Environment Protection Engineering

Vol. 35 2009 No. 3

ANDRZEJ KŁOS*, MAŁGORZATA RAJFUR*,
MARIA WACŁAWEK*, WITOLD WACŁAWEK**

IMPACT OF ROADWAY PARTICULATE MATTER ON DEPOSITION OF POLLUTANTS IN THE VICINITY OF MAIN ROADS

This paper presents the results of biomonitoring studies involving the assessment of the effect of traffic on the deposition of heavy metals (Cd, Cu, Mn, Ni, Pb and Zn). In our experiment, mosses and lichens growing in the vicinity of a major road were exposed to traffic for over 100 days. The increase of metal concentration was determined using Relative Accumulation Factors. It was discovered that the concentrations of Zn, Cu, Ni, Pb and Zn decreased along with the distance from the road in the windward direction. In the opposite direction, the highest increase in pollutants (Zn, Pb and Cd) was observed over the distance of 50–150 m, while Cu and Ni concentration is the highest close to the road. No relevant variation in the concentration of Mn was observed. For the purposes of comparison the concentrations were also determined in soil.

1. INTRODUCTION

The economical transformations of the recent years in Poland have been accompanied by a dynamic increase in the number of vehicles in the roads.

On the basis of the data from Central Statistical Office in 2007 the number of vehicles in Poland has risen by 14% in comparison with the situation in 2005 and by 28% in comparison with 2000. The total number of in-service vehicles in Poland amounts to 19.5 million. Opole province holds the third position in the country in terms of the number of vehicles per capita – 427 vehicles per 1000 population (Statistical Yearbook, 2008)

The impact of motor traffic on quality of environment involves both exhaust gases and dust from the abrasion of tyres, brakes and roadway surface. The motor traffic

* Chair of Biotechnology and Molecular Biology, Opole University, ul. Kard. B. Kominka 4, 45-032 Opole, Poland, tel.: 77/401 60 42, e-mail: aklos@uni.opole.pl

** Chair of Chemical Physics, Opole University, ul. Oleska 48, 45-052 Opole, Poland, tel.: 77/452 71 34, e-mail: waclawek@uni.opole.pl

related factors affecting the volume of air pollution from a roadway sources include: traffic volume, vehicle speeds, vehicle mix, technical condition of vehicles (in Poland 80% of cars are 5-year-old or more), and, in addition, the roadway geometry and the surrounding terrain. Among other factors influencing atmospheric pollution dispersion the climate or microclimate type and topography of the road vicinity shold be mentioned.

The pollution emission rates per 1 km length of road are as follows: for carbon monoxide from around 3 g/km for passenger cars to 30 g/km for buses and lorries, for nitrogen oxides: from 0.5 g/km for motorbikes and passenger cars to 2.5 g/km for buses and lorries. The emissions of hydrocarbons are from 0.4 g/km for passenger cars to 3 g/km for lorries. In order to determine the emission levels for xenobiotics in the atmospheric aerosol direct and indirect methods of chemical analysis are used. The reference indirect measurement method to determine sulphur dioxide is the method with UV spectrophotometric detection (Ambient air – ISO/DIS 10498), and chemiluminescence method for the concentration of nitrogen dioxide (PN-ISO 7996:2001). The assessment of these pollutants is also conducted with the passive Amay probes (Krochmal and Kalina, 1996; Krochmal and Kalina, 1997). However, the disadvantage to these methods is associated with the large financial outlay necessary to conduct the studies, in particular in the case when they are spatial studies conducted on numerous sites at the same time.

A considerable hazard to the environment is associated with the emission of heavy metals, mostly Cu, Ni, Pb and Cd as well as of S (Pomorska and Duda, 2004). 3% of the total Pb (19.857 Mg), ca 1.6% of Ni (4.499 Mg), ca 0.7% of Cu (2.669 Mg) and ca 0.4% of Cd emissions (0.219 Mg) (OLENDRZYŃSKI et al. 2003) were due to motor traffic in 2001. As a result of fuel combustion and tyre abrasion some amounts of Zn are also emitted to atmosphere (POLKOWSKA et al. 2007; PRATT and LOTTERMOSER 2007). The deposition of heavy metals emitted due to motor traffic has been determined in the soil (ZUPANČIČ 1999; TURER et al. 2001; PIRON-FRENET et al. 1994) and in precipitation, runoff and ground waters (POLKOWSKA et al. 2007).

The methods of assessing the environmental pollution are currently, often replaced with biomonitoring methods. The plants used as the indicators are usually mosses and lichens. The studies rely on the exposition of the plant material transplanted from areas with unpolluted environment (active biomonitoring) or on the use of bioindicators naturally inhabiting the examined area (passive biomonitoring). The assessment focuses on the analysis of the chemical composition of the bioindicators. In July, 2008 a report concerned with spatial and temporal variations in the concentration of heavy metals in mosses was published. The program involved the area of Europe and gathered research institutions from 20 European countries. On the basis of the collected results it was concluded that in general the lowest concentrations were observed in (northern) Scandinavia, the Baltic States and northern parts of the United Kingdom (HARMENS et al. 2008). In addition, the analysis concerns the changes in the physiol-

ogy and morphology of the bioindicators. Biomonitoring studies undertaken in urban areas have offered valuable insights into the problem. Such studies have been conducted in Portugal (PACHECO et al. 2001), Italy (BERGAMASCHI et al. 2007; SCHINTU et al. 2005), India (SHUKLA and UPRETI 2007), Greece (PIRINTSOS et al. 2006) and Argentina (HEBE et al. 2002), to mention just a few.

Lichens and mosses have also been used for assessment of the impact of motor traffic on the dispersion of pollutants in the vicinity of roads. Such a study was conducted over the years from 1994 to 1995 along the 55th kilometer of the Lille-Paris (F) A1 motorway (CUNY et al. 2001). On the basis of the changes in the concentration of analytes in the exposed lichen samples the authors indicated that the levels of Cd and Pb depositions are affected not only by the volume of the traffic but the vehicle speeds as well. Another example of how biomonitoring can be effectively used is the study conducted along the M3 motorway in Hungary (NASZRADI et al. 2004) and the studies conducted along a road in Accra, Ghana (AFFUM et al. 2008).

An example of the application of passive biomonitoring is a study which was conducted in Finland. The objective of the study was an assessment of the impact of motor traffic on the deposition of Pt and Rh emitted from car catalytic converters (NIEMELÄ et al. 2007). The concentration of elements from the platinum group (Pt, Pd and Rh) as well as 17 other elements (including Zn, Cu, Ni, Pb and Cd) were determined in 32 moss samples taken along 12 main roads in Australia (ZECHMEISTER et al. 2006). The biomonitoring studies conducted in July and November of 1998 along local roads in the environs of Grenoble (F) indicated that the concentration of pollutants in the vicinity of main roads is determined by the volume of the traffic, vehicle mix and distance from the road (GOMBERT et al. 2003).

Over the period from 1990 to 1994 a pilot study was conducted in north-west Italy along a newly opened mountain motorway A32 (a 70 km stretch of motorway in the Alps) which focused on the impact on the vegetation in the examined area (CAMPO et al. 1996). The studies revealed that the highest concentration of heavy metals: Cr, Pb and Cd in the vegetation could be noted at the distance of 10 m from the road. Additionally, the comparison between the various species of plants indicated that mosses and lichens can serve as the most representative indicator of the environmental pollution with trace elements.

The above studies clearly indicate that the deposition roadway pollution decreases with distance away from the road.

The object of the biomonitoring studies presented in this research was the assessment of the deposition of heavy metals: Zn, Cu, Ni, Pb and Cd, which enrich the local atmospheric aerosol due to motor traffic in the perpendicular direction to a stretch of the trunk ring road of Opole. In the studies mosses and lichens transplanted from the area of Bory Niemodlińskie were applied. The concentration of heavy metals was also determined in the surface 5 cm layer of the soil. A comparative studies involved as well the determination of Mn contents; the chemical element is used in car catalytic converters.

2. MATERIALS AND METHODS

The studies were conducted in the area of the northern ring road of Opole. This road, 14.85 km in length, is a section of three trunk roads: 45, 46 and 94. The area of sampling is affected both by urban emission sources (ca 6 km from town center) and by industrial sources (cement and lime works and electric power station).

Epiphytic lichen *Hypogymnia physodes* and epigeic moss *Pleurozium schreberi* were applied for the research. The samples of lichens and mosses were collected from the same sites, in Bory Niemodlińskie, situated south-west of Opole. The basic criterion for the selection of the particular site for the collection of moss and lichen for sampling was associated with the low concentration of heavy metals in this area. The lichens were collected together with their natural substrata of their vegetation (dry spruce branches).

The mosses were cleaned of mechanical impurities and placed in plastic bags; the mass of a sample was 1 g, whereas the lichens were left on the dry branches and tied to form bundles in which the mass of the lichens was 2 g. Such lichen and moss samples (two in a given site) were placed 1.5 m above ground level, on the border of a forested area, in the perpendicular direction to the road (figure 1).

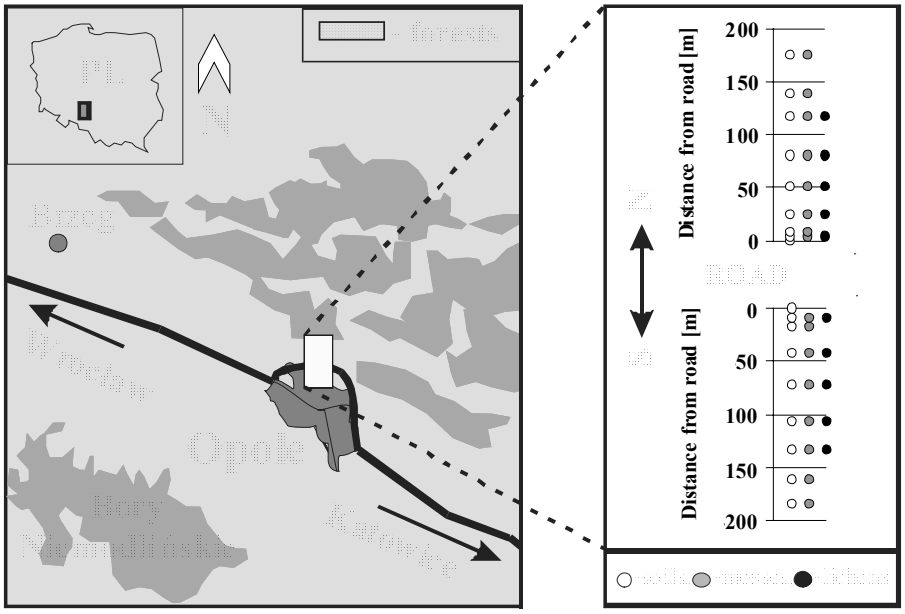

Fig. 1. Distribution of moss and lichen samples near the northern ring road of Opole

The analysis involved samples of mosses and lichens which were exposed over the period from November 30, 2007 to April 10, 2008. After the period of the exposition the samples were cleaned of mechanical impurities, dried at 373 K and homogenized

in an agat mortar. Samples of 5 cm thick layer of surface soil were taken at the sampling points marked in the map (figure 1) and on the edge of the asphalt surface of the road. The soil after drying at 373 K was subsequently passed through a 2 mm mesh sieve, homogenized and again passed through a sieve, this time with a 0.2 mm mesh.

The mineralization of the homogenized lichen, moss and soil samples (each 0.6 g) was performed with a CEM Mars X microwave oven in aqua regia. The determination of heavy metals: Zn, Cu, Ni, Mn, Pb and Cd in the solutions after the mineralization was carried out with the Unicam Model Solaar 969 atomic absorption spectrometer (AAS).

The diagram of the analytic procedure is presented in figure 2.

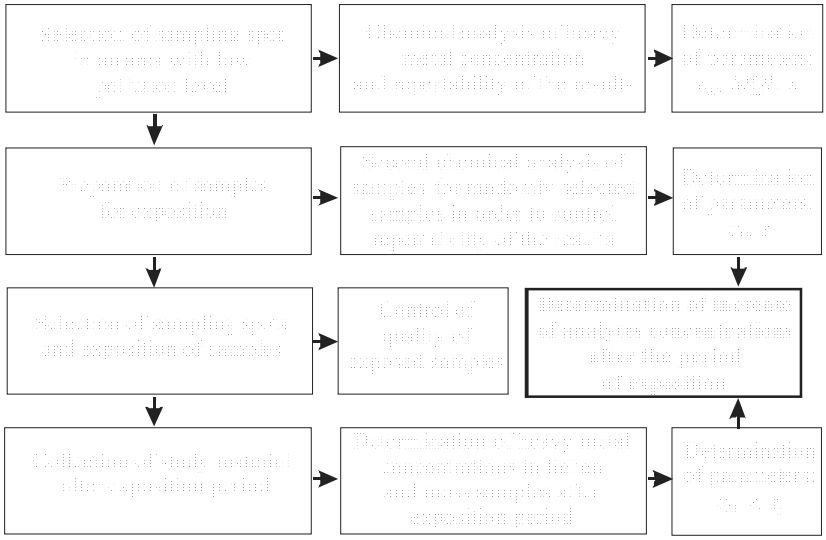

Fig. 2. Diagram of analytical procedure

Quality assurance/quality control

In order to fulfill the requirements associated with quality assurance/quality control (QA/QC) the sampling was repeated seven times with regard to randomly selected samples of mosses and lichens selected for exposition. On every occasion the same analytic procedure was followed. The procedure was also repeated seven times in two sampling spots in which lichen and moss samples were taken. In the remaining samples the procedure was repeated three times. Calibration was performed with the standard solution from ANALYTIKA Ltd. (Czech Republic). In addition, comparative study was conducted with AAS and INAA (Instrumental Neutron Activation Analysis) in 2006. Concentrations of Zn and Mn, among others, were established in moss and lichen samples. INAA studies were conducted at Frank Laboratory of Neutron Physics, Dubna, Russia.

The graphical results in figure 3 have been borrowed from our not yet published studies (FRONTASYEVA and KŁOS, unpublished data).

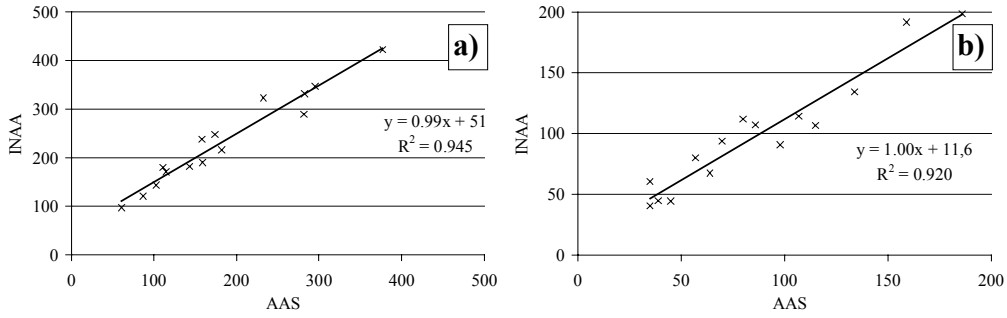

Fig. 3. Comparison between concentrations [mg/kg d.m.] of analytes accumulated in samples of lichens, mosses and soil determined with AAS and INAA methods for: a) Mn, b) Zn

The QC of INAA results were ensured by carrying out a concurrent analysis of the reference materials Lichen 336 IAEA (International Atomic Energy Agency). Deviation: the NAA/certified value expressed in [%] between the results obtained by INAA and the certified value amount to, respectively: Mn 13.2 %, Zn 0.2 % (KŁOS et al. 2008). Concentrations of Cu, Ni, Pb and Cd were determined after the apparatus validation by comparing the data from it with those coming from the INAA measurements.

Statistical elaboration of experimental data

The research involved the determination of the *LOQ* (*limit of quantification*) values as well as of those of *MQL* (*method quantification limit*). The value of *LOQ* was determined for samples prepared in accordance with recommendations of KONIECZKO and NAMIEŚNIK (2007) using the formula:

$$LOQ = 3\ (x_{\text{mean}} + 3 \cdot s) \tag{1}$$

where: x_{mean} – mean, s – standard deviation.

The values of *MQL* are summarised in Table 1.

Table 1

Values of *MQL* determined for moss and lichen samples [mg/kg of d.m.]

	Zn	Cu	Ni	Mn	Pb	Cd
Moss	0.505	0.085	0.058	1.12	0.108	0.033
Lichen	0.564	0.080	0.053	1.02	0.133	0.032

The uncertainty of the measurement was assessed from the standard deviation s:

$$s = \sqrt{\frac{\sum_{i=1}^{n} (x_i - x_{\text{mean}})^2}{n-1}} \tag{2}$$

while the standard deviation of the analytic method was calculated to be:

$$s_{am} = \sqrt{\frac{1}{n-k}\sum_{i=1}^{k} s_i^2 (n_i - 1)} \tag{3}$$

where: k – number of parallel series of measurements.

From the experimental data the *Relative Accumulation Factors* (*RAF*) were calculated

$$RAF = \frac{(c_{x,1} - c_{x,0})}{c_{x,0}} \tag{4}$$

where: $c_{x,0}$ – concentration of analyte prior to the exposition; $c_{x,1}$ – concentration of analyte after the exposition.

3. RESULTS

Tables 2 and 3 contain a summary of the results of measurements of heavy metal concentrations in mosses and lichens prior to and after the period of exposition referred to 1 kg of dry mass (d.m.). The tables contain the values of standard deviation s, calculated from formula (2) and the value of standard deviation of the analytic method s_{am}, calculated from formula (3).

Table 2

Results of heavy metal concentrations in moss samples prior to and after exposition [mg/kg d.m.]; *Mean* (*s* [%], percentage of standard deviation); number of samples: $n = 3$ (* $n = 7$)

	Distance from road								Concentration before deposition*
	Direction North								
[m]	4	8	25	51*	80	117	139	175	
Zn	76 (5.2)	95 (2.6)	183 (5.7)	367 (6.2)	352 (5.4)	355 (6.4)	162 (6.7)	80 (3.4)	54 (9.6)
Cu	23.3 (8.6)	30.8 (6.4)	26.7 (5.4)	22.5 (9.9)	20.8 (6.9)	20.8 (6.3)	15.0 (7.1)	11.7 (7.7)	10.8 (7.3)
Ni	9.2 (7.1)	12.5 (7.1)	9.2 (11.3)	7.5 (9.9)	7.5 (9.7)	7.5 (8.8)	7.5 (7.3)	5.8 (8.1)	5.1 (6.6)
Mn	407 (8,3)	211 (9.3)	228 (7.9)	222 (10.6)	259 (8.0)	217 (10.0)	207 (6.3)	252 (5.6)	268 (10.5)
Pb	20.0 (8.5)	20.8 (8.1)	30.0 (6.2)	30.0 (9.2)	31.7 (6.3)	25.8 (3.6)	13.3 (6.4)	10.8 (4.4)	10.8 (7.0)
Cd	5.8 (11,0)	5.0 (10.6)	3.3 (11.4)	4.2 (10.1)	5.0 (9.9)	5.0 (8.1)	4.2 (9.5)	3.3 (7.7)	2.4 (10.1)

Direction South									
[m]	8	17*	42	72	106	133	161	183	
Zn	118 (8.2)	114 (7.4)	115 (10.6)	108 (7.3)	104 (6.9)	113 (8.4)	117 (4.5)	84 (6.3)	54 (9.6)
Cu	35.0 (5.6)	32.5 (4.1)	25.0 (6.3)	17.5 (5.7)	19.2 (4.3)	19.2 (2.8)	14.2 (3.2)	14.2 (6.9)	10.8 (7.3)
Ni	18.3 (3.6)	17.5 (6.1)	9.2 (8.2)	8.3 (5.5)	7.5 (7.4)	7.5 (4.3)	6.7 (9.3)	6.7 (9.2)	5.1 (6.6)
Mn	222 (6.6)	238 (8.2)	213 (5.3)	241 (3.0)	256 (5.8)	209 (6.2)	218 (6.6)	241 (6.5)	268 (10.5)
Pb	25.0 (4.9)	25.0 (6.4)	24.2 (4.4)	24.2 (1.7)	25.8 (9.0)	23.3 (2.4)	25.8 (6.0)	17.5 (5.6)	10.8 (7.0)
Cd	9.3 (8.1)	7.6 (8.8)	6.4 (10.9)	5.3 (7.7)	4.7 (8.7)	5.3 (7.1)	4.7 (5.4)	4.7 (5.4)	2.4 (10.1)
s_{am}	Zn		Cu		Ni		Mn		Pb	Cd
[%]	8.2		6.9		8.1		7.9		7.3	9.5

Table 3

Results of heavy metal concentrations in lichen samples prior to and after exposition [mg/kg d.m.]; *Mean* (*s* [%], percentage of standard deviation); sample number: $n = 3$ (* $n = 7$)

Distance from road						Concentration before deposition*
Direction North						
[m]	4	25	51*	80	117	
Zn	197 (7.9)	300 (4.8)	300 (8.9)	318 (5.2)	367 (6.2)	62 (8.9)
Cu	18.3 (4.5)	10.0 (7.0)	10.0 (9.2)	10.0 (7.5)	9.2 (9.3)	6.3 (7.3)
Ni	9.2 (7.0)	7.5 (6.9)	8.3 (9.1)	9.2 (6.0)	5.8 (7.2)	6.4 (6.6)
Mn	170 (7.1)	108 (8.8)	113 (10.4)	117 (9.6)	125 (6.3)	124 (10.5)
Pb	16.7 (5.6)	21.7 (5.0)	20.0 (8.5)	20.0 (8.0)	24.2 (4.6)	9.6 (7.0)
Cd	9.4 (5.9)	9.2 (6.6)	12.5 (10.7)	13.2 (7.4)	11.8 (8.9)	2.5 (10.1)
Direction South						
[m]	8	42*	72	106	133	
Zn	197 (7.9)	173 (5.3)	140 (6.8)	138 (7.0)	137 (6.0)	62 (8.9)
Cu	17.5 (5.1)	10.0 (6.7)	9.2 (9.5)	6.7 (8.4)	6.7 (8.3)	6.3 (7.3)
Ni	20.8 (5.8)	9.2 (6.2)	7.5 (8.1)	7.5 (6.3)	7.5 (5.3)	6.4 (6.6)
Mn	123 (10.0)	123 (7.1)	125 (7.1)	123 (6.5)	119 (8.4)	124 (10.5)

Pb	22.5 (7.3)	18.3 (3.6)	15.0 (6.0)	13.3 (3.8)	14.2 (5.1)	9.6 (7.0)
Cd	9.3 (8.2)	8.9 (8.2)	6.8 (9.6)	6.8 (6.2)	4.0 (7.7)	2.5 (10.1)

s_{am} [%]	Zn	Cu	Ni	Mn	Pb	Cd
	7.6	7.3	7.1	8.2	6.4	9.6

Table 4

RAF parameters indicating increase in analytes concentration in mosses and lichens after the exposition

Metal:	Zn	Cu	Ni	Mn	Pb	Cd
The distance south [m]	Moss					
8	1.18	2.23	2.67	–0.17	1.31	2.73
17	1.11	2.00	2.50	–0.11	1.31	2.03
42	1.14	1.31	0.83	–0.21	1.23	1.57
72	0.98	0.62	0.67	–0.10	1.23	1.10
106	0.92	0.77	0.50	–0.04	1.39	0.87
133	1.09	0.77	0.50	–0.22	1.15	1.10
161	1.15	0.31	0.33	–0.18	1.39	0.87
183	0.55	0.31	0.33	–0.10	0.62	0.87
The distance north [m]	Moss					
4	0.40	1.15	0.83	0.52	0.85	1.30
8	0.75	1.85	1.50	–0.21	0.92	1.00
25	2.37	1.46	0.83	–0.15	1.77	0.33
51	5.77	1.08	0.50	–0.17	1.77	0.67
80	5.49	0.92	0.50	–0.03	1.92	1.00
117	5.55	0.92	0.50	–0.19	1.39	1.00
139	1.98	0.39	0.50	–0.23	0.23	0.67
175	0.48	0.08	0.17	–0.06	0.00	0.33
The distance south [m]	Lichens					
8	2.01	2.02	2.26	–0.01	1.25	2.70
42	1.65	0.72	0.43	–0.01	0.83	2.55
72	1.14	0.58	0.17	0.01	0.50	1.73
106	1.12	0.15	0.17	–0.01	0.33	1.73
133	1.09	0.15	0.17	–0.04	0.42	0.59
The distance north [m]	Lichens					
4	2.01	2.16	0.43	0.37	0.67	2.80
25	3.59	0.72	0.17	–0.13	1.17	2.67
51	3.59	0.72	0.30	–0.09	1.00	4.00
80	3.85	0.72	0.43	–0.06	1.00	4.27
117	4.62	0.01	–0.09	0.01	1.42	3.70

On the basis of the collected results it is possible to conclude that after the period of exposition the concentrations of Zn, Cu, Ni, Pb and Cd have increased. The change in the concentration of Mn was not observed. The concentration level of heavy metals in

the distance of 180 m from the road is similar in the northern and southern directions. This could also indicate urban pollution as the background source of the pollutants.

The figures 4–9 contain a comparison between the *RAF* values (formula 4). The values of RAF are summarised in Table 4.

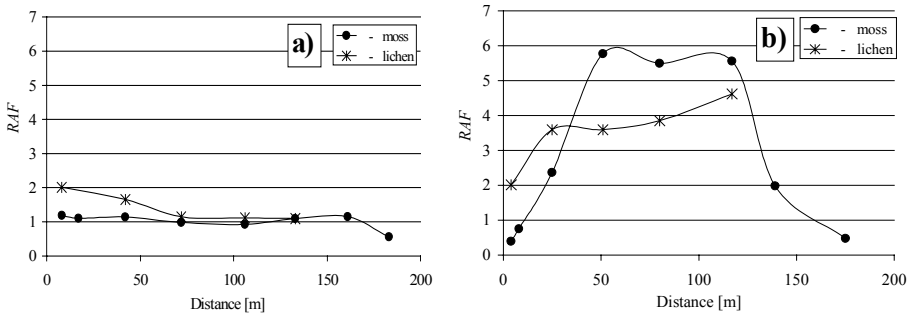

Fig. 4. Dependence of Zn concentration in the exposed moss and lichen samples on the distance from the road edge: a) distance in south direction, b) distance in north direction

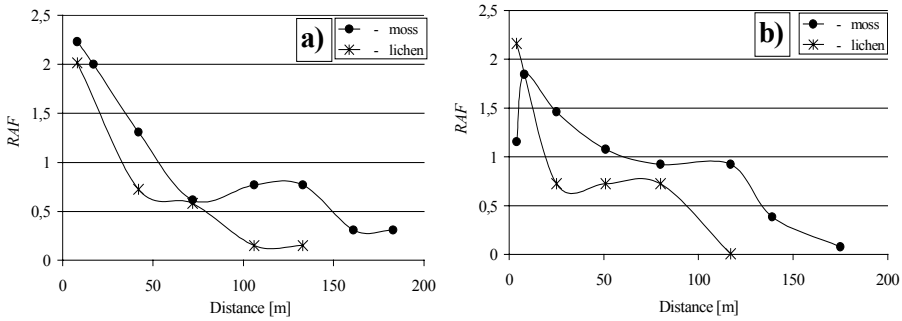

Fig. 5. Dependence of Cu concentration in the exposed moss and lichen samples on a distance from the road edge: a) distance in south direction, b) distance in north direction

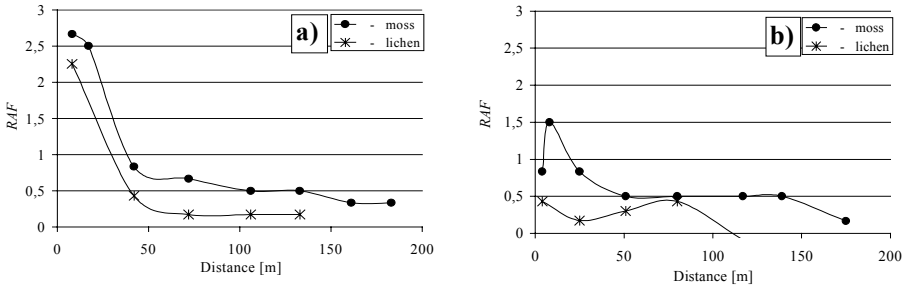

Fig. 6. Dependence of Ni concentration in the exposed moss and lichen samples on a distance from the road edge: a) distance in south direction, b) distance in north direction

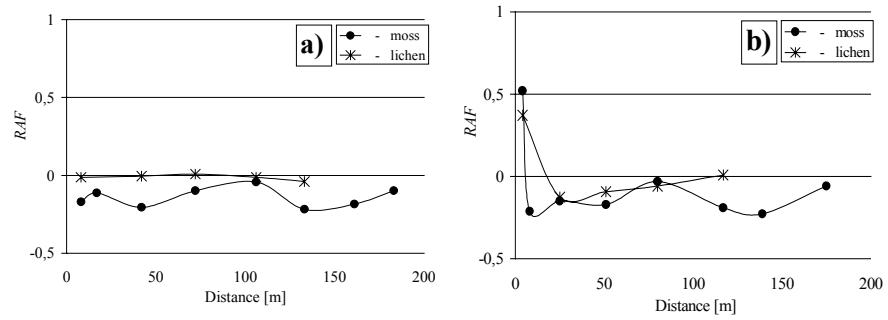

Fig. 7. Dependence of Mn concentration in the exposed moss and lichen samples on a distance from the road edge: a) distance in south direction, b) distance in north direction

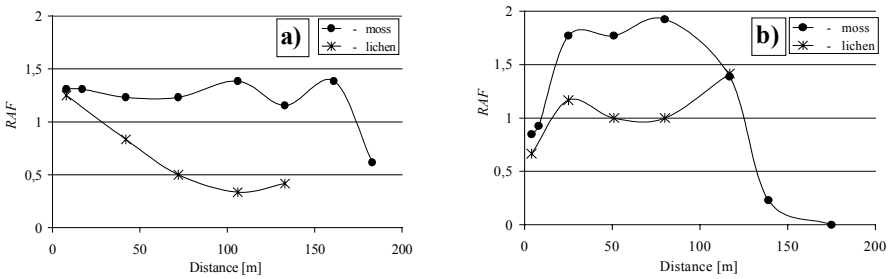

Fig. 8. Dependence of Pb concentration in the exposed moss and lichen samples on a distance from the road edge: a) distance in south direction, b) distance in north direction

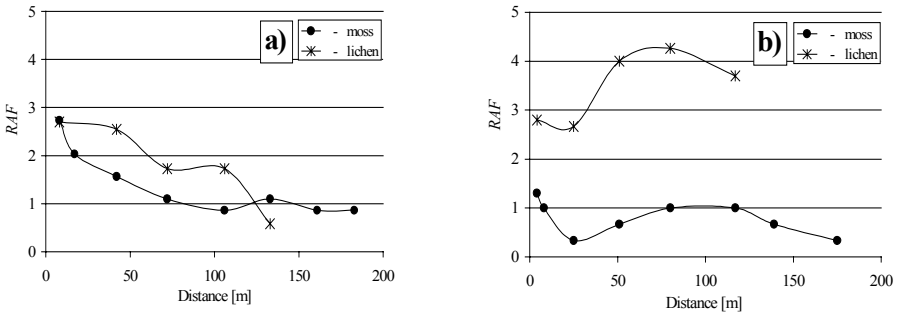

Fig. 9. Dependence of Cd concentration in the exposed moss and lichen samples on a distance from the road edge: a) distance in south direction, b) distance in north direction

The figures indicate that the concentration of the examined analytes increased in the samples of mosses and lichens after the exposition, except for the case of Mn (figure 7).

Table 5 contains data on the concentration of the examined analytes in the soil samples. The used symbols denote: c_0 – concentration of analytes in the samples collected directly on the edge of the roadway, x_{mean} – mean concentration of analytes in the soil samples collected on the sites of lichen exposition, s – standard deviation from the mean value, (S) and (N) – geographical (south and north) direction.

Table 5

Parameters of soil pollution in the vicinity of the road
c_0 – concentration of analytes in the samples collected directly on the edge of the roadway,
x_{mean} – mean concentration of analytes in the soil samples collected on the sites of lichen exposition,
$s(x_{mean})$ – standard deviation from the mean value, (S) and (N) – geographical (south and north) direction

Parameter	Zn	Cu	Ni	Mn	Pb	Cd
$c_{0,(S)}$ [mg/kg d.m.]	383	76	70	325	97	5.5
$x_{mean,(S)}$ [mg/kg d.m.]	61	11	17	259	34	3.1
$s_{(S)}$ [%]	17.0	20.4	16.0	16.0	25.0	16.2
$c_{0(N)}$ [mg/kg d.m.]	433	139	155	443	180	6.0
$x_{mean,(N)}$ [mg/kg d.m.]	142	20	38	499	60	4.0
$s_{(N)}$ [%]	29.4	44.4	65.1	36.6	18.2	17.7

The calculated standard deviations from the mean values for seven samples of soil collected on a single site at the distance of 51 m north from the road, were as follows: Zn (±20.8%), Cu (±23.2%), Ni (±38.3%), Mn (±27.9%), Pb (±21.8%) and Cd (±18.3%). These values are comparable with the values of the standard deviation $s_{(S)}$ and $s_{(N)}$.

The concentrations of examined analytes in the soil collected on the edge of the roadway were also determined on the sites, from where the moss and lichen samples were taken. The results are as follows: Zn (123 mg/kg d.m.), Cu (16.8 mg/kg d.m.), Ni (14.4 mg/kg d.m.), Mn (382 mg/kg d.m.), Pb (12.1 mg/kg d.m.) and Cd (1.4 mg/kg d.m).

4. DISCUSSION

The presented results confirm the impact of the motor traffic on the deposition of heavy metals Zn, Cu, Ni, Pb and Cd in the vicinity of main roads (POMORSKA and DUDA 2004; OLENDRZYŃSKI et al. 2003; POLKOWSKA et al. 2007; PRATT and LOTTERMOSER 2007). But the concentration of Mn has not changed considerably in the majority of the moss and lichen samples studied (figure 6). Manganic oxide is contained in car catalytic converters (JANICKA and WALKOWIAK 2005); however, its measured concentration in the soil on the edge of the road is similar to the concentration of this element in the forest soils, from which the samples of moss and lichen were transplanted. The maximum concentrations of these analytes in the soils collected in another sampling site in the area of Bory Stobrawskie (figure 1) situated

north-east of Opole, are higher, i.e. Zn (199 mg/kg d.m.), Cu (22.7 mg/kg d.m.), Ni (18.0 mg/kg d.m.), Mn (324 mg/kg), Pb (17.4 mg/kg d.m.) and Cd (2.2 mg/kg d.m.) (KŁOS et al. 2008). The present data indicate that save for Mn the concentrations of the remaining heavy metals in the soil collected in vicinity of the road are several times higher than the concentrations of them in the forest soil and the soil collected further away from the road. The data from the reference (ZUPANČIČ 1999) indicate that the changes in the concentrations of heavy metals with the distance from the road can be described with a logarithmic function. The results of this research do not confirm the applicability of the model, which probably is caused by the large uncertainty of our data expressed in terms of the standard deviation for the mean value (table 5).

No correlation was found between the concentration of analytes in the biological material and the soil, which can be accounted for by the short exposition period as well as the fact that the pollutants can translocate due to precipitation into deeper layers of the soil.

More detailed analysis is necessary to rationalize the results for heavy metals: Zn (figure 4), Cu (figure 5), Ni (figure 6), Pb (figure 8) and Cd (figure 9), accumulated in mosses and lichens over the exposition period. The plants mostly accumulate the mobile forms of the metals, which enter the structure of mosses and lichens due to ion exchange (KŁOS et al. 2007a). The studies conducted in the vicinity of main roads have indicated that the lead emission due to motor traffic penetrates into the deeper layer of the soil (PIRON-FRENET et al. 1994), which could explain the lack of the correlation between the concentration of the examined analytes in the plant material and the surface 5-cm-soil layer. The distribution of the concentrations of heavy metals accumulated in mosses and lichens over the exposition period depends on the climate conditions, mainly on the intensity and volume of precipitation as well as force and direction of the winds (PIRON-FRENET et al. 1994). Over the period of the exposition (mild winter) the direction of the winds was from the south and west, which is specific for the examined area. In the southern direction the concentration of the examined analytes decreased with the distance from the road except for Mn. Such a distribution of pollutants follows the model from other studies, e.g., (NIEMELÄ et al. 2007). The distribution of pollutant concentration in the northern direction indicates the correlation between Cu and Ni as well as Cd, Pb and Zn. The concentration of Cu and Ni in lichens decrease with the distance from the road with a maximum in mosses at the distance of 8 m, whereas for Pb and Zn the concentration reaches a maximum at the distance of 50–150 m from the road. The small increase of Pb and Zn concentrations in the mosses exposed at the distance of 50–100 m from the motorway is confirmed by the studies conducted in the vicinity of M3 motorway in Hungary (NASZRADI et al. 2004). Such a distribution of pollutants could result from the physical similarities between the particles (state of aggregation, size, mass), which contain the examined analytes. The particles are entrained by the wind and transferred over the road due to air circulation and back-

wash. An important role is also attributed to the convection resulting from the differences in the temperatures of the asphalt and the surrounding.

The sites selected for the exposition of mosses and lichens is situated in the northwestern part of the town, which forms an undeveloped urban sprawl area. The central part of the town along with industrial zone is situated in the east and north direction from the place of exposition. It should be assumed that in the sites of the moss and lichen exposition the distribution of the deposition of wet and dry pollutants originating from the town and remote emission sources tends to be uniform since the samples have been distributed evenly over the 400 m road stretch on the both sides of the road (figure 1). The great probability of the existence of the effect of the surrounding pollution associated with remote emission sources is confirmed by the *RAF* factors determined for the analytes accumulated in mosses and lichens exposed at the distance of 100–200 m south of the road: $RAF_{Zn} \approx 0.6$, $RAF_{Cu} \approx 0.2$, $RAF_{Ni} \approx 0.3$, $RAF_{Mn} \approx -0.1$, $RAF_{Pb} \approx 0.5$, $RAF_{Cd} \approx 0.8$.

The comparison between the increase of the concentration of analytes in mosses and lichens indicates that the concentration of Zn, Cu, Ni and Pb tends to be higher in mosses while the concentration of Cd is higher in lichens. In both groups no increase in the concentration of Mn was found. The studies conducted in Sofia, Bulgaria, indicate that lichens tend to accumulate more Zn and Mn (CULICOV and YURUKOVA 2006), whereas in lichens and mosses exposed for 3 months in the urban area of Acerra (southern Italy) the increase in the analyte concentrations was higher in mosses (BASILE et al. 2008). The reasons for the higher concentration of analytes in mosses than in lichens as well as the commonly observed lack of correlation between the concentrations of analytes result from the lower resistance of the lichens to the stress associated with the change in the environment. Lichens are more susceptible to pollution, which often leads to the atrophy of lichens as a result of exposition. As a consequence, this leads to the leaching of the analytes from the dead thallus due to precipitation. Some references (e.g., BASILE et al. 2008) conclude that active biomonitoring should apply mosses rather than lichens.

The technique of moss and lichen exposition applied here follows the procedure applied in other active biomonitoring studies (e.g., HORVAT et al. 2000; PANTELICĂ and CERCASOV 2001; PANTELICĂ et al. 2004; CULICOV and YURUKOVA 2006). The biological material is often exposed in specially prepared containers (e.g., SOLGA et al. 2006; ZECHMEISTER et al. 2006; KŁOS et al. 2007b). This procedure is applied for the purpose of standardizing exposition methods. It also serves in order to discard some climate related factors.

The determined concentrations of heavy metals in samples of mosses and lichens (tables 2 and 3) were considerably higher than the boundary value for the *MQL* of analytic method (table 1). Standard deviation for the analytic method s_{am} calculated for all examined heavy metals does not exceed 10%.

5. CONCLUSIONS

The conducted studies indicate the usefulness and cost-effectiveness biomonitoring for assessing the deposition of pollutants in the vicinity of main roads. On the basis of an analysis of the variability of the chemical composition of mosses and lichens exposed in the area of main roads it is possible to determine the places and relative distribution of the deposition of pollutants emitted into the air due to motor traffic.

REFERENCES

[1] AFFUM H.A., ODURO-AFRIYIE K., NARTEY V.K., ADOMAKO D., NYARKO B.J.B., *Biomonitoring of airborne heavy metals along a major road in Accra, Ghana*, Environmental Monitoring and Assessment, 2008, 137, 15–24.

[2] *Ambient air – Determination of sulfur dioxide-Ultraviolet fluorescence metod*, ISO/DIS 10498.

[3] BASILE A., SORBO S., APRILE G., CONTE B., CASTALDO COBIANCHI R., *Comparison of the heavy metal bioaccumulation capacity of an epiphytic moss and an epiphytic lichen*, Environmental Pollution, 2008, 151, 401–407.

[4] BERGAMASCHI L., RIZZIO E., GIAVERI G., LOPPI S., GALLORINI M., *Comparison between the accumulation capacity of four lichen species transplanted to a urban site*, Environmental Pollution, 2007, 148, 468–476.

[5] CAMPO G., ORSI M., BADINO G., GIACOMELLI R., SPEZZANO P., *Evaluation of motorway pollution in a mountain ecosystem*, Pilot project: Susa Valley (Northwest Italy) years 1990–1994, Science of the Total Environment, 1996, 189–190, 161–166.

[6] CULICOV O.A., YURUKOVA L., *Comparison of element accumulation of different moss- and lichen-bags, exposed in the city of Sofia (Bulgaria)*, Journal of Atmospheric Chemistry, 2006, 55, 1–12.

[7] CUNY D., VAN HALUWYN CH., PESCH R., *Biomonitoring of trace elements in air and soil compartments along the major motorway in France*, Water, Air and Soil Pollution, 2001, 125, 273–289.

[8] GOMBERT S., ASTA J., SEAWARD M.R.D., *Correlation between the nitrogen concentration of two epiphytic lichens and the traffic density in an urban area*, Environmental Pollution, 2003, 123, 281–290.

[9] HARMENS H., NORRIS D. and the participants of the moss survey, *Spatial and temporal trends in heavy metal accumulation in mosses in Europe (1990–2005)*. The ICP Vegetation reports to the Working Group on Effects of the Convention on Long-range Transboundary Air Pollution. Centre for Ecology and Hydrology Environment Centre Wales Deiniol Road, Bangor (Gwynedd, UK), 2008.

[10] HEBE A., CARRERAS M., PIGNATA L., *Biomonitoring of heavy metals and air quality in Cordoba City, Argentina, using transplanted lichens*, Environmental Pollution, 2002, 117, 77–87.

[11] HORVAT M., JERAN Z., ŠPIRIČ Z., JAĆIMOVIĆ R., MIKLAVČIČ V., *Mercury and other elements in lichens near the INA Naftaplin gas treatment plant, Molve*, Croatia Journal of Environmental Monitoring, 2000, 2, 139–144.

[12] JANICKA A., WALKOWIAK W., *Usuwanie wielopierścieniowych węglowodorów aromatycznych z gazów spalinowych silnika o zapłonie samoczynnym na drodze procesów katalitycznych*, Journal of KONES Internal Combustion Engines, 2005, 12, 87–94.

[13] KŁOS A., RAJFUR M., WACŁAWEK M., WACŁAWEK W., *Heavy metal sorption in the lichen cationactive layer*, Bioelectrochemistry, 2007a, 71, 60–65.

[14] KŁOS A., RAJFUR M., WACŁAWEK M., WACŁAWEK W., *Application of lichen for the determination of precipitation pH by the exposure method*, [in:] Pawłowski L., Dudzińska M.R., Pawłowski A., Environmental Engineering, 2007b, 507–513, Taylor & Francis, London.
[15] KŁOS A., RAJFUR M., WACŁAWEK M., WACŁAWEK W., *The influence of unidentified pollution sources on the irregularity of biomonitoring tests results*, Water, Air, and Soil Pollution, 2008, 191, 345–352.
[16] KONIECZKO P, NAMIEŚNIK J. (eds.), *Assessment and quality control in analytic measurements*, WNT, Warszawa, 2007.
[17] KROCHMAL D., KALINA A., *Application of a passive sampling method for determination of air pollution by NO_2 and SO_2 in the whole area of Poland*, Chemia i Inżynieria Ekologiczna, 1996, 3, 325–336.
[18] KROCHMAL D., KALINA A., *A method of nitrogen dioxide and sulphur dioxide determination in ambient air by use of a passive samplers and ion chromatography*, Atmospheric Environment, 1997, 31, 3473–3479.
[19] Mały rocznik Statystyczny Polski (Little Statistical Yearbook) 2008, GUS, Warszawa.
[20] NASZRADI T., BADACSONYI A., NÉMETH N., TUBA Z., BATIČ F., *Zinc, lead and cadmium content in meadow plants and mosses along the M3 motorway (Hungary)*, Journal of Atmospheric Chemistry, 2004, 49, 593–603.
[21] NIEMELÄ M., PIISPANEN J., POIKOLAINEN J., PERÄMÄKI P., *Preliminary study of the use of terrestrial moss (Pleurozium schreberi) for biomonitoring traffic-related Pt and Rh deposition*, Environmental Contamination and Toxicology, 2007, 52, 347–354.
[22] OLENDRZYŃSKI K., DĘBISK B., KARGULEWICZ I., SKOŚKIEWICZ J., FUDAŁA J., HAŁAWICZKA S., CENOWSKI M., *Inwentaryzacja emisji zanieczyszczeń powietrza za rok 2001 na potrzeby statystyki krajowej i zobowiązań międzynarodowych w ramach Konwencji w sprawie transgranicznego zanieczyszczenia powietrza na dalekie odległości. Instytut Ochrony Środowiska*, (Institute of Environmental Protection), Krajowe Centrum Inwentaryzacji Emisji (National Emission Centre), Warszawa, 2003.
[23] PACHECO A.M.G., FREITAS M.C., BARROS L.I.C., FIGUEIRA R., *Investigating tree bark as an air-pollution biomonitor by means of neutron activation analysis*, Journal of Radioanalytical and Nuclear Chemistry, 2001, 249, 327–331.
[24] PANTELICĂ A., CERCASOV V., *Experimental setup and elemental analysis of lichen bioaccumulators before exposure*, Report WP2 IDRANAP 03-01/2001, European Commission Center of Excellence Inter Disciplinary Research and Applications Based on Nuclear and Atomic Physics, 2001.
[25] PANTELICĂ A., CERCASOV V., STEINNES E., BODE P., WOLTERBEEK B., WENTZ I., *Comparative characterisation of air pollution at six industrial sites in Romania*, Report WP2 IDRANAP 79-04/2004, European Commission Center of Excellence Inter Disciplinary Research and Applications Based on Nuclear and Atomic Physics, 2004.
[26] PIRINTSOS S.A., MATSI T., VOKOU D., GAGGI C., LOPPI S., *Vertical distribution patterns of trace elements in an urban environment as reflected by their accumulation in lichen transplants*, Journal of Atmospheric Chemistry, 2006, 54, 121–131.[27] PIRON-FRENET M., BUREAU F., PINEAU A., *Lead accumulation in surface roadside soil: its relationship to traffic density and meteorological parameters*, Science of the Total Environment, 1994, Vol. 144, 1–3, 297–304.
[28] POLKOWSKA Ż., DUBIELLA-JACKOWSKA A., ZABIEGAŁA B., NAMIEŚNIK J., *Skład zanieczyszczeń wprowadzanych do środowiska wzdłuż dróg o różnym natężeniu ruchu pojazdów mechanicznych*, Ecological Chemistry and Engineering, 2007, 14, S3, 315–338.
[29] POMORSKA K., DUDA A., *Wpływ motoryzacji na poziom zanieczyszczeń gazowych powietrza*, Chemia i Inżynieria Ekologiczna, 2004, 11, S4, 545–555.
[30] *Powietrze atmosferyczne – Oznaczanie stężenia masowego tlenków azotu – Metoda chemiluminescencyjna*, PN-ISO 7996:2001.

[31] PRATT C., LOTTERMOSER B.G., *Mobilisation of traffic-derived trace metals from road corridors into coastal stream and estuarine sediments, Cairns, northern Australia*, Environmental Geology, 2007, 52, 437–448.

[32] SCHINTU M., COGONI A., DURANTE L., CANTALUPPI C., CONTU A., *Moss (Bryum radiculosum) as a bioindicator of trace metal deposition around an industrialised area in Sardinia (Italy)*, Chemosphere, 2005, 60, 610–618.

[33] SHUKLA V., UPRETI D.K., *Heavy metal accumulation in Phaeophyscia hispidula en route to Badrinath, Uttaranchal, India*, Environmental Monitoring and Assessment, 2007, 131, 365–369.

[34] SOLGA A., BURCHARDT J., FRAHM J.P., *A new approach to assess atmospheric nitrogen deposition byway of standardized exposition of mosses*, Environmental Monitoring and Assessment, 2006, 116, 399–417.

[35] TURER D., MAYNARD B., SANSALONE J.J., *Heavy metal contamination in soils of urban highways: Comparison between runoff and soil concentrations at Cincinnati, Ohio*, Water, Air, and Soil Pollution, 2001, 132, 293–314.

[36] ZECHMEISTER G.H., HAGENDORFERC H., HOHENWALLNER D., HANUS-ILLNARC A., RISS A., *Analyses of platinum group elements in mosses as indicators of road traffic emissions in Austria*, Atmospheric Environment, 2006, 40, 7720–7732.

[37] ZUPANČIČ N., *Lead contamination in the roadside soils of Slovenia*, Environmental Geochemistry and Health, 1999, 21, 37–50.