates additional need for wash vehicles. Roads, tyres, and studs wear out faster in the case of surfaces that are clean of snow and are wet [6, 9]. This leads to a need for greater expenditures on the maintenance of roads and roadsides.

The erosion of the pavement of roads is a source of dust consisting of the mineral substances and the binding agent of the pavement material. Asphalt consists of small particles of mineral material and bitumen. The type of pavement also plays an essential role, for example asphalt surfaces that include oil shale bitumen are considered somewhat more dangerous to the environment than the ones including oil bitumen. The worn out layers of Estonian pavements contain up to 7.5% bitumen (Estonian Asphalt Norms AL ST 1-02). The proportion of HM in bitumen is small, only the concentration of nickel and vanadium is on average over 1 mg/kg in raw oil.

Several problems are associated with the use of de-icing salts for snow and ice removal from roads. Some of the problems are the corrosion of road surfaces

and vehicles and damage to roadside vegetation and aquatic systems near the roads [6, 10]. The most usual de-icing salt is sodium chloride. First it is extremely soluble, and secondly, it is cheaper than the other de-icing salts. The unpleasant fact is that sodium is an undesirable element for vegetation displacing other cations such as calcium, magnesium, and potassium in soil and rendering these other cations unavailable for plant uptake [11]. A large amount of salt in soil will cause the shift of osmotic pressure and decrease the water supply in plants.

It is difficult to assess the size of the problem of environmental pollution originating from road traffic, especially because we are not dealing with point pollution but the origin is spread all over the road network and has to do with parameters that are not easily controlled. Exhaust gases and dust are dispersed by the wind, washed onto the ground by rain, and transferred on in the soil due to chemical processes. The wind and traffic carry dust along a width of over 30 m of the roadside area, causing elevated HM contents in the soil and snow samples taken from the roadside.

Roadside pollution with HM arising from traffic is a widely known fact and has been in the focus of many investigators [12–16]. Once emitted, metals can reside in the environment for a long time. Future improvements in that field may depend on preventing the formation of the pollutants, rather than on attempting to reduce their concentration once they have been created.

The behaviour of a metal depends on its chemical character and the soil matrix: ions or compounds that complex with metals (e.g., Cl^- , HS^- , SO_4^{2-} , etc.) and partial pressures of gases (e.g., O_2 , CO_2 , H_2S , NH_3). The main individual compounds of metals are the hydroxides, oxyhydroxides, carbonates, and sulphides in alkaline and reduced soils, and sulphates and chlorides in acidic soils. For example zinc may be transported as a sulphate complex in sulphate-rich run-off waters, and zinc carbonate/bicarbonate complexes may be important in carbonate-rich soils. Some metals such as iron, manganese, and chromium change their oxidation steps as the redox status of soil changes. So, Fe(II) and Mn(II), existing in reduced soils, form more soluble compounds Fe(III) and Mn(IV) in oxidized soils. Approximate prediction of the behaviour of HM in soil is possible by measuring the soil conditions such as the pH, redox potential, and the content of organic matter and other main constituents. Unfortunately, we must usually manage with limited knowledge about the investigated system by drawing conclusions about the probable transport and accumulation of HM in soil. Moreover, the selection of metals (e.g., Fe, Cd, Cu, Pb, Zn, Co, Ni, Cr) is also limited. An optimized selection of variables was made to get the answers to questions set up in the present work. In addition to the selected HM the pH of soil, chloride content in the soil, and the area of distribution of HM around the road were regarded to estimate the pollution level caused by traffic in that region.

The pollution research was carried out at the Department of Transportation of Tallinn University of Technology (TUT) during the years 2001–2003.

MATERIALS AND METHODS

The study area and schedule

The locations of the sites of sampling were selected according to the different purposes of the studies carried out in 2001, 2002, and 2003:

- The samples in 2001 were taken to find out the pollution level of the areas near the roads with different traffic volumes in crowded areas. The study was ordered by the Department of Sustainable Development and Planning of Tallinn City Government.
- The purpose in 2002 was to expand the database used for the study of HM on roadsides and to assess possible environmental risks. The study was ordered by the Ministry of the Environment of the Republic of Estonia.
- The purpose in 2003 was to determine the effect of chlorides on the environmental situation according to the proportions of Cl and HM in the soil and snow samples and also to assess the change of the proportions of HM in crowded areas through time. The study was ordered by Tallinn Municipal Services Department and the Ministry of the Environment of the Republic of Estonia.

The locations selected by the study group of the Institute of Transportation of TUT were identified, recorded to easily recognizable static objects, and photographed. All 79 soil samples were taken from roadsides and analysed chemically.

The samples were collected as follows:

29 March–7 Apr 2001	33 samples of soil (23 from densely populated areas and 10 from areas bordering highways),
11 Feb and 15–25 March 2002	16 samples of soil,
18 March–30 Apr 2003	25 samples of soil (Table 2),
12 Oct 2003	5 samples of soil (Table 3), and
13 Feb–12 March 2003	5 samples of snow (Table 4).

The years differed in the amount of precipitation (Fig. 1) and temperatures (Fig. 2), which resulted in differences in organizing road maintenance in winter. The winters in the period 2001–2003 were different, the number of fluctuations of ground surface temperatures over 0°C differed, and the ground melted at different times (Figs. 1 and 2). Such factors as ground surface temperatures and the amount of precipitation especially influence the spread of smaller dust particles.

The winter of 2002/2003 was cold (the ground was frozen deeply and for a long time, and it was dry). The small amount of precipitation in February and March meant that the wind could carry pollution further away from the roads. This may be the reason why the concentrations of HM in the soil samples taken in spring 2003 were relatively smaller than in previous years.

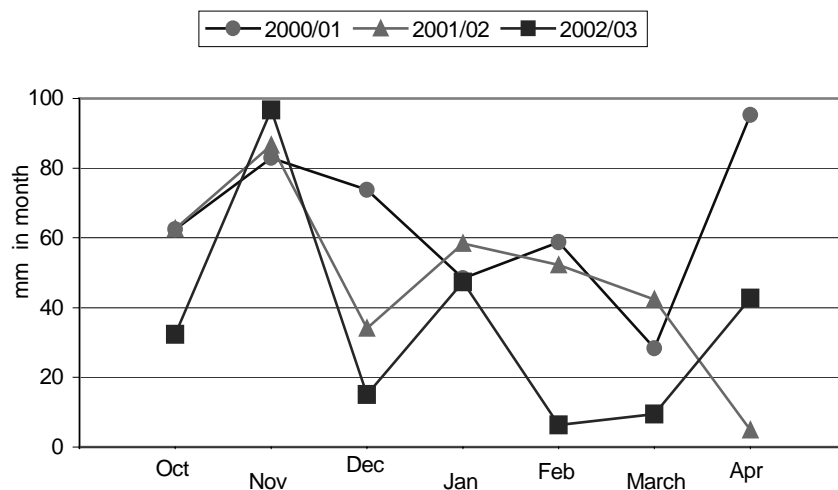


Fig. 1. Winter precipitation in Tallinn in 2000–2003 (data from the Estonian Meteorological and Hydrological Institute).

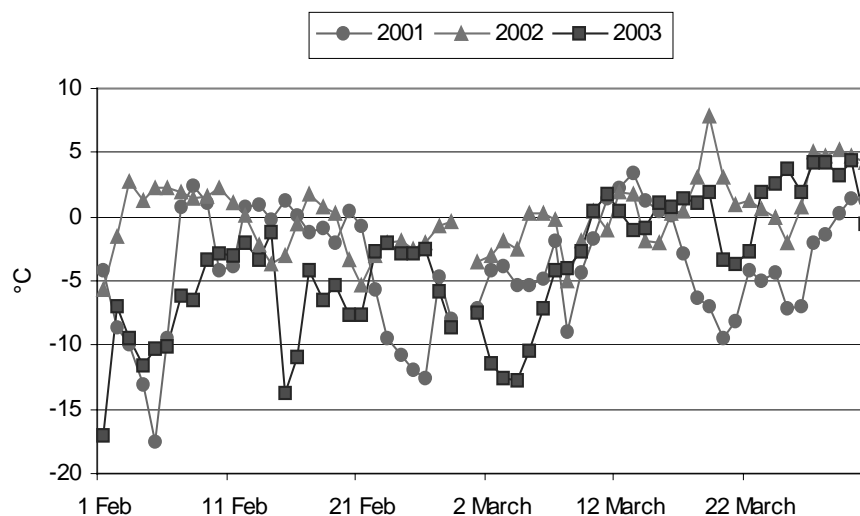


Fig. 2. Average daily ground temperatures in Tallinn in February–March 2001–2003 (data from the Estonian Meteorological and Hydrological Institute).

Information on the sampling sites in 2003 is summarized in Table 1. The concentrations of chloride, HM (selected considering the aim of the study), and the pH of soil and snow samples are given in Tables 2, 3, and 4.

Table 1. Sampling sites in 2003 with information about traffic volume and road width

Site No.	Date of sampling	Site characteristics	Road lanes	Cars per day	Sample No.	Distance to road pavement, m
S1	27 March	Urban forest area, the road is bordered by pine forest on one side and a birch grove on the other	1 + 1	3 400	1	5
	27 March				2	20
S2	24 March	Highway type road, level area, buildings on one side of the road and brushwood on the other	1 + 1	5 100	3	5
	4 March				4	15
S3	25 March	Roadside on a higher level than the road, no drainage	1 + 1	12 000	5	15
S4	30 March	Steep incline of the road, kerbstones, urban forest	1 + 2	14 500	6	20
S5	27 March	Highway type road, level area, pasture on one side, shrubbery on the other	2 + 2	15 000	7	5
	27 March				8	20
S6	23 March	Urban park, wide sideway road reconstructed in 2002, kerbstones, new roadside filling	3 + 2	16 700	9	5
	23 March				10	10
	30 March				11	30
S7	18 March	Steep incline of the road, roadside slightly higher, grass, some old trees	2 + 2	22 000	12	5
	18 March				13	15
S8	30 Apr	Highway near crossing a river with steep banks	2 + 2	22 700	14	20
	24 March				15	30
S9	15 March	Urban centre, a verdant area with old trees in between traffic directions	3 + 3	27 000	16	8
S10	18 March	Highway on higher level than a park	3 + 3	33 000	17	5
S11	27 March	Road bordered by urban forest on one side and buildings on the other	3 + 3	37 000	18	8
S12	24 March	Roadside of a relatively new part of road, level and disordered grassland	3 + 3	48 600	19	8
	24 March				20	29
S13	14 March	Highway type road, sampling area up to 27 m from the road in level grassland beyond which a forest starts	2 + 2	49 600	21	5
S14	18 March	Road leading out of the urban centre, a verdant area near dwelling houses	3 + 3	67 000	24	10
	27 March				25	20
S15	12 March	Steep incline in a highway type road	1 + 1	4 800	See Table 4	8

The sites under investigation (Table 1) were selected at the roads with asphalt pavement. The age of the roads varies. For example, road S12 was constructed in 1997 and S13 was open to traffic around 1960. The samples were collected at distances of up to 30 m from the pavement edge. The speed limits of motor vehicles were 70 km/h (on sites S5, S8, S10, S13), 30 km/h (on site 15), and 50 km/h (on the other sites).

Collection of samples

Soil samples (ISO 11464:1994(E)). At least 500 g of fresh soil was collected at distances of 4–30 m from the pavement at depths of 3–5 cm in spring immediately after the melting of the soil. The reference samples were gathered in autumn at a depth of 10 cm. The samples were transported to the laboratory in tightly closed plastic bags, dried in the air, stones and other additives larger than 2 mm were removed, and subsampled by hand (quartering). For the preparation of laboratory samples portions of 200 to 300 g were separated. For the preparation of a test sample the laboratory sample was split until the required sizes of samples were obtained. The test sample not less than 2 g in mass was ground in an agate mortar.

Snow samples were collected 3 m from the road from areas 10×10 cm at 10 cm depth. The snow samples were melted at room temperature in a glass container. The meltwater was filtered through a plankton net with a hole diameter of 90 nm. The filtrate was passed through filterpaper (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 used for analysis of heavy metals. The filtrate was used for the determination of chloride. The loss of heavy metals by filtration was not determined.

Methods of chemical analysis

The pH of the samples was determined by the routine potentiometric method using a glass electrode and silver–silver chloride reference electrode in a 1:5 (V/V) suspension of soil in a solution of 1 mol/dm³ potassium chloride. The suspension was vigorously mixed for 5 min, and after 2 h the pH was measured with a pH meter (ISO 10390:1994).

Chloride was titrated amperometrically in a solution produced by digesting a mean sample of soil by diluted (1 mol/dm³) nitric acid or in the snow melt. The titration was carried out using silver nitrate as the titrant and a rotating platinum-wire electrode. As the reference electrode, a mercury sulphate–mercury electrode was used [14].

Heavy metals were determined in the soil and in the particulate matter of snow. The samples were digested by nitric acid (63%) and diluted by distilled water. The conventional atomic absorption spectrometry (AAS) was used. Zinc, copper, and nickel were determined by the flame method, and cadmium, lead, and cobalt were determined by the electrothermal method in a graphite cuvette [14, 17].

RESULTS AND DISCUSSION

Results of chemical analyses

Tables 2–4 give the results of analyses of roadside soil in spring and autumn 2003 and of snow collected in roadside. In some places the samples were collected at different distances from the road.

The concentrations of chloride and HM and the pH were determined in the Laboratory of Chemical Analysis of Testing and Calibration Centre of TUT, which has competence according to EVS-EN ISO/IEC 17025:2000 to conduct tests in the field of elements determination using AAS methods, registration

Table 2. Concentration of chloride and heavy metals (mg/kg) and the pH of soil samples collected at several distances (*L*) from roads of different traffic volume in March 2003

Sample No.	<i>L</i> , m	pH _{KCl}	Cl	Zn	Cu	Cd	Pb	Co	Ni
1	5	7.32	173	54	26	0.23	12	1.9	–
2	20	6.98	59	79	32	0.46	9.4	1.3	–
3	5	7.48	995	425	53	2.2	112	–	22.4
4	15	7.22	84	145	60	3.88	62.4	10.3	–
5	15	7.02	30	59	32	0.24	7.7	2.6	–
6	20	6.61	100	488	86	3.05	85	5	–
7	5	7.5	153	103	42	0.53	28.9	8.3	–
8	20	7.2	61	67	34	0.31	14.9	4.1	–
9	5	7.04	53	94	61	0.3	11.4	3.3	–
10	10	6.32	33	176	63	0.24	53.2	3.7	–
11	30	6.18	41	148	43	0.48	55.3	2.9	–
12	5	7.34	724	191	42	2.7	108	–	16.7
13	15	6.89	488	562	155	6.2	72	–	33.4
14	20	7.7	72	122	70	1.13	36	7.4	–
15	30	7.19	135	123	50	0.33	16.6	5.9	–
16	8	7.02	158	217	210	1.3	121	6	–
17	5	7.45	200	127	57	0.34	39.2	6	–
18	8	7.5	459	219	53	4.3	57	–	12.1
19	8	7.58	221	182	141	0.43	24.9	7.5	–
20	29	7.19	34	74	36	0.16	17.5	2.6	–
21	5	7.6	430	173	55	0.22	12.2	5.6	–
22	27	7.11	42	45	50	0.17	7.4	2.3	–
23	20	7.02	124	111	49	1.14	32	9.2	–
24	10	7.28	58	165	100	0.35	49.6	7.9	–
25	20	6.9	371	179	73	1.59	71	6.3	–

– Not determined.

Table 3. Concentration of heavy metals and chloride (mg/kg) in soil (at 10 cm depth, distance from road surface 8–20 m) collected on 6 October 2003

Sample No.	Traffic volume, cars per day	Cl	Zn	Cu	Cd	Pb	Co	Ni	Cr	Fe
4	5 100	550	39	41	0.09	47	29	14.8	81	26 800
6	14 500	132	65	65	0.65	68	7.2	4.8	12	12 602
13	22 000	415	108	125	2.77	72	61	47.5	50	17 978
14	22 700	83	78	87	2.32	51	42	31	43	13 010
18	37 000	115	37	34	0.26	32	15	3.6	7.3	5 030

Table 4. Concentration of heavy metals and chloride (mg/kg) in snow samples collected in 2003

Site No.	Date of sampling	Cl	Zn	Cu	Cd	Pb	Co	Cr	Ni
S14	3 March	1700	182	141	0.43	24.9	7.5	15.4	–
S11	3 March	2880	163	44	4.3	24	–	–	10.3
S6	12 March	500	258	85	0.35	18	9.8	18	–
S9	12 March	850	324	123	0.24	18	7.3	20.6	–
S15	12 March	720	86	58	0.2	12.4	4.2	11.4	–

– Not determined.

number L116, the present accreditation shall remain in effect until 16 Jan 2008. The methods used for the determination of the concentration of chloride and pH are not accredited

Traffic as a source of heavy metal pollution

The summary statistics of chemical analyses is shown in Table 5.

The data vary in a large range (maximum–minimum), resulting in high values of standard deviations. Therefore the values of medians are more representative, for example for comparison with the background data given in Table 6.

The average of the roadside samples taken from Rae rural municipality, Harju County, in 2002 and 2003 shows the changes in a background suburban area close to Tallinn compared to the studies conducted by the Estonian Geological Survey in 1991. Table 6 reveals that in approximately 10 years the concentration of Pb in the soil in the area closely surrounding Tallinn has declined but the concentrations of Zn and Ni have doubled.

In the samples taken in 2001–2003 in urban conditions the median concentrations of zinc and copper were the most elevated exceeding three times the Estonian average (Fig. 3). The median of lead had decreased during three years; however, it still exceeded the Estonian soil average concentration two times. The considerable growth of the concentration zinc in 2003 compared with the previous years is reflected also in the growth of the concentration of cadmium. The average concentrations of HM received in spring 2003 in urban conditions exceeded the Estonian averages (Tables 5 and 6) as follows: copper 6.3, zinc 4.6, cadmium 3.8,

Table 5. Summary statistics of the soil pH, and concentrations of chlorides and heavy metals (mg/kg) in roadside soil in spring 2003

	Soil pH _{KCl}	Cl	Zn	Cu	Pb	Cd
Average	7.15	212	173	67	45	1.29
Standard deviation	0.37	242	131	43	35	158
Minimum	6.18	30	45	26	7	0.16
Maximum	7.7	995	562	210	121	6.2
Median	7.19	112	134	53	36	0.46

Table 6. Comparison of the average heavy metal concentrations (mg/kg) in roadside in 2001–2003 with results of earlier investigations

	Zn	Cu	Pb	Cd	Ni	Co	Cr
Estonian soils, average 1997*	37.3	10.6	16.4	0.34	21.9	7.92	42
Soils in surroundings of Tallinn, 1997*	16	6.16	12.5	0.23	16.4	3.75	24.4
Soils in surroundings of Tallinn, 1991**							
median (<i>N</i> = 158)	35	22	22	–	12	7	28
average (<i>N</i> = 158)	45	23	26	–	12	5.9	29
Rae municipality, 2002–2003***							
average	72	23.5	17	0.22	26	5	23.2
2001–2003 spring, average (<i>N</i> = 74)***	155	65.8	54.6	0.7	27.3	5.2	137
Tallinn, 2003 spring							
median (<i>N</i> = 25) ^{Table 5}	134	53	36	0.46	–	–	–
average (<i>N</i> = 25) ^{Table 5}	173	67	45	1.29	–	–	–
2003 autumn							
average (<i>N</i> = 5) ^{Table 3}	65	70.4	54	1.21	2.5	30.8	40.5

*[18], **[19], ***[20–22], Tables 3 and 5 of this work.

– Not determined.

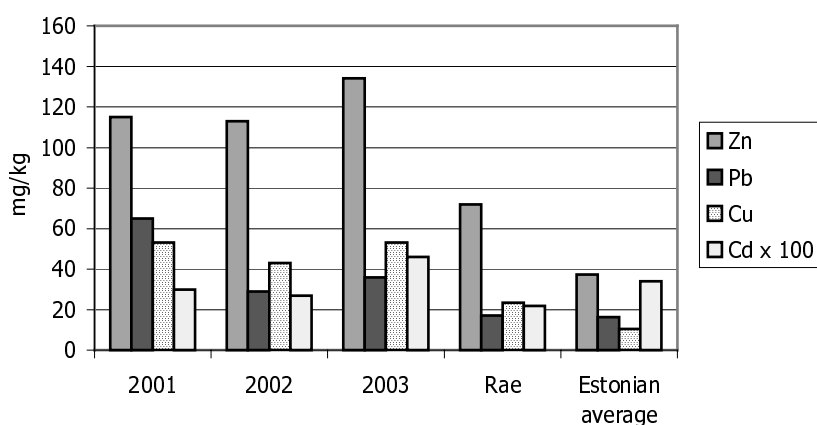


Fig. 3. Medians of heavy metal concentrations in roadside soil in urban areas in 2001, 2002, and 2003 compared with the relevant concentrations in Rae rural municipality [21, 22] and the averages for Estonian soil [18].

and lead 2.7 times. This is evidently caused by technogenic pollution mainly caused by traffic. The average concentrations of Cu and Cd were high, the values fluctuated within a large range, being unexpectedly high in some samples.

Snow samples were collected in five sites, and the HM content of snow (Table 4) was compared with the content in soil in spring 2003. The large differences found can be explained mainly by different distances of sampling

places from pavement. In spite of the differences, snow has several advantages over soil as it is free of terrestrial components and catches pollutants straight from the air. Snow also accumulates pollutants for a long time. In our case the concentrations were influenced also by snow dumped from the road. The concentrations of chloride and HM found in snow were in many cases higher than in the soil of the same site. The concentrations of HM in snow were lowering in the order: Zn > Cu > Pb > Co > Cd.

Traffic volume and heavy metals

The correlations between the HM concentrations in roadside soil and traffic volume (cars per day) are shown in the correlation matrix (Table 7). The correlation decreased in 2002 in the order: $r_{Zn} > r_{Pb} > r_{Fe} > r_{Cd} > r_{Cr}$. Consequently the best indicators for traffic as the source of HM pollution are the first three HM: zinc, lead, and iron.

For decades lead contamination of roadsides has received a great deal of attention. Leaded petrol has been an important source of lead pollution. In 1986 the lead content of petrol in Finland was lowered from 0.7 g to 0.15 g/L and in the unleaded petrol the concentration is less than 0.013 g/L [23]. Since that time the percentage of vehicles with catalytic converters has been sharply increasing. Notwithstanding the increasing use of unleaded petrol, the metal burden in roadside soil still seems to be continuously considerable. The main part of lead is the result of accumulation during a long time. Therefore lead is not any longer regarded as the best indicator of trends and changes in traffic pollution.

Iron can be used as an indicator of vehicle emissions as it is a product of attrition and corrosion of the main construction materials of cars. Iron is the main element in the bodies of studs. Iron is found for example in the diabase of Eurajoe, which is widely used as a mineral in asphalt concrete in Estonia.

However, iron is not a typical trace element due to its terrestrial origin. The natural iron content in Estonian soils is 5000–10 000 mg/kg [18]. Iron concentration in roadside soil was determined in the years 2001 and 2002. In 2001 the analysis of soil samples taken 4–8 m from the road pavement gave the average of iron concentration 9456 ± 2995 mg/kg (median 9627 mg/kg) and

Table 7. Correlation coefficients (r , $p < 0.05$) between traffic volume and HM concentrations

Year of sampling	Number of samples and area of sampling	Traffic volume, cars per day	Zn	Cd	Pb	Cr	Fe
2001	23, crowded areas	500–42 500	0.514	0.520	0.228	0.589	0.716
2001	33, crowded area + highway	500–42 500	0.544	0.621	0.190	0.452	–
2002	16, crowded area + highway	890–621 000	0.770	0.467	0.721	0.273	0.596

– Not determined.

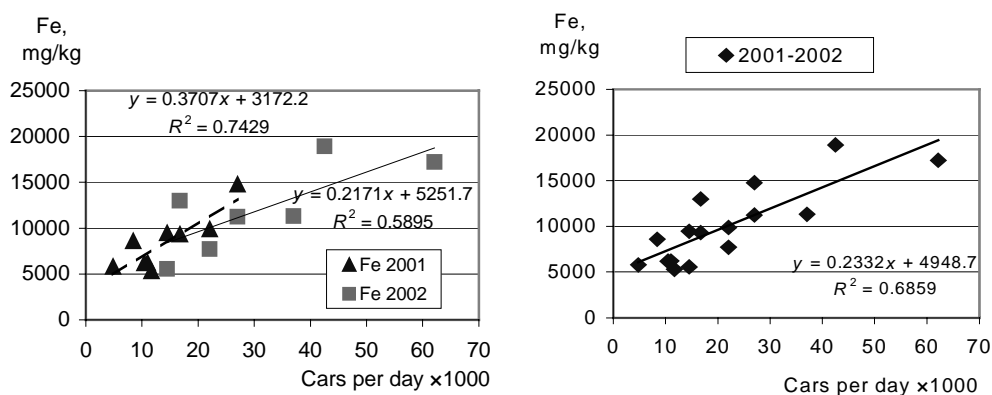


Fig. 4. Iron concentration in roadside soil depending on the traffic volume at a distance of 30 m from the pavement edge [20, 21].

15–30 m from the road, 10572 ± 7446 mg/kg (median 8948 mg/kg). Although the concentration of iron is still in the average ranges of Estonia, it belongs to the maximum values. The study of the correlation of iron with the traffic intensity indicated high correlation as can be seen in Fig. 4 and in Table 7.

In recent years the modern automobile industry has introduced galvanically coated steel using mostly zinc as the protective element for iron. In the normal atmosphere zinc forms a basic zinc carbonate film, which greatly retards its corrosion rate. Also tires of motor vehicles are a source of zinc pollution. In practice the concentration of zinc in roadsides is rising. The rise is related to the traffic volume (Table 6) and exceeds significantly the Estonian average in soils. An example can be given about London where the growth of the traffic volume from 20 000 to 120 000 cars/day was accompanied by a rise in the load of zinc in roadsides up to 6.2 times [24].

To conclude, zinc can be used as an element to demonstrate the pollution effect of traffic. Considering the importance of the non-vehicle emissions in influencing the environmental situation, the concentration of zinc in the soil is an important parameter in assessing the environmental impact of traffic.

Distribution area of heavy metals in roadside

Heavy metals originating from traffic are distributed in roadsides by the atmosphere within a distance that depends on the size of particles. The concentration of pollutants in soil can vary greatly according to the strength and direction of the wind, the width of the road, and the height of the buildings. The highest concentration of HM was measured directly at the side of the road. In roadsides that are not built up the concentration of HM is significant even at a distance of 100 m from the road [14].

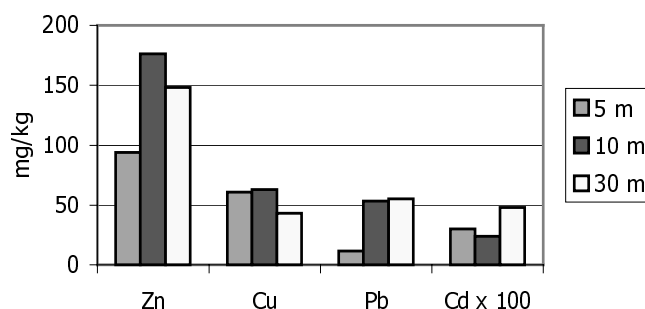


Fig. 5. Concentration of zinc, copper, lead, and cadmium at different distances from the pavement (sites 6, samples 9, 10, and 11, Table 2).

In the present study the concentration of HM was determined at distances from 4–5 m up to ~30 m from road with traffic volumes in the range 500–62 100 cars/day.

To characterize the distribution of the concentration of HM in the roadside area site S6 (see Table 1) is shown in Fig. 5. This area is characterized by slow speed (50 km/h) of vehicles and residential low buildings situated along the street at about 50 m distance from the road. The samples were collected from a park bordered by roads, at distances 5, 10, and 30 m from the pavement edge. Zinc and copper had the highest concentrations at a distance of 10 m, lead and cadmium at 30 m. Obviously lead particles originating from the fuel burning products are small and rise to higher levels in the atmosphere and fall down at greater distances as products of corrosion than zinc and copper. The higher concentration at a distance of 30 m for cadmium can be explained by a secondary source of pollution (e.g. heating systems of the homes) or long-term accumulation of Cd.

In our studies the highest concentrations of HM in the soil were found at 8–15 m from the pavement. The spread of HM further than 30 m from the pavement was not a subject of these studies.

The main factors (pH, chloride) limiting the mobility of heavy metals in soil

The accumulation of HM 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 acidic–alkaline conditions of soil, the degree of aeration, and the components of soil with high adsorption properties versus HM, ion exchange or precipitation of metals on mineral surfaces. The soluble compounds of HM usually move into the deeper horizons or wash out with rain or snow at some distances from the roadside. The great amount of chlorides spread on the roads during the snowing period is also of importance as a factor influencing the fate of HM in soil.

The form in which the HM are in soil depends to a great deal on the degree of the aeration of soil. In the case of high traffic the degradation of the motor fuel residues will lower the oxygen content in soil. Organic pollutants need oxygen for oxidation. The simultaneous rise of the pH (and lowering of the hydrogen ion concentration) with the decreasing of the pressure of oxygen in soil is caused by the consumption of hydrogen ions by the reduction of oxygen. In that way the rise of the pH and the lowering of the redox potential of the soil near the road are a result of traffic pollution.

The concentration of carbon dioxide increases simultaneously in the atmosphere and soil. The metals can occur in the form of hydroxides or carbonates depending on the parameters of soil. The hydroxides are of major interest because they are for most HM insoluble under these conditions. The hydroxides of metals can be ranged by the ability to dissolve in water at room temperature as follows: $\text{Fe(II)} > \text{Ni, Co} > \text{Pb} > \text{Zn} > \text{Cr(III)} > \text{Fe(III)}$. The solubility of hydroxides is a function of pH. In our study the range of the soil pH was between 6.2 and 7.7, and soil had suboxic properties. From the investigated metals the equilibria Fe(II/III) and Cr(III/VI) are redox dependent. The solubility of iron(II)hydroxide and zinc(II)hydroxide in that pH region will decrease about a thousand times if the pH rises as it happens in winter [25]. Iron(III)hydroxide and chromium(III)hydroxide are entirely precipitated already at pH 6.2.

In the year 2003 the trends of the concentrations of chloride and soil pH were similar (Table 2). The de-icing salt spreads from the road as spray and dust through the atmosphere or with run-off waters, and its concentration decreases with distance as does the alkalinity of the soil. This can be explained by the diminishing of the influence of the products of incomplete combustion of fuel in the engine.

The large amount of de-icing salt used in wintertime that accumulates in the roadside soil also has a considerable influence on the solubility of most HM. The ratios of millimoles of chloride ions and HM ions in soil by medians are: 10 Cl:823 Fe:6.5 Zn:2.6 Cr:0.5 Pb. Millimoles of the elements were calculated using the data of 2003 (Tables 3 and 5). Consequently, chloride ions are in excess compared with HM, except iron. Taking into consideration that the maximum value of chloride in soil was found to be almost nine times as high as the median (Table 5), chloride may be recognized as a critical parameter controlling the fate of HM in soil. Most HM can form soluble chlorides or chloride complexes in the presence of chloride ions in a suitable pH region, except lead, which forms an insoluble lead(II)chloride. The high correlation between the lead and chloride concentrations in spring 2003 ($r = 0.62$; $p < 0.01$) can obviously be explained by the accumulation of lead as lead chloride in the roadside. In autumn the study of the sites with a high salt use indicated a drop of the salt content in soil during summer through wash-out but the content of lead had not altered significantly. Zinc as a more mobile element had decreased nearly everywhere during summer. Supposing that the aeration of soil improves in summer and the soil becomes more acidic, the solubility of zinc compounds will also rise and zinc may be washed out from the soil. Assimilation of zinc by plants will also be possible. The same trend

is shown by cadmium, which has a high correlation with zinc ($r_{\text{spring}} = 0.50$; $r_{\text{autumn}} = 0.94$; $p < 0.01$). The high correlation can be explained by the similar chemical properties of zinc and cadmium.

Corrosion as a main source of heavy metal pollution and the role of de-icing salt in it

The spray of de-icing salt potentially promotes corrosion of the metallic parts of vehicles creating a concentrated electrolytic coating. When a metal surface is in contact with an electrolyte, differences develop between local areas of the surface; a more reactive (less noble) area referred to be anodic. Zinc is electrochemically more reactive than most of the constituent metals in vehicles (Cd, Co, Cu, Cr, Fe, Ni) and will oxidize first sending the ions into solution, for example the corrosion of zinc in contact with iron. By that way the high de-icing salt concentration is one of the most important factors causing corrosion of metallic parts of vehicles and emission of HM from traffic. The mechanism for zinc corrosion is largely determined by the formation and stability of the basic carbonate film ($\text{ZnCO}_3 \cdot 3\text{Zn(OH)}_2$) on the zinc surface. This compound is soluble in acidic conditions and in the presence of chloride ions.

Chemical analysis of samples collected during three years indicated that correlation between chloride and zinc in soil is strong: $r_{2001} = 0.438$ ($n = 14$) $< r_{2002} = 0.785$ ($n = 12$) $< r_{2003} = 0.792$ ($n = 25$) (see also Fig. 6).

A noteworthy finding was a high concentration of iron in soil in autumn in places where the concentration of chloride was continuously high (Table 3). This suggests that the corrosion process of the road furniture takes place also in summer.

There is a deficiency of information about the part of the wear of tires and pavement in HM pollution. It will be a task for further investigations to find some indicator elements to explain the problem. A research carried out in seven European countries [4] shows that the classifications of HM recovery (compared

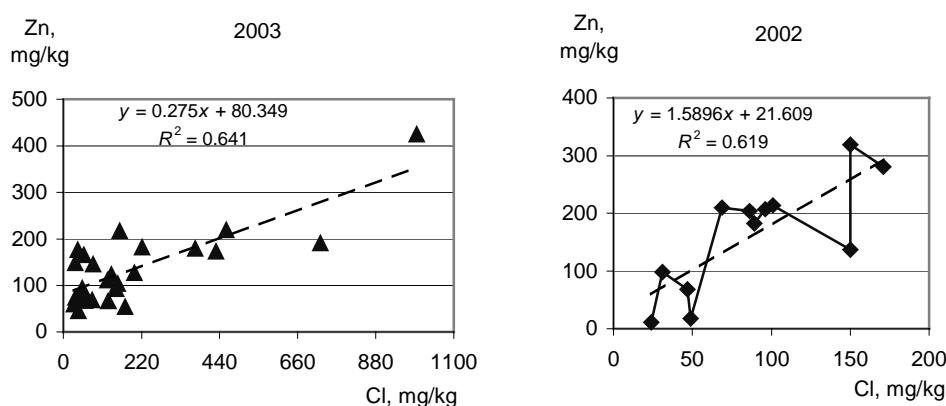


Fig. 6. Correlation of chloride and zinc in roadside soil [22].

with calculated values) in sites are similar despite differences in traffic volume, share of heavy traffic, climate, and topography. This indicates similarities in the dispersal mechanisms and environmental behaviour near the roads.

Figure 7 shows the change of the concentration of elements at sites (Table 1) with different traffic conditions and surroundings.

Some maximum concentrations can be explained by the specific character of traffic, for example roads running uphill (S15 and S7) or streets (S9) where the sampling point was between two traffic directions with trolley buses and the traffic was of high volume but slow with frequent brakes.

The highest value of copper in site S9 can be explained by trolley bus traffic in this street and attrition of copper contacts. High zinc concentrations can be found in places where also the chloride content is higher and the corrosion of cars is expected to take place more intensively than in other sites. The sites with very high chloride concentrations have also elevated lead levels.

Correlation matrices were calculated between the metals to detect the presence of collinearity. A correlation exists in case the absolute value of the coefficient is greater than 0.5 ($p < 0.05$).

Correlation Tool from Microsoft Excel Analysis Tool Pack [26] was used to calculate the correlation matrices.

Table 8 gives the coefficients of correlation between the metals in different years and in spring and autumn 2003 in places with high zinc and chloride concentrations in spring. Except chromium, a strong correlation exists between the other metals, especially in autumn. The median of cadmium was in urban conditions in strong correlation with zinc ($r_{2003, \text{autumn}} = 0.94$, Table 8). Zinc and its compounds are usually accompanied with trace amounts of cadmium. It must be noted that cadmium belongs among especially toxic elements and thus its monitoring is extremely important.

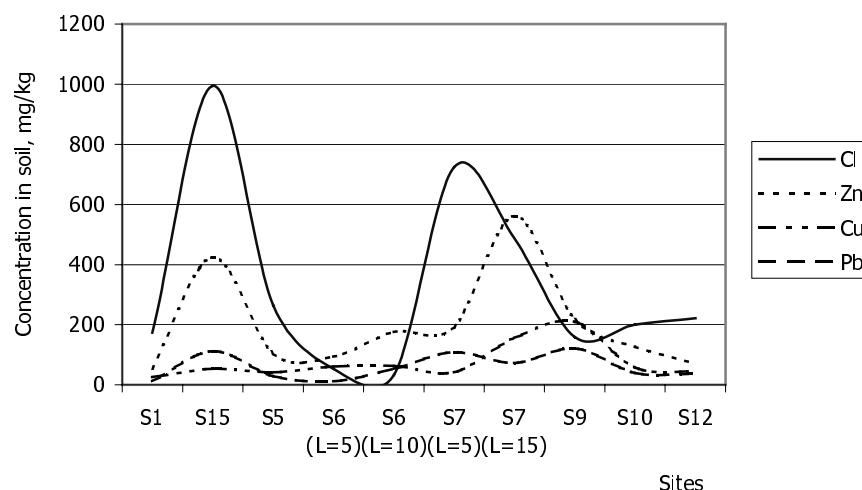


Fig. 7. Zinc, copper, lead, and chloride concentration in different sites (Table 1).

Table 8. Correlation matrix of heavy metals in roadside soil in spring 2001, 2002, and 2003 and in autumn 2003. Bold shows correlations greater than 0.5

Year	Correlation coefficient r ($p < 0.05$)						
	Element	Zn	Cu	Cd	Pb	Ni	Cr
2001	Zn	1					
	Cu	-0.192	1				
	Cd	0.307	-0.121	1			
	Pb	0.446	-0.25	0.521	1		
	Ni	0.596	-0.281	0.222	0.592	1	
	Cr	0.837	-0.122	0.178	0.397	0.472	1
	Fe	0.887	-0.152	0.354	0.454	0.423	0.941
2002	Zn	1					
	Cu	-0.052	1				
	Cd	0.423	-0.092	1			
	Pb	0.781	-0.343	0.528	1		
	Ni	0.002	0.716	0.221	-0.052	1	
	Cr	0.163	0.114	0.434	0.291	0.269	1
	Fe	0.603	0.145	0.591	0.591	0.391	0.567
2003 $N = 25$	Zn	1					
	Cu	0.502	1				
	Cd	0.745	0.335	1			
	Pb	0.671	0.499	0.581	1		
$N = 21$	Co	0.254	0.355	0.514	0.371		
2003 autumn $N = 5$	Zn	1					
	Cu	0.996	1				
	Cd	0.939	0.951	1			
	Pb	0.798	0.773	0.566	1		
	Ni	0.869	0.908	0.916	0.529	1	
	Cr	0.089	0.163	0.132	0.106	0.468	1
	Co	0.763	0.814	0.843	0.385	0.982	0.555

CONCLUSIONS

- Accumulation of heavy metals (Zn, Pb, Cd, Cr, Ni, Cu, Co) hazardous to the environment in roadside was determined. Correlation amongst the HM used as construction materials in car production confirms that traffic is a common source for those.
- The average concentrations of HM in soil received in spring 2003 in urban conditions exceeded the Estonian averages several times: copper 6.3, zinc 4.6, cadmium 3.8, and lead 2.7 times. This is evidently caused by technogenic, mainly traffic pollution.
- The fate of HM pollution caused by traffic (dissolution in the soil solution, accumulation, migration) depends on the chemical properties of

HM compounds as well as the properties and structure of soil. The quantity of chlorides used in road maintenance and the pH of the soil influence the mobility and transportation of HM.

- In winter when salt was used for de-icing, an increased concentration of HM (especially Zn and Fe) in soil was observed. The growth of zinc concentration in soil was accompanied by an increase in cadmium.
- Lead, used for a long time as an indicator of traffic pollution, is not a sufficient indicator for characterizing the environmental impact of traffic any more.
- Zinc can be used as the indicator element to demonstrate the traffic pollution effect in spring. It is suggested that simultaneously the concentration of chlorides in the soil and/or groundwater should be observed.

ACKNOWLEDGEMENTS

This work was supported by the Ministry of the Environment of the Republic of Estonia and by Tallinn Municipal Services Department.

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Raskmetallid teeäärtes pinnases

Maire-Liis Hääl, Helvi Hödrejärvi ja Harri Rõuk

Autoliiklus põhjustab mitmete keskkonnale ohtlike raskmetallide sisalduse kasvu teeäärsete alade pinnases. Põhiliselt kuuluvad liiklusest põhjustatud saaste hulka Fe, Zn, Pb, Cd ning osaliselt Cr, Ni ja Co. On leitud, et teekatete jäätmisvastaste reagentide (NaCl) kasutamine talvel suurendab liiklusvahendite ja teepäraldiste korrosiooni tõttu raskmetallide, eriti raua ja tsingi kontsentratsiooni pinnases. Tsink võib osutada sobivaks näitajaks liiklusest põhjustatud raskmetallide saaste avastamisel ja jälgimisel kevadel. Suveperioodil on pinnase aereerimise ja happesuse tõusu tagajärjel tsingiühendite liikuvus suurem kui talvel.