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Variation of trace element accumulation in topsoil near the Vilnius–Kaunas highway

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The aim of the research was to distinguish from a group of 22 trace elements (Ag, B, Ba, Co, Cr, Cu, Ga, Li, Mn, Mo, Nb, Ni, Pb, Sc, Sn, Sr, Ti, V, Y, Yb, Zn and Zr) the main elements associated with traffic pollution and road construction, which are well accumulated in topsoil, basing on their real total contents determined by OAES in four different cross-sections of the Vilnius–Kaunas highway connecting the two largest cities of Lithuania in two sampling periods (1991 and 2005) as well as to analyse the areal and temporal variation of their accumulation. The main elements are the following: Pb, Zn, Cu, Mo, Sn, Sr. The main regularity of their areal variation in all cross-sections is the highest additive index of their accumulation (Z6) in the nearest zone (at a distance <15 m from the hard shoulder). The main regularity of the temporal variation is the highest increase of Z6 in a cross-section with unfavourable conditions for dispersion of pollutants, where there is a relief barrier on the both sides of the highway. Monitoring of cross-sections is recommended.

Key words: trace elements, roadside topsoil, areal and temporal variation, traffic pollution, road construction, Lithuania

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INTRODUCTION

Roadside topsoil is polluted by heavy metals and other potentially harmful chemical elements and can become a secondary pollution source of the atmosphere, hydrosphere and roadside biota. Investigations of this issue are usually aimed at distinguishing traffic-associated elements-pollutants, their influence zone and the main factors predetermining their accumulation. The elements-indicators revealed by different investigators are diverse mainly due to different sampling media and territories (Zechmeister et al., 2005; Tausz et al., 2005; Bosco et al., 2005), also a wider group of determined traffic-derived elements, e. g., Pt, Pd, Rh (Morcelli et al., 2005). To distinguish the main traffic-associated pollutants, investigations of roadside soil outside urban territories are important, because they are less affected by other pollution sources as compared with urban territories (Yongming et al., 2005). Roadside pollution investigations in Lithuania were abundant. Mainly soil and vegetation was analysed (Sunkieji..., 2001; Lubytė et al., 1996; Motuzas et al., 2001; Vaičys et al., 1995; Pauliukevičius, Masiliūnas, 1998; Kliaugienė (Brannvall), Baltrėnas, 2004). Investigation of pollution near the Vilnius–Kaunas highway is especially important, because data of 2002 (http://www.vilnius.lt/dipolis/dok/v-k_bukle.doc) indicate that, unlike the general situation in Lithuania, the flow of motor vehicles on this highway has been constantly increasing (except for the crisis in 1999–2000) and in the period 1989–2002 has grown up more than twice. Element contents in soil near this highway were investigated in 1991 by the Institute of Geology under the guidance of V. Baltakis and with participation of the authors (topsoil in 10 cross-sections) and by Agrochemical Research Centre in 1993 (three depth layers in two cross-sections) with repeated sampling of the upper layer in 1999 (Sunkieji..., 2001). The results obtained differ not only due to the different location of the cross-sections, but mainly due to the different analytical procedures applied. In the first case, optical atomic emission spectrophotometry (OAES) enabled to determine the real total contents of 28 elements compared to atomic absorption spectrophotometry (AAS) which was applied to determine only acid-extractable contents of Pb, Zn, Cu, Cd, Cr and Ni. AAS analytical results did not reveal any regularities in the temporal variation of element contents near the highway were.

The aim of the present research was to distinguish from the group of 22 trace elements (Ag, B, Ba, Co, Cr, Cu, Ga, Li, Mn, Mo, Nb, Ni, Pb, Sc, Sn, Sr, Ti, V, Y, Yb, Zn and Zr) those that mostly accumulate in topsoil near the Vilnius–Kaunas highway and are associated with *traffic (T)* or *road construction (RC)*, and to reveal their areal and temporal variation, basing on repeated sampling in cross-sections with different dispersion conditions and on real total contents of elements. The main *TRC-associated* and *soil-accumulated (SA)* elements will be called *TRCSA-indicators*. The following *preliminary checklist* of 11 elements was compiled taking into account a group of publications on primary sources of traffic-associated pollutants (Salma, Maenhaut, 2006; Zechmeister et. al., 2005; Stormwater…, 2005; Heinrichs, Brumsack, 1996; Lytlea et al., 1995; Sternbeck et al. 2002; Ward, 1990): **Pb, Zn, Cu, Sn, Mo, Ni, Cr, Co, Mn, V, Ba.** According to these references, the sources include diesel or gasoline (Pb, Zn, Cu, Mo, Ni, Cr, Co), lubricating oil (Zn, Cu, Ni, Mo, V, Ba), motor oil and grease (Zn), brake lining wear (Pb, Zn, Cu, Sn, Mo, Ni, Cr, Mn, Ba), bearing wear (Cu), brushing wear (Cu, Ni), tire wear (Pb, Zn, Cu, Mo), corrosion of welded metal plating (Cu, Ni, Cr, V), asphalt paving (Ni), anti-detonating compounds (Mn), wheel weights (Pb).

OBJECTS, METHODS AND DATA

Topsoil was sampled by the authors in 2005 at the same four cross-sections of the highway as in 1991 (Fig. 1). They differ in conditions for dispersion of pollutants (Fig. 2): SD is favourable for dispersion, DS is semi-favourable, where wide spreading is possible only to the leeward side of the road; the remaining two are unfavourable as there are either a forest barrier (FB cross-section) or a relief barrier (RB cross-section). The cross-sections differ also in average transport intensity; it has increased everywhere (Table 1). The samples were taken from the central reservation part (CRP) and both sides of the road a distance of no more than 70 m from the hard shoulder, i. e. the width of the highway protection belt (HPB) recommended in the Law of Roads of Lithuania. Each cross-section was subdivided into the nearest zone N (<15 m), the transitional zone T (15–35 m) and the distant zone D (35–70 m). The D zone occupies half of the width of the HPB. The width of the N zone was chosen so as to include ditches closest to the highway in all cross-sections and basing on investigations of 1991. It corresponds to the width of the *target zone*, which is used in the typology of the Dutch roads and which is beyond the so-called *free zone*, but before the agricultural or natural area (Blok, 2005). Unlike the Dutch road typology, the N zone includes the CRP, both soft shoulders with man-made ground affected by de-icing salt and part of the natural or agricultural area. The nearest zone was subdivided into three sub-zones: N1 (CRP and the territory at a distance of <2.5 m), N2 (2.5–7.5 m) and N3 (7.5–15 m). The N2 sub-zone usually includes the roadside ditch or relief depression, and the N3 sub-zone can be very different. As the samples were taken from both the windward and the leeward side of the highway, nine segments were distinguished (Table 1). Samples were taken from the upper 10 cm layer and were composite, i. e. consisted of 5 sub-samples taken from sites located on the line parallel to the highway at a distance of 1 m from each other. All composite samples were homogenized, dried at room temperature and screened through 1 mm nylon sieves. The screened part was ashed at 450 °C and ground. OAES analysis of total contents was done at the laboratory of the Institute of Geology and Geography. To reveal the element paragenetic associations, the recommended method of factor analysis was used (Zinkutė, 2002), while to find out significant areal and temporal differences, both parametric (ANOVA and t test) and non-parametric (U test) statistical methods were applied. In most cross-sections sandy soil prevailed, but also sandy loamy or loamy soil occurred; besides, in some places, especially in the D cross-section, soil was rich in organic matter. To calculate the concentration coefficients (CC), different regional background values of sandy, sandy-loamy or loamy soils were used, and for samples rich in organic matter (when loss on ignition exceeded 30%) the background values adjusted according to land use (Kadūnas et al., 1999). Areal variation was analysed in two directions: perpendicular to the highway (in generalised segments) and parallel to the highway (comparing segments of different cross-sections).

RESULTS AND DISCUSSION

Different ways were tried to reveal the *main TRCSA-indicators* of the Vilnius–Kaunas highway, first of all the following: 1) determination of accumulating associations (as defined in Zinkutė, 2002) in the whole investigated HPB during both periods and finding their common members (with Sr, **Ni,** Y**, **Zn** as a result); 2) determination of accumulating associations in the N zone during both periods and finding their common members (**Zn, Pb,** Sr, **Ni,** Y**, Sc*); 3) comparison of the median CC values in N, T and D zones and finding elements common to both periods elements, which have the highest CC medians in N zone compared to T and D zones (**Zn, Pb,** Sr, **Ni,** Y**, **Sn, Cr*, V*, Ba,** Yb**). All these ways seem ineffective for the following reasons: 1) too little elements from the *preliminary checklist* included (they are in bold); 2) too much typical *lithogenic (allotigenic)* or *clastogenic (allotigenic accessory)* elements (Baltakis, 1993; Kadūnas et al., 1999) included (the first ones are marked by *, the second ones by **). Though some of typical allothigenic elements (Cr, Ni, V, Co) have primary traffic-associated sources, they not necessarily are *mainly traffic-associated* because: 1) accumulation of V and Ni can also be predetermined by diffuse pollution from the Elektrėnai heat and power plant (EHPP); 2) typical allothigenic elements, which depend on the content of clay fraction, have highly variable background values, so their accumulation can be of natural origin. This is in agreement with investigations of Lithuanian urban territories where higher levels and growth of *non-ferrous metals* (Pb, Zn, Cu, Sn, Ag) compared to *ferrous* (Cr, Co, Ni, Mo, V) were revealed (Taraškevičius et al., 2003), also with a wide traffic-associated group distinguished during investigations of the Vilnius–Kaunas highway in 1991: Pb–Zn–Ag–Sn–Cu–(Mo–Sr–Cr–Ni) with the lowest input of Cr and Ni (Baltakis, Radzevičius, 1995). None of typical allothigenic accessory elements is on the *preliminary checklist*

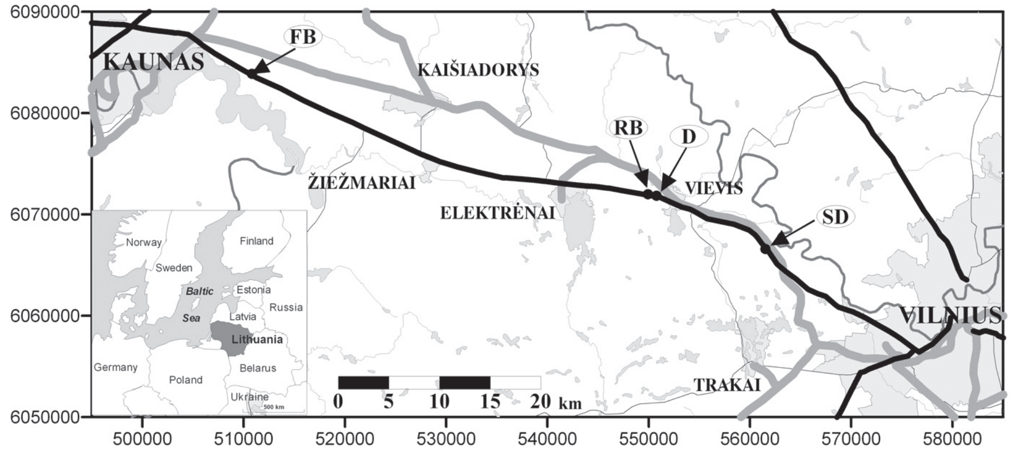

Fig. 1. Location of the study cross-sections of the Vilnius–Kaunas highway.
Cross-sections (distance from Vilnius in parentheses): D (41.8 km) – favourable for dispersion of pollutants, SD (28.2 km) – semi-favourable for dispersion of pollutants, FB (84.6 km) – unfavourable with forest barrier, RB (42.1 km) – unfavourable with relief barrier

1 pav. Tirtų greitkelio Vilnius–Kaunas profilių išsidėstymas.
Profiliai (skliausteliuose nurodytas atstumas nuo Vilniaus): D (41,8 km) – palankus teršalų sklaidai, SD (28,2 km) – pusiau palankus teršalų sklaidai, FB (84,6 km) – nepalankus su miško barjeru, RB (42,1 km) – nepalankus su reljefo barjeru

Table 1. **Characterization of different segments of cross-sections and the number of topsoil samples taken there**
1 lentelė. **Skirtingų profilių atkarpų apibūdinimas ir jų paviršinio dirvožemio ėminių skaičius**

Segment (abbreviation)	Cross-section	D		SD		RB		FB		Grand total
	Traffic intensity	8020[a]	16965[b]	8620[a]	15650[b]	8020[a]	16965[b]	13540[a]	18465[b]	
	Year	1991	2005	1991	2005	1991	2005	1991	2005	
Windward distant (WD)		CM(2)	CM(3)	MT(4)	M(2)	A(9)	CM(2)		MF(2)	24
Windward transitional (WT)		CM(2)	A(1)	GSL(2)	GSL(1)	A(1), GTSL(3)	A(1), GTSL(1)	MF(2)	MF(1)	15
Windward at a distance of 7.5–15 m (WN3)		**D(1),** CM(1)	CM(2)	GSL(2)	GSL(2)	GTSL(2)	GTSL(1)	G(1)	G(1), MF(1)	14
Windward at a distance of 2.5–7.5 m (WN2)		G(1)	G(1)	**D(1),** GSL(1)	**D(1)**	**D(1)**	**D(1),** GSL(2)	D(1)	D(1)	11
Windward and leeward at a distance of <2.5 m and central reservation (N1)		**C(1), S(2)**	**C(1), S(2)**	**C(1), S(2)**	**C(1), S(2)**	**C(1), S(2)**	**C(1), S(2)**	**C(1), S(2)**	**C(1), S(2)**	**24**
Leeward at a distance of 2.5–7.5 m (LN2)		G(1)	G(1)	D(1)	D(1)	**D(1),** GBSL(1)	**D(1),** GBSL(1)	**D(1),** G(1)	**D(1),** GWF(1)	12
Leeward at a distance of 7.5–15 m (LN3)		**D(1),** CM(1)	CM(1)	M(2)	M(2)	GBSL(2)	GBSL(2)		MF(1)	12
Leeward transitional (LT)		CM(3)	CM(1)	M(3)	M(2)	GBSL(2), A(3)	GBSL(1), CM(1)	MF(1)	MF(1)	18
Leeward distant (LD)		CM(3)	A(2)	M(2)	M(2)	A(5)	CM(2)		MF(2)	18
Grand total		19	16	21	16	33	18	10	15	148

Explanations. The types of cross-sections are explained in the text; the number of samples is given in parentheses; characterization of land: C – central reservation, S – soft shoulder, D – ditch, G – grassland, GSL – grassland on the slope, GBSL – grassland with bushes on the slope, GTSL – grassland with trees on the slope, GWF – grassland near the wire fence, M – meadow, MT – meadow with trees, CM – cultivated meadow, A – arable land or garden, MF – mixed forest. The main points of the profiles are in bold. The changes in land use are shaded. Approximate data on traffic intensity: a – data obtained by V. Baltakis from the Ministry of Communications before sampling in 1991 (basing on traffic intensity at 35 km for SD cross-section, at 45 km for D and RB cross-sections and at 93 km for FB cross-section), b – data of 2002–2005 obtained from the website of Lithuanian Road Administration under http://www.lra.lt/lt.php/eismo_saugumas/juodosios_demes/82 (basing on traffic intensity at 18–30 km for SD cross-section, at 37–45 km for D and RB cross-sections and at 83.9–84.2 km for FB cross-section).

Paaiškinimai. Profilių tipai paaiškinti tekste; ėminių skaičius nurodytas skliaustuose; žemės apibūdinimas: C – centrinė skiriamoji juosta, S – neasfaltuotas kelkraštis, D – griovys, G – žolynas, GSL – žolynas ant šlaito, GBSL – žolynas su krūmais ant šlaito, GTSL – žolynas su medžiais ant šlaito, GWF – žolynas prie vielinės tvoros, M – pieva, MT – pieva su medžiais, CM – kultūrinė pieva, A – ariama žemė ar daržas, MF – mišrus miškas. Svarbiausios profilių vietos paryškintos, žemės panaudojimo pokyčiai pateikti fone. Apytikriai duomenys apie transporto intensyvumą: a – duomenys, kuriuos gavo V. Baltakis iš Susisiekimo ministerijos prieš ėminių ėmimą 1991 m. (SD profiliui parinktas transporto intensyvumas 35 km, D ir RB profiliams – 45 km, o FB profiliui – 93 km), b – 2002–2005 m. transporto intensyvumo duomenys iš Lietuvos automobilių kelių direkcijos tinklalapio http://www.lra.lt/lt.php/eismo_saugumas/juodosios_demes/82 (SD profiliui parinktas transporto intensyvumas 18–30 km, D ir RB profiliams – 37–45 km, o FB profiliui – 83,9–84,2 km).

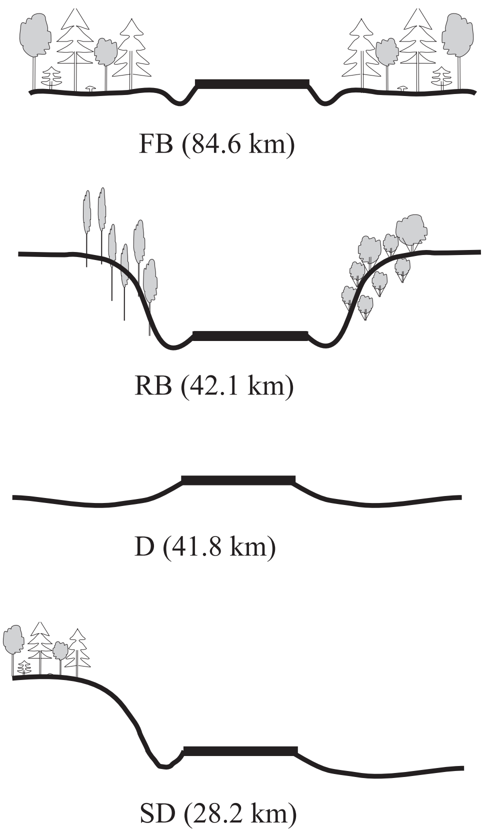

Fig. 2. Outline of cross-section types of the Vilnius–Kaunas highway. Explanation of cross-sections is given in Fig. 1

2 pav. Greitkelio Vilnius–Kaunas tirtų profilių tipų eskizai. Profilių paaiškinimas pateiktas 1 pav

of traffic-associated elements. Though Sr is not related to traffic (TR), it can be associated with road construction (RC): with the gravelly man-made ground, road grit and salt deposited during winter maintenance (Wahlin et al., 2006). Abundant association of *possible TRCSA-indicators* (N/b–Zn–Pb–Cu)–(Sr–Ba–As)–(P–Cd–Sn–Hg–Ag), where N/b is the bitumoid fraction of oil products, distinguished by cluster analysis in topsoil of Vilnius (Taraškevičius et al., 2003) is without allothigenic-accessory elements, but includes elements associated with carbonates (Sr and Ba). Break wear as the primary source of Ca and Ba (Zechmeister et al., 2005) and de-icing mixtures also indicate that elements associated with carbonates are *possible TRCSA-indicators*. Revealing the *main TRCSA-indicators* according to accumulating associations could be insufficiently effective because of regional, but not local background values applied. The third way eliminated from the *possible TRCSA-indicators* not only Zr, Nb, Ti, B (their highest accumulation level in both periods was in more distant zones), but also Co, Mn, Li, Ga and Ag (their accumulation pattern was different in two periods). As the primary sources of Mn (constituent of antidetonating compounds) and Co (diesel) are mentioned by investigators, it means that soil does not reflect their pollution due to insufficient accumulation.

A comparison of average CC in T and D zones in each sampling period using ANOVA revealed no differences, while the non-parametric U-test revealed the only difference for Mn indicating that T and D zones can be united for comparison with N zone to reveal the *main TRCSA-indicators.* Despite the differences in element arrangement according to various ratios (average or median contents or CC) in each period, also different groups of elements with a significantly higher content or accumulation in N zone, which were revealed by the parametric and non-parametric statistical methods or log-transforming data (Table 2), the following *main TRCSA-indicators* of the Vilnius–Kaunas highway can be listed on the basis of their highest repeatability in sequences of Table 2: **Pb, Zn, Cu, Sr, Mo, Sn.**

To check whether this assumption is right, PCA was performed for both time periods not only for samples from the whole HPB, but also from N zone alone (Table 3). In spite of the banning of leaded gasoline in Lithuania in the end of the last century, the factor with the highest loading of Pb was considered to be traffic-related, because there are other primary traffic-associated sources of Pb, also due to its previous accumulation. The distinguished *main TRCSA-indicators* either belong to the *factor kernel* (Zinkutė, 2002) or have significant ($p < 0.05$) positive loadings on the traffic-related factor (except for Sn in N zone in 1991), though some other pollutants (Cr, Ni), which are on the *preliminary checklist*, sometimes are also essentially correlated with the same factor. The same factor is often significantly loaded by some typical allothigenic (Li, Ga, Sc) or allothigenic-accessory (Y, Yb) elements or Ag. Separation of Ag from the *main TRCSA-indicators* and its negative loading on the mixed factor of allothigenic, allothigenic-accessory and carbonates-associated elements in 2005 in the whole HPB territory indicates its other possible sources.

The additive index of accumulation of the *main TRCSA-indicators* (Z6) has increased in the whole HPB: its average value 1.12 times and median value 1.06 times. Variation of the median values of Z6 in generalised segments indicates the highest influence of traffic in N1 (CRP and soft shoulders) followed by N2 (which usually includes the ditches) and the further gradual de-

Table 2. **Trace elements with significantly higher contents or concentration coefficients in the nearest zone compared to combined transitional-distant zone**

2 lentelė. **Mikroelementai, kurių kiekiai ar koncentracijos koeficientai yra didesni artimojoje zonoje, lyginant su jungtine pereinamąja ir tolimąja zona**

Method	1991	2005
ANOVA for log-transformed data	**Pb, Zn, Sr, Mo,** Ag, **Sn**	**Pb, Zn, Cu, Sr, Mo**
U-test for non-transformed data	**Pb, Zn, Sr, Mo**	**Zn, Pb, Cu, Sr,** Ga
ANOVA for CC	**Pb, Zn, Sr, Cu,** Sc, **Mo,** Ni, Y, Ba, **Sn,** Cr, Ag	**Zn, Cu, Pb, Sr,** Y, Ga, Ni, **Mo,** Yb, Li, V, Co, **Sn,** Ba
U-test for CC	**Pb, Zn, Sr,** Y, Sc, **Cu, Mo,** Ni, Cr	**Zn, Cu, Pb, Sr,** Y, Ga, Yb, Co, Li, Mo, Ba, **Sn**

Explanations. CC – concentration coefficients; the significance level is 0.05; supposed main TRCSA-indicators are in bold; Pb, Zn and Sr are mentioned 8 times, Mo – 7, Cu – 6, Sn and Y – 4, other elements – 1–3 times.

Paaiškinimai. CC – koncentracijos koeficientai; reikšmingumo lygmuo – 0,05; paryškinti, spėjama, pagrindiniai, su transporto tarša ir kelio konstrukcijomis susiję elementai; Pb, Zn ir Sr paminėti 8 kartus, Mo – 7, Cu – 6, Sn ir Y – 4, kiti elementai – 1–3 kartus.

Table 3. **Paragenetic associations of elements in topsoil from the Vilnius–Kaunas highway protection belt**
3 lentelė. **Elementų paragenetinės asociacijos greitkelio Vilnius–Kaunas apsauginės juostos paviršiniame dirvožemyje**

F(V%)	Elements with positive loadings	Elements with negative loadings
	All recommended highway protection belt, 1991	
F1(21.0)	Ni*, Sc*, V*, **Cu,** (**Zn,** Co*, B*, Mn, Ga*, **Sr**)	Nb**, Zr**, (Li*, **Sn,** Ti**)
F2(16.6)	Ga*, Li*, Co*, Cr*, (B*, Nb**, Ti**, **Sn,** Ba, Ni*)	
F3(16.4)	Yb**, Y**, Mn, Ti**, (Zr**, V*, Cr*, Ag, Co*, Nb**, B*)	(**Pb**)
F4(15.4)	**Pb,** Ag, **Zn, Mo,** (**Cu,** Cr, **Sr, Sn**)	(Zr)
F5(12.4)	**Sr,** Ba, **Sn,** (**Mo,** Nb*)	B*, (Ti**, **Cu,** Yb**)
	All recommended highway protection belt, 2005	
F1(24.3)	Co*, Mn, Ba, Sc*, Ni*, Cr*, Li*, Yb**, (Ga*, **Sn,** V*, Y**, Ti**)	
F2(21.5)	**Pb, Zn, Cu, Mo, Sr,** Ga*, **Sn,** (Y*, Yb**, Li*, Cr*)	(Zr**, Ti**)
F3(12.4)	B*, Ti**, V*, (Yb**, Sc*, Cr*, Y**, Ag, Ga*)	(**Sr**)
F4(11.7)	Zr**, Nb**, (**Sn,** Ti**, Ag, Ba, Yb**)	(Ni*, Sc*, V*)
F5(7.6)	Y**, (Yb**, **Sr,** Co*, Ga*)	Ag
	N zone, 1991	
F1(29.5)	Yb**, Ti**, Zr**, Y**, Mn, Nb**, (B*)	(**Pb**)
F2(25.1)	**Zn,** Ag, **Mo, Pb, Cu,** (Cr*, **Sr,** Ni*, Ga*, Sc*)	
F3(12.3)	Cr*, V*, Ni*, Sc*, Co*, (Ga*, Sr, Ba, Mn)	(Nb**)
F4(8.9)	Ba, **Sn, Sr,** (Mn)	B
F5(6.0)	Li*, Ga*, (Nb**, Cr*)	
	N zone, 2005	
F1(29.6)	Co*, Yb**, Ni*, Y**, Sc*, V*, Ga*, Li*, B*, Ti**, Cr*, (Mn)	
F2(21.6)	**Pb, Cu, Zn, Sr, Mo,** (Li*, **Sn,** Ga*)	Zr**, (Ti**)
F3(13.2)	Ba, Mn, **Sn,** (Cr*, Ga*, Sc*, Co*, Ag, Ti**)	
F4(9.8)	Nb**, Ag, (B*, Zr**, Ti**)	

Explanations. The associations were distinguished by PCA with varimax rotation when all distinguished factors have eigenvalues higher than 1; F(V%) – factor (percentage of variance explained by the factor); only elements with significant ($p < 0.05$) loadings are listed; the technogenic factors and the supposed main TRCSA-indicators are in bold; * – typical members of allotigenic association, ** – typical members of allotigenic-accessory association.

Paaiškinimai. asociacijos buvo išskirtos pagrindinių komponenčių metodu su varimakso posūkiu, kai visų išskirtų veiksnių tikrinės reikšmės didesnės už 1; F(V%) – veiksnys (veiksnio paaiškinamos dispersijos procentinis kiekis); išvardyti tik elementai su reikšmingomis ($p < 0,05$) veiksnio apkrovomis; paryškinti technogeniniai veiksniai ir, spėjama, su transporto tarša ir kelio danga susiję bei dirvožemio akumuliuoti elementai-indikatoriai; * – tipiniai alotigeninės asociacijos elementai, ** – tipiniai alotigeninės-akcesorinės asociacijos elementai.

crease in N3, T and D sub-zones (Fig. 3). The main regularity of temporal variation is a decrease of Z6 in T and D and an increase in N1 and N2 sub-zones with the opposite tendencies in WN3 and LN3 segments. The increase of Z6 in WN3 can be explained by the relief barriers in the windward part of two cross-sections and the decrease in T and D zones by a possible prevalence of mobile forms, their uptake by plants and export with harvest in zones used for agriculture, also leaching. The same areal regularity as for Z6 in generalised segments is observed for most of the *main TRCSA-indicators*, especially Zn, Pb and Sr (Fig. 4). For Sn this tendency is less pronounced. A somewhat higher accumulation of Cu and Mo in WD segment in 1991 can be explained by the impact of the EHPP which is located to the windward direction from the highway. The temporal variation of Z6 is predetermined by Zn, Pb and Cu which have an analogous distribution pattern in segments, except for Pb in CRP and soft shoulders where its contents decreased (maybe due to leaching of previously accumulated Pb from the upper layers, its runoff with stormwater and disturbance of soil cover). Mo and Sn show opposite tendencies of temporal variation in all segments: accumulation of Sn increases and of Mo decreases (maybe due to the high Mo and low Sn uptake by plants).

A comparison of areal and temporal variability of Z6 and Pb, Zn, Cu in different cross-sections reveals the influence of natural and anthropogenic factors on accumulation in roadside topsoil (Fig. 5). The areal distribution pattern of Z6 in both time periods in most of cross-sections is asymmetric (except for DS).

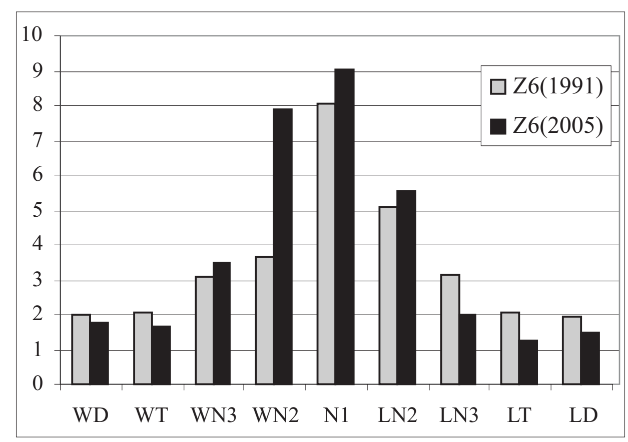

Fig. 3. Variability of the additive index Z6 of Zn, Pb, Cu, Mo, Sn and Sr accumulation in segments of all cross-sections.
Explanation of segments is given in Table 1
3 pav. Zn, Pb, Cu, Mo, Sn ir Sr suminio kaupimosi rodiklio Z6 kaita visų magistralės profilių atkarpose.
Atkarpų paaiškinimas pateiktas 1 lentelėje

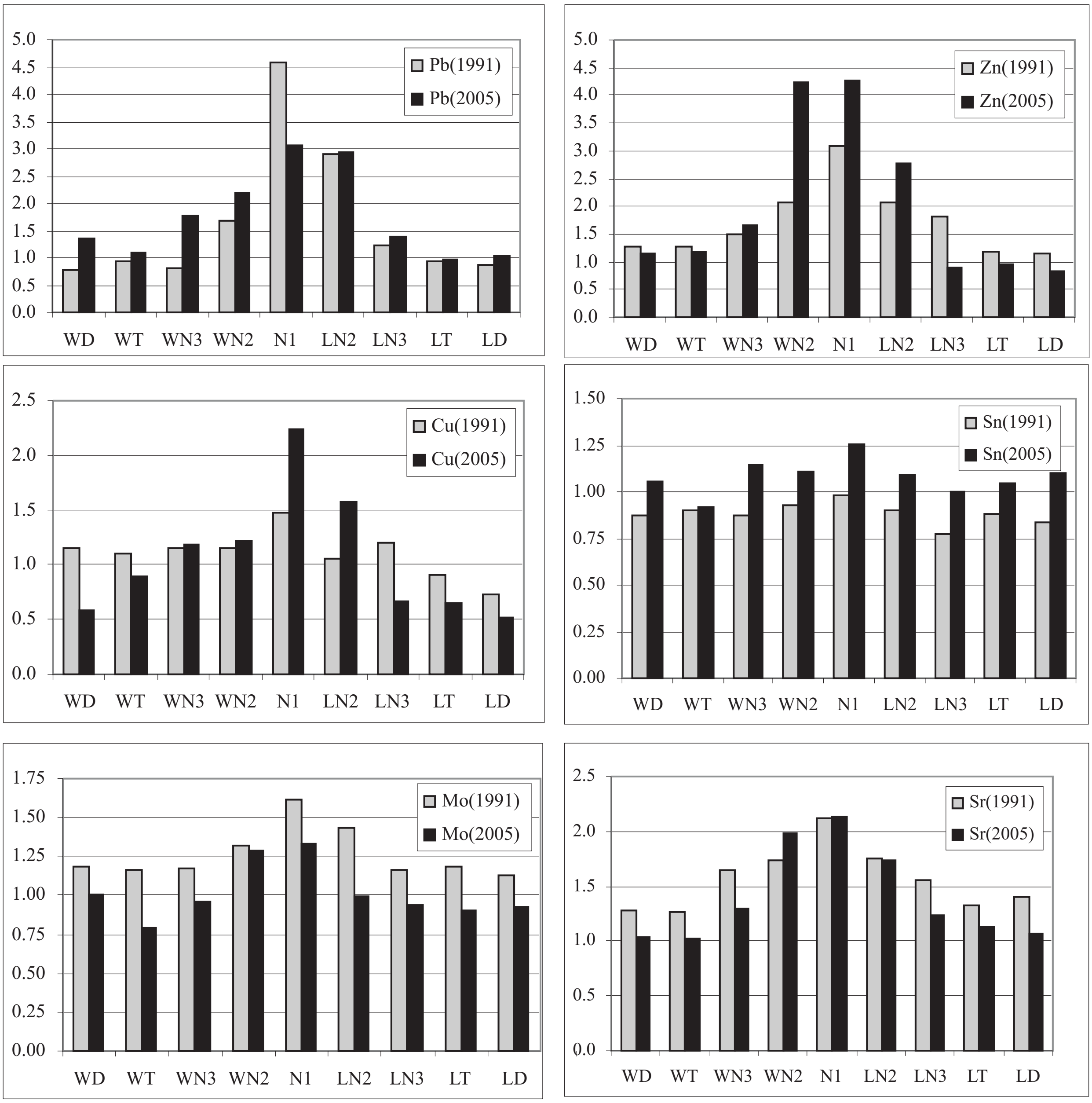

Fig. 4. Variability of median concentration coefficients of Pb, Zn, Cu, Sn, Mo and Sr in segments of all cross-sections.
Explanation of segments is given in Table 1

4 pav. Pb, Zn, Cu, Sn, Mo ir Sr koncentracijos koeficientų medianų kaita visų profilių atkarpose.
Atkarpų paaiškinimas pateiktas 1 lentelėje

In D cross-section, the mode during both periods is observed in LN2, higher values are observed in its leeward segments of the N zone compared to respective windward, especially in 1991. The accumulation in these segments depends mainly on Zn and Cu which have a similar distribution pattern, partly on Pb. The regularities of areal distribution are the same in the RB cross-section; in 1991 they depended on Pb, in 2005 on Pb, Zn and Cu. In the FB cross-section, the modes of Z6 are in the windward segments: WN3 in 1991 (Cu at the outskirts of the forest) and WN2 in 2005 (Zn in a ditch). One of the samples in LN2 taken near the wire fence recently constructed to protect the wildlife from traffic contained elevated levels of Pb, Cu and Zn. The higher accumulation of Zn and Cu in WD and WT in 1991 may be explained by the influence of EHPP pollution.

The D and RB cross-sections are close to each other, but greatly differ in dispersion conditions. In 1991, contamination was the highest in D cross-section and the lowest in RB. They do not differ in traffic intensity, but differ in soil type (in D cross-section it has a heavier texture and is rich in organic matter) and in land use. The latter probably predetermined the high accumulation of *TRCSA-indicators* in D cross-section in 1991 when it was mainly occupied by cultivated meadow compared to more distant segments of the RB cross-section occupied by arable land or a garden (Table 1). However, in 2005 accumulation level has decreased in all segments, indicating a possible uptake of part of the *main TRCSA-indicators* by plants combined with leaching and absence of relief barriers. Presumably, the uptake of Zn and Cu by plants and their mobility was higher compared to Pb and Sn the CC values of which slightly

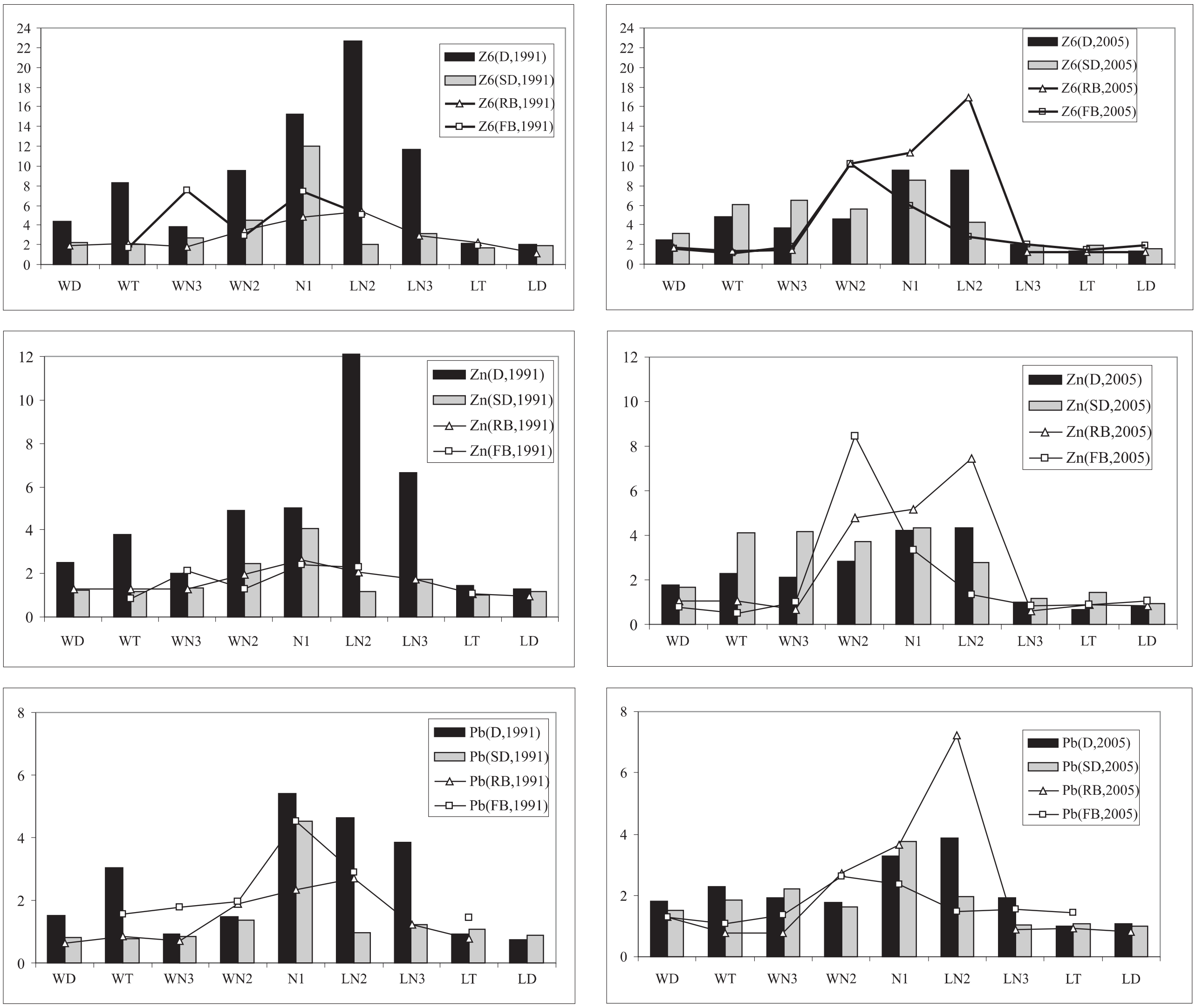

Fig. 5. Variability of medians of the additive index Z6 of Pb, Zn, Cu, Sn, Mo, Sr accumulation and of Zn and Pb concentration coefficients in cross-sections.

Explanations: the letters in parentheses indicate a cross-section (their types are given in Fig. 2), followed by year of sampling; explanation of segments is given in Table 1

5 pav. Zn, Pb, Cu, Mo, Sn ir Sr suminio kaupimosi rodiklio Z6 bei Zn ir Pb koncentracijos koeficientų medianų kaita profiliuose.

Paaiškinimai: raidės skliaustuose nurodo profilį (jų tipai pateikti 1 pav.), po jų parašyti ėminių rinkimo metai; atkarpų paaiškinimas pateiktas 1 lentelėje

increased in different segments of the D cross-section. The initial accumulation level in the RB cross-section was rather low; its decrease due to plant uptake, and leaching was observed only in D, T and N3 sub-zones, meanwhile in N1 and N2 sub-zones, on the contrary, it became the highest among respective sub-zones of all cross-sections, indicating a great influence of the relief barrier (together with the highest increase of traffic intensity). The increase of Zn, Pb and Cu was found mainly on the leeward while of Sr and Mo mainly on the windward slope. The growth of most of the *main TRCSA-indicators* was observed in N1 and N2, only the contents of Pb, Mo and Sn increased in the N3 sub-zone. The initial level of accumulation in SD cross-section was rather high, in 2005 it increased in all the windward segments with a relief barrier (but lower compared to RB), also in N1 and some of the leeward segments, i. e. on a wider territory. This growth was mainly due to an increase of Pb and Sn, meanwhile Zn and Cu grew up only in N1 and N2 sub-zones. The accumulation level of the FB cross-section was variable and due to insufficient sampling cannot be explained. An increase of accumulation was observed only in WN2 where the growth of Zn and Pb was detected in a ditch. The contents of Zn and Cu also increased in the N1 sub-zone.

CONCLUSIONS

Statistical methods enabled to distinguish the following main elements related to traffic and road construction and accumulated by soil *(main TRCSA-indicators)* near the Vilnius–Kaunas highway: Pb, Zn, Cu, Sn, Mo and Sr. Their highest levels and highest areal and temporal variation are observed in the nearest zone (<15 m). The areal variation of these indicators and the additive index of their accumulation (depending mostly on Pb and Zn) in generalised segments perpendicular to the highway indicates the highest accumulation in the central reservation part (CRP) and soft shoulders, followed by sub-zones which usually include the ditches, and its further gradual decrease in more distant sub-zones. The main regularity of temporal variation of the additive index of accumulation in generalised segments is its increase in the CRP, soft shoulders and sub-zones usually including the ditches, and a decrease in transitional and distant subzones, though there are differences in the temporal variability of various *main TRCSA-indicators*. The lower accumulation of Zn, Cu and Mo in the transitional and distant zones can be explained by their uptake by cultivated plants. The distribution of the same indices in cross-section segments is usually asymmetric and different, indicating areal variation observed also along the highway. It is predetermined by the influence of relief and forest barriers, prevailing winds, soil type, land use, vegetation, traffic intensity and other diffuse pollution sources. The following regularity was observed in temporal changes of the additive index of accumulation of the *main TRCSA-indicators*: relief barriers near the highway do not favour the spread of pollutants and increase their accumulation in the nearest zone. Therefore roadside topsoil monitoring should be continued in the cross-sections differing in the conditions for dispersion of pollutants.

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MIKROELEMENTŲ KAUPIMOSI KAITA PAVIRŠINIAME DIRVOŽEMYJE PRIE GREITKELIO VILNIUS–KAUNAS

S a n t r a u k a

Skirtingai nei daugelyje autotransporto taršos tyrimų, nagrinėjančių nedidelį mikroelementų skaičių, siekiant atskleisti taršos polielementiškumą, šiame straipsnyje analizuojama gausi jų grupė: Ag, B, Ba, Co, Cr, Cu, Ga, Li, Mn, Mo, Nb, Ni, Pb, Sc, Sn, Sr, Ti, V, Y, Yb, Zn, Zr. Darbo tikslas – remiantis greitkelio Vilnius–Kaunas tyrimais, išskirti elementus, kurių didžiausias kaupimasis paviršiniame dirvožemyje yra susijęs su transportu, ir apibūdinti jų kaupimosi kaitą areale (profiliuose ir jų atkarpose) ir laike (nuo 1991 iki 2005 m.). Bendri elementų kiekiai paviršiniame dirvožemyje nustatyti optinės atominės emisinės spektrofotometrinės analizės būdu. Profiliai skiriasi teršalų sklaidos sąlygomis bei kitų gamtinių ir antropogeninių veiksnių poveikiu. Profiliai padalyti į tolimąją (D), tarpinę (T) ir artimąją (N) zonas. Smulkiau suskirsčius N zoną, profiliuose gautos 5 pazonės: N1 (<2,5 m), N2 (2,5–7,5 m), N3 (7,5–15 m), T (15–35 m) ir D (35–70 m). Atsižvelgus į tai, ar jos pavėjinėje, ar priešvėjinėje pusėje, gautos 9 atkarpos, besiskiriančios žemėnauda, augalija ir dirvožemiu. Elementų koncentracijos koeficientai (CC) apskaičiuoti tinkamai parenkant įvairias fonines reikšmes. Lyginant CC medianas zonose, nustatytas gausus su transporto tarša ir kelio konstrukcijomis susijusių elementų pogrupis. Jis patikslintas lyginant N zoną su jungtine T + D zona ir išskiriant paragenetines asociacijas. Išskirti pagrindiniai elementai-indikatoriai, susiję su autotransporto tarša (Pb, Zn, Cu, Sn, Mo) bei kelio konstrukcijomis (Sr). Suminio šių elementų kaupimosi rodiklio Z6 reikšmę nulemia Pb ir Zn. Apibendrinus profilių atkarpas, išaiškėjo indikatorių, o ypač jų Z6, kaitos dėsningumas areale – tolstant nuo asfaltuotos juostos jis laipsniškai mažėjo, taip pat pagrindinis Z6 kaitos laike dėsningumas – augo N1 ir N2 pazonėse ir mažėjo T ir D pazonėse. Pb, Zn, Cu, Sn, Mo ir Sr pasiskirstymai apibendrintose atkarpose šiek tiek skiriasi. Z6, Zn, Cu ir Mo mažėjimą T ir D pazonėse galėjo nulemti biogeocheminė akumuliacija augaluose. Tų pačių kintamųjų pasiskirstymas įvairių profilių atkarpose dažniausiai yra asimetriškas ir skirtingas, t. y. kaita areale palei greitkelį priklauso nuo reljefo bei miško barjerų, vyraujančių vėjų krypties, dirvožemio tipo, augalijos, transporto intensyvumo ir kitų išsklaidytos taršos šaltinių. Dėsningumas išryškėjo tik lyginant Z6 pasiskirstymo pokyčius laike: nustatyta, kad reljefo barjerai sukuria nepalankias sąlygas teršalų ir dulkių sklaidai ir nulemia, laikui bėgant, elementų prieaugį N zonoje, todėl siūloma tęsti paviršinio dirvožemio stebėjimą minėtuose profiliuose.

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ИЗМЕНЧИВОСТЬ НАКОПЛЕНИЯ МИКРОЭЛЕМЕНТОВ В ПОВЕРХНОСТНОЙ ПОЧВЕ ОКОЛО АВТОСТРАДЫ ВИЛЬНЮС–КАУНАС

Р е з ю м е

В отличие от большинства исследований, в которых загрязнение почвы автотранспортом рассматривалось на примере небольшого числа выделяемых микроэлементов, авторами была изучена их многочисленная группа: Ag, B, Ba, Co, Cr, Cu, Ga, Li, Mn, Mo, Nb, Ni, Pb, Sc, Sn, Sr, Ti, V, Y, Yb, Zn, Zr. Цель исследования – выявить элементы, накопление которых в поверхностной почве автострады Вильнюс–Каунас в наибольшей степени связано с автотранспортом, а также осуществить анализ их площадной (в профилях и сегментах) и временной изменчивости. Валовые содержания элементов определялись методом оптического атомного эмиссионного спектрофотометрического анализа. Изученные профили различаются по условиям рассеяния загрязняющих элементов и по влиянию других природно-антропогенных факторов. В профилях выделены зоны: дальняя D, переходная T и ближняя N, а после разделения зоны N выделены 5 подзон: N1 (<2,5 м), N2 (2,5–7,5 м), N3 (7,5–15 м), T (15–35 м) и D (35–70 м). Учитывая их расположение с наветренной и подветренной сторон от автострады, выделено 9 сегментов. Для подсчета коэффициентов концентрации (CC) использованы разные соответствующие фоновые значения. При сравнении медиан CC в трех зонах выявлена подгруппа элементов, накопление которых, возможно, связано с транспортом; эта подгруппа была уточнена при сравнении N и объединенных T + D зон и определении парагенетических ассоциаций. Выделены основные элементы-индикаторы, связанные с загрязнением транспортом (Pb, Zn, Cu, Sn, Mo) и дорожными конструкциями (Sr). Суммарный показатель их накопления Z6 в наибольшей степени зависит от Pb и Zn. Генерализация сегментов профилей выявила закономерности площадной изменчивости накопления элементов-индикаторов, и особенно показателя Z6 – уменьшение с увеличением расстояния от асфальта, и временной изменчивости Z6: увеличение в N1 и N2 и уменьшение в подзонах T и D. Уменьшение Z6, Zn, Cu, Mo в подзонах T и D, вероятно, обусловлено их аккумуляцией в растениях. Распределение переменных в сегментах отдельных профилей чаще всего различается и является асимметричным, т. е. изменчивость их содержания вдоль автострады зависит от многих факторов. Общая закономерность выявлена только при сравнении временных изменений Z6: барьеры рельефа предопределяют увеличение накопления металлов в зоне N во времени. Предлагается продолжить мониторинг поверхностного слоя почв в профилях.