GEOLOGIJA. 2005. T. 49. P. 10–20

Geochemija • Geochemistry • Геохимия

The structure of technogenous geochemical anomalies in topsoil of Panevëþys metal processing enterprises

Rimantë Zinkutë

Zinkutė R. The structure of technogenous geochemical anomalies in topsoil of Panevėžys metal processing enterprises. *Geologija*. Vilnius. 2005. No. 49. P. 10–20. ISSN 1392-110X.

The levels and peculiarities of topsoil pollution on the territories of 16 metal processing plants of Panevėžys are discussed using the data on trace element contents determined by DC Arc ES (B, Ga, P, Mn, Ti, V, Cr, Co, Ni, Cu, Zn, Pb, Mo, Ag, Sn, Zr, Y, Sc, Ba) or XRF (Sr, As, U) during geochemical mapping of the town. Both the pollution type and the geochemical structure of the complex pedogeochemical anomalies distinguished according to a partial contamination index of 10 metals (Cu, Zn, Pb, Ag, Sn, Mn, Cr, Ni, Co, Mo) are investigated. The pollution type is analyzed in a generalized way, by distinguishing the maximum pollutants and metal pollution codes, while geochemical structure is revealed through priority pollutants – metals that form wide and contrasting anomalies (usually Cu, Zn, Pb, sometimes Ni, Mo, Cr, Sn, Ag). The spatial pattern of the structure is partly reflected in the areas occupied by aureoles of three associations such as ACu (Cu–Zn–Sn–Ag–Mn), ANi (Ni–Mo–Cr–Co) and APb (Pb), in their arrangement in descending order and the prevailing association. This information can be useful when planning the remediation of areas where contamination exceeds the allowable level or while revealing the polluting elements that can be most hazardous.

Key words: topsoil, metal processing enterprises, heavy metals, complex anomalies, geochemical structure

Received 2 November 2004, accepted 20 December 2004
Rimantė Zinkutė, Institute of Geology and Geography, T. Ševčenkos 13, 03223 Vilnius, Lithuania

INTRODUCTION

Complex multielement anomalies in topsoil reflect atmospheric pollution from point sources, *i.e.* industrial enterprises. For risk assessment, both the *area* and *contrast* of an anomaly must be taken into account. These indices as well as the *form* of anomalies are different: they depend on technological processes, the amount of emissions, location of industrial shops within the territory of the plant, existence of other enterprises in close neighbourhood, as well as on different natural factors. On the other hand, even anomalies with quite a different areas can be characterised and compared according to their *geochemical structure*. Such analysis can be important for decision-making from two points of view: 1) for planning the remediation methods of a polluted territory; 2) for estimating the risk of pollution of the surrounding territory with different elements. A corresponding plan of actions can be then adopted, *e.g.*, reduction of emissions or improvement of technological processes.

Certain regularity can be expected in the atmospheric pollution and in topsoil anomalies of industrial enterprises, if more or less *stable technologies* are used there. However, usually they change; besides, presently most of industrial enterprises are not even functioning. As topsoil is an accumulating medium for pollutants, trace element anomalies in it not always fully reflect the current technological processes of the enterprise. On the other hand, it is important to investigate the geochemical structure of anomalies not in order to reveal the technological processes, but mainly because these territories can become *secondary pollution sources*.

THE CHOICE OF THE OBJECTS AND THE AIM OF RESEARCH

To study the influence of urbanisation and industrialisation on the structure of technogenous geochemical anomalies, it was necessary to choose appropriate objects. Panevėžys was chosen as a town where a great number of industrial enterprises (even 45) have been analysed for their topsoil pollution level (Radzevičius et al., 1997). The most important thing seemed to reveal the structure of anomalies formed by the *main polluters* of the town. A comparison of six different groups of industrial enterprises (16 belong to metal processing, 10 to transport, 2 to energetics, 9 to food, 3 to light and 5 to building industry) showed that mainly the enterprises more or less involved in metal processing are the main chemical polluters of the environment in Panevėžys (Zinkutė, Radzevičius, 2001). This tendency was proven also in other towns of Lithuania (Kadūnas ir kt., 1995), especially in various industrial districts of Vilnius. Besides, unlike in most other industrial enterprises, the prevalence of the siderophiles Mo, Ni and Co is sometimes possible in accumulating associations of metal processing plants, *e.g.*, in the fuel equipment plant in the Žirmūnai district of Vilnius (Taraškevičius, Šiaudinienė, 2001). Therefore, it is mainly in metal processing plants where a *much more complicated* geochemical structure can be expected.

Therefore, it was quite natural to choose the metal processing plants of Panevėžys as the objects of the current research. They are situated in four different industrial districts, mostly in western (5), eastern (6) and southern (4) and only one in the central district. As they occupy a different area, the number of samples taken was unequal (Table 1). Only samples *within plant territories* were be taken into account, as outside them overlapping with pollution of other enterprises was possible. The *technological type* of the enterprises differed, *i.e.* different metal processing methods were used: mechanical processing (M), casting (C), galvanic processing (G) or electrical engineering (E). The main technological types were CM and M, more rare GM and ME; one type was unique – GME. In each of three main districts there are enterprises with various technological types and with different area.

Various aspects of pollution by metal processing plants have been analysed before: first of all the distribution pattern of elements in topsoil, their accumulation level and associations (Kadūnas ir kt., 1995), followed by studies devoted to a comparison of different plants in order to find their common or specific geochemical features (Zinkutė, Radzevičius, 2001; Zinkutė, 2002), to explain the distribution of *point pollution codes* (Zinkutė, 1999) or to introduce *object pollution codes* (Zinkutė, 2002), to reveal *T-specific, M-specific, typical* and *prevailing* elements (Zinkutė et al., 2002). Actually all these studies were useful for revealing pollution type and geochemical structure on the territories of metal processing plants.

The aims of this research were the following: 1) to compare the pollution types of metal processing plants in different industrial districts of Panevėžys on the basis of generalised information obtained on the whole territory of each enterprise; 2) to characterise the pollution types of complex geochemical anomalies in topsoil of these enterprises and to reveal their geochemical structure from a new aspect by listing their priority elements, which form both wide and contrasting anomalies. Such analysis already was done in 2001 for the conference "Metals in the environment" (Zinkutė, Tverkutė, 2001), but a full article was not yet published. As a new hygienic norm has been adopted recently (Lietuvos …, 2004), and as some of the results have already been published since 2001, the former contribution had to be revised.

METHODS

Sampling, sample preparation and analytical methods. They have been described in "Geochemical atlas of Panevėžys" (Radzevičius et. al., 1997). The samples were analysed for the total content of 22 elements: B, Ga, P, Mn, Ti, V, Cr, Co, Ni, Cu, Zn, Pb, Mo, Ag, Sn, Zr, Y, Sc, Ba (DC Arc Emission Spectrometry) and Sr, As, U (XRF). In some of the samples the elevated content of W, Cd, Sb, As, Bi enabled to detect them by DC Arc ES.

Evaluation of topsoil contamination level. It was based of *additive contamination indices* using the recommended levels (Lietuvos …, 2004). The *total contamination index* (Z22) was calculated by summing up the *concentration coefficients* (CC) of all 22 elements analysed in Panevėžys, while the *partial contamination indices* were found according to subsets of these elements. CC values were computed for each element dividing its amount determined in sample by a *local background value*, which was determined on the water-intake territory after consecutive elimination of anomalies (Зинкуте, 1999). In each point the elements with CC > 2 were included into a *point accumulating association* (Zinkutė, 2002). Geohygienic state was evaluated for elements in comparison with their *maximum permitted concentrations* (MPC) in soil given in hygienic norm (Lietuvos …, 2004).

Characterization of the whole territories of metal processing enterprises. Each enterprise was first of all characterised by a median value of Z22. Then *object accumulating associations* (descending sequences of CC medians which are greater than 1.3) were found for each plant. Due to a complex comparison of *object accumulating associations*, their generalisation seemed to be useful. So each metal processing enterprise was characterised by a ***maximum pollutant*** (element with the highest CC median). However, such information was not enough. As accumulation and a good correla-

Table 1. **Description and contamination level of metal processing plants in Panevëþys**
1 lentelė. **Panevëþio metalo apdorojimo gamyklø duomenys ir jø uþterðtumo lygis**

District Rajonas	Code Kodas	Title Pavadinimas	N	S* (ha)	Type Tipas	Production Produkcija	Z22	Z10	Z10 input Z10 įnašas	Per cent of samples where Z10 is: Procentas mėginių, kai:			
										>16	16–32	32–128	>128
W	TM1	"Tikslioji mechanika" (I site)	34	S (4.3)	GME	Electronic devices	314	312	99.2	94.1	5.9	17.6	70.6
W	LK	"Lietkabelis"	26	M (9.0)	M	Cables	122	120	98.3	92.3	15.4	30.8	46.2
W	Au2	"Aurida" (II site)	46	L (25.2)	CM	Auto-compressors	53.2	50.1	94.4	78.3	13.0	54.3	10.9
W	Au1	"Aurida" (I site)	25	M (8.9)	CM	Auto-compressors	26.2	22.8	87.3	68.0	24.0	32.0	12.0
W	TM2	"Tikslioji mechanika" (II site)	34	L (19.5)	M	Precise mechanical devices	8.72	5.03	57.7	17.6	0	14.7	2.9
E	Met	"Metalistas"	27	M (6.2)	GM	Locks	115	111	97.0	81.5	11.1	25.9	44.4
E	Ekr	"Ekranas"	91	L (42.0)	ME	TV-tubes, crystal	71.7	50.5	70.4	83.5	14.3	42.9	26.4
E	DS	Gas-main construction	5	S (1.4)	M	Bituminisation of pipes	31.4	28.8	91.9	60.0	20.0	40.0	0
E	Ket	"Panevėžio ketus"	17	M (5.6)	CM	Cast iron production	29.7	27.0	90.8	70.6	23.5	17.6	29.4
E	Av	Aviation repair plant	25	L (14.8)	GM	Aircraft repair	13.89	11.7	84.1	36.0	16.0	16.0	4.0
E	Arem	Motor transport repair works	29	M (8.7)	M	Motor transport repair	9.29	5.63	60.6	27.6	6.9	17.2	3.4
S	Pr	"Praktika"	26	S (4.6)	CM	Portative boring machine-tools	46.1	42.8	93.0	69.2	3.8	53.8	11.5
S	Akl	Blind society plant"	40	S (3.6)	GM	Consumer goods	16.1	13.6	84.4	47.5	10.0	20.0	17.5
S	Re	"Remeksta"	26	L (13.5)	M	Domestic appliances repair	10.23	7.86	76.8	26.9	11.5	15.4	0
S	K	Deaf society plant	27	M (5.8)	CM	Consumer goods	9.22	5.92	64.2	14.8	3.7	0	11.1
C	El	"Elektro-technika"	11	S (1.5)	ME	Desk lamps	15.62	12.7	81.5	45.5	0	27.3	18.2

Districts: W – western, E – eastern, S – southern, C – central. N – number of topsoil samples taken. S* – approximate area: L – large (>10 ha), M – medium (5–10 ha), S – small (<5 ha). Type – technological type, which is indicated by combination of letters (C – casting, G – galvanic processing, E – electrical engineering, M – mechanical processing). Z22 – total contamination index, Z10 – partial contamination index by 10 metals: Cu, Zn, Sn, Ag, Mn, Ni, Mo, Cr, Co, Pb. Z10 input – percentage of Z10 from Z22
Rajonai: W – vakarinis, E – rytinis, S – pietinis, C – centrinis. N – paimtų paviršinio dirvožemio sluoksnio mėginių skaičius. S* (ha) – apytikris plotas: L – didelis (>10 ha), M – vidutinis (5–10 ha), S – mažas (<5 ha). Tipas – technologinis tipas, kurį nusako raidžių kombinacija (C – liejimas, G – galvaninis apdorojimas, E – elektrotechnika, M – mechaninis apdorojimas). Z22 – bendras užterštumo rodiklis, Z10 – 10 metalų (Cu, Zn, Sn, Ag, Mn, Ni, Mo, Cr, Co, Pb) dalinis užterštumo rodiklis. Z10 įnašas – Z10 procentas nuo Z22.

tion of Cu, Zn, Pb, Sn, Mo, Ni, Mn, Cr, Ag, Co (most of which are typical of alloys) was usually observed on the territories of the enterprises (Zinkutė, Radzevičius, 2001), the *partial metal contamination index Z10* was computed according to these 10 elements, and a generalisation according to three paragenetic associations of ten metals was accomplished. These associations were distinguished by the cluster analysis (Ward method from a correlation matrix of the logarithms of concentrations recalculated to air-dry material) using data on all 16 enterprises (Zinkutė, Radzevičius, 2001). ***Metal average pollution*** codes (MAP-codes) were determined on the basis of these three metal-associations. Besides, the percentage of samples where the MPC of metals (Lietuvos …, 2004) were exceeded was determined. Thus, each metal processing enterprise was characterised by: 1) ***maximum metal-pollutant*** (one of the 10 mentioned metals, in rare cases – other element); 2) ***metal average pollution code*** (MAP-code) showing a relative importance of each of the three metal associations according to the mean values of the average CC of their elements (Zinkutė, 2002); 3) ***hygienic codes of metal associations*** (metals in each metal association arranged in descending order according to the percentage of samples were their MPCs are exceeded); 4) information about elements that are rarely detected by an analytical equipment applied (most often W and Cd).

Distinguishing of complex anomalies and characterization of their geochemical structure.

Complex anomalies, which characterise metal processing on the territories of the study objects, can be distinguished on the basis of the concentration levels of these 10 elements. The easiest way was chosen to include the points with Z10 >16. The pollution type in these complex anomalies was characterised in the same way as on the whole territories (maximum metal-pollutant, MAP code). The geochemical structure of complex anomalies can be characterised in two ways: analysing *spatial distribution regularities* and by *generalisation*. There are two problems if the first way is chosen: 1) some areas are too small for subdivision; 2) changes in the geochemical field are too great (earlier investigations have shown a high variability of *point accumulating associations*). Of course, some information about the spatial geochemical structure was obtained from maps, on which not only the overlap of aureoles of the partial contamination indices computed for three metal associations, but also the arrangement of these associations according to the descending areas of their aureoles, as well as association with the greatest partial contamination in each site could be seen. A more detailed analysis according to *point average pollution codes* (PAP codes) was not done, as their variability is also great (Zinkutė, 2002). Therefore, the main aim was not the spatial subdivision of complex anomalies, but the *generalisation of their geochemical structure* and elucidation of their regularities. The generalisation was realised by analysing the width and contrast level of metal anomalies within a complex anomaly. Two indices were calculated for each metal in a complex anomaly: ***area index Ia*** – per cent of contaminated (CC > 2) samples (roughly reflects the area of metal anomaly); ***contrast index Ic*** – per cent of unallowably (CC > 16) contaminated samples among contaminated (CC > 2) samples. Element anomaly was considered to be wide (W) when Ia ≥ 75%, medium (M) when 50 ≤ Ia<75 (%), small (S) when 10 ≤ Ia < 50 (%), and insignificant (*) when Ia < 10 (%). Element anomaly was considered to be contrasting (C) when Ic ≥ 25 (%), medium contrasting (M) when 0 < Ic < 25 (%) and not contrasting (*) when Ic = 0 (%). Preparing remediation plans for zones of investigated plants unallowably polluted by metals (Z10 > 16) attention should be given to the elements that form within these zones wide and contrasting (WC) anomalies. They can be called ***priority metals.***

RESULTS AND DISCUSSION

According to median values of Z22 and Z10, the greater part of 16 objects is dangerously contaminated, but the differences among various enterprises both in Z22 and in Z10 are great (Table 1). Plants with a greater variety of different technological processes are usually characterised by higher medians of Z22 and Z10; *e.g.*, the highest Z22 is observed in TM1. However, great differences of these indices are found even within the same type, because they depend not only on technological processes ever used but also on the amount of emissions, the time of functioning and the present status of a plant (*e.g.*, LK is characterised by the greatest volume of emissions among M-type plants, it has been functioning for a long time and still is operating). Especially great differences in the values of both indices can be found if sampling has been done on the whole large territory of the plant, because the median pollution levels depend on the location of industrial blocks within the area. For example, the largest plants have both high (Ekr, Au2) and low (TM2, Av) Z22 and Z10 medians. The input of metal pollution in various plants is also different: Z10 makes up from 57.7% (TM2) to 99.2% (TM1) of Z22. It is smaller (<80%) also if total contamination is low (K, TM2) or if another type of activities exists in the enterprise (*e.g.*, glass melting in Ekr, transport activity in Arem and Re).

Complex anomalies (Z10 > 16) are observed in all study objects (Figs. 1–4). Some of them occupy only part of the territory of the enterprise, *e.g.*, TM2 (Fig. 1), K, Re, Akl (Fig. 2), Arem (Fig. 3), but most of them are large and include almost the whole plant, sometimes even part of the adjacent territory, *e.g.*, Au2, Au1 (Fig. 1), Met, Ekr (Fig. 3), El (Fig. 4). The largest complex anomaly in the western district was found in Au2 (Fig. 1), in the southern in Pr (Fig. 2),

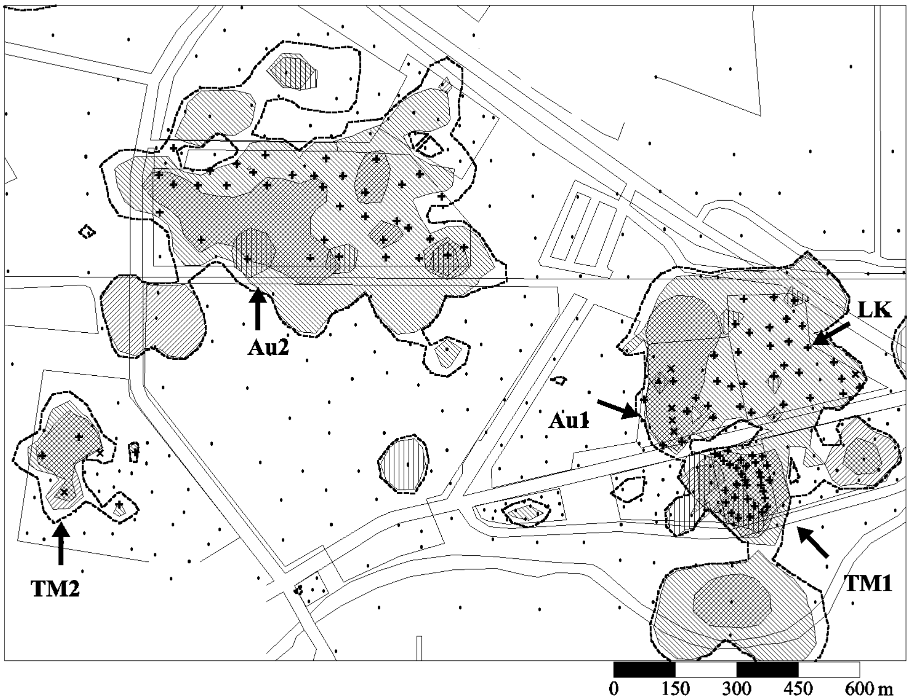
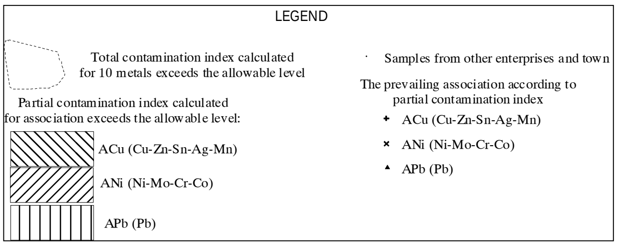
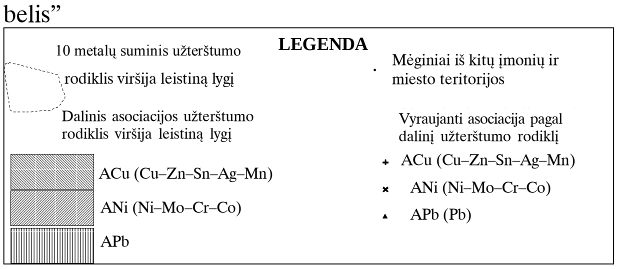


Fig. 1. Complex anomalies formed by Cu, Zn, Sn, Ag, Mn, Ni, Mo, Cr, Co, Pb in topsoil of metal processing plants of the western industrial district of Panevėžys
1 pav. Panevėžio vakarinio pramoninio rajono metalo apdorojimo įmonių dirvožemyje suformuotos kompleksinės Cu, Zn, Sn, Ag, Mn, Ni, Mo, Cr, Co, Pb anomalijos.



Codes of the enterprises: TM1 – "Tikslioji mechanika" (I site), TM2 – "Tikslioji mechanika" (II site), Au1 – "Aurida" (I site), Au2 – "Aurida" (II site), LK – "Lietkabelis"



Įmonių kodai: TM1 – „Tikslioji mechanika" (I aikštelė), TM2 – „Tikslioji mechanika" (II aikštelė), Au1 – „Aurida" (I aikštelė), Au2 – „Aurida" (II aikštelė), LK – „Lietkabelis"

in the eastern in Ekr (Fig. 3). In the central district the anomaly of El was not very large (Fig. 4). The most contrasting metal contamination was observed in the western district (maximum Z10 median in TM1), it was lower in the eastern (Met) district, followed by the southern (Pr) and the central (El) districts. Extremely large and contrasting anomalies are formed when several metal processing enterprises are close to each other (TM1, LK and Au1).

The following three paragenetic associations were distinguished according to the correlation of metal content on the territories of the plants: ACu (Cu–Zn–Sn–Ag–Mn), ANi (Ni–Mo–Cr–Co) and APb (Pb). Some plants of electrical engineering (Ekr, TM1) are characterised by a very wide group of elements exceeding their MPC (Table 2). A comparison of pollution types estimated on the whole territories of metal processing enterprises revealed different regularities in various districts (Table 2).

The main pollutant in the ***western*** district is the same – Cu. Either ACu or ANi prevail in the MAP-codes. The role of ANi is the greatest in Au1 and TM2, lower in TM1 and the lowest in Au2 and LK, where APb has more influence. According to hygienic codes of metal associations, mostly metals from ACu (usually Cu, as in TM1, LK and Au2, or Sn, as in Au1) are characterised by the greatest percentage of samples in which their MPC is exceeded, except TM2, where Ni from ANi has affected a greater part of the territory (probably a specific technology used in the new site of the precise mechanics plant). In most plants, except TM2 and LK, Cr has the greatest influence in the hygienic code of ANi, followed either by Mo in Au2 and Au1 (casting) or by Ni in TM1 (galvanic shop).

Almost in all objects of the ***eastern*** district, except Met, MAP-codes are the same – PbCuNi, showing the prevailing role of APb, though Pb is not everywhere the main pollutant but only in the enterprises from the eastern (Ekr, DS) or northern (Arem) parts of the district, meanwhile in the enterprises from the western (Met, Ket) or southern (Av) parts of this district Zn is the main pollutant. The prevalence of APb, also the highest among 10 metals, percentage of topsoil samples in Ekr, DS and Av with Pb content exceeding its MPC can be explained by a strong influence of Pb pollution in "Ekranas" (related to special glass production) on the adjacent DS, as well as by the intensive transport in the eastern part of the district. The MAP-code of Met is quite different – CuNiPb and Cr from ANi shows there the greatest (in comparison with other 10 metals) percentage of samples in which its MPC is exceeded. The enterprises of the district are

Fig. 2. Complex anomalies formed by Cu, Zn, Sn, Ag, Mn, Ni, Mo, Cr, Co, Pb in topsoil of metal processing plants of the southern industrial district of Panevėžys

Legend is the same as in Fig. 1. Codes of the enterprises: Pr – "Praktika", Akl – Blind society plant, Re – "Remeksta", K – Deaf society plant

2 pav. Panevėžio pietinio pramoninio rajono metalo apdorojimo įmonių dirvožemyje suformuotos kompleksinės Cu, Zn, Sn, Ag, Mn, Ni, Mo, Cr, Co, Pb anomalijos.

Sutartinius ženklus žr. 1 pav. Įmonių kodai: Pr – „Praktika", Akl – Aklųjų draugijos gamykla, Re – „Remeksta", K – Kurčiųjų draugijos gamykla

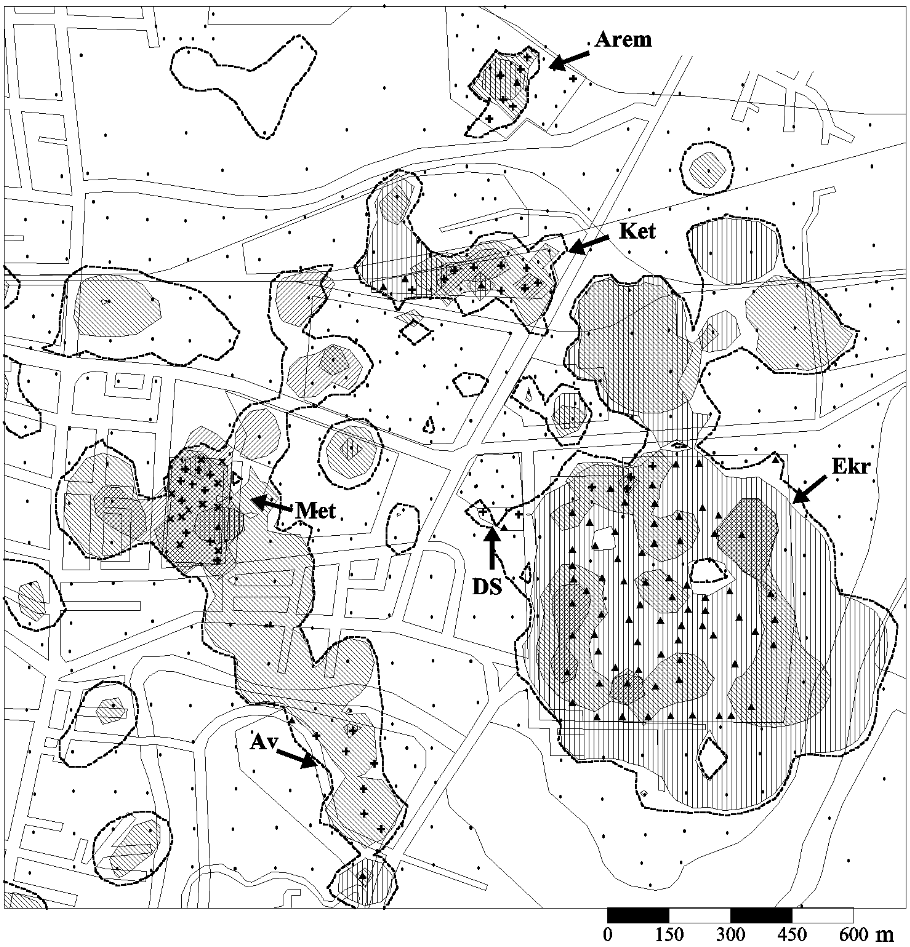


Fig. 3. Complex anomalies formed by Cu, Zn, Sn, Ag, Mn, Ni, Mo, Cr, Co, Pb in topsoil of metal processing plants of the eastern industrial district of Panevėžys

Legend is the same as in Fig. 1. Codes of the enterprises: Met – "Metalistas", Ekr – "Ekranas", DS – Gas-main construction, Ket – "Panevėžio ketus", Av – Aviation repair plant, Arem – Motor transport repair enterprise

3 pav. Panevėžio rytinio pramoninio rajono metalo apdorojimo įmonių dirvožemyje suformuotos kompleksinės Cu, Zn, Sn, Ag, Mn, Ni, Mo, Cr, Co, Pb anomalijos.

Sutartinius ženklus žr. 1 pav. Įmonių kodai: Met – „Metalistas", Ekr – „Ekranas", DS – dujotiekio statyba, Ket – „Panevėžio ketus", Av – aviacijos remonto gamykla, Arem – autoremonto gamykla

Fig. 4. Complex anomaly formed by Cu, Zn, Sn, Ag, Mn, Ni, Mo, Cr, Co, Pb in topsoil of "Elektrotechnika" metal processing plant in the central industrial district of Panevėžys
Legend is the same as in Fig. 1. El – "Elektrotechnika"
4 pav. Panevėžio centrinio pramoninio rajono „Elektrotechnikos" metalo apdorojimo gamyklos dirvožemyje suformuotos kompleksinės Cu, Zn, Sn, Ag, Mn, Ni, Mo, Cr, Co, Pb anomalijos.
Sutartinius ženklus žr. 1 pav. El – „Elektrotechnika"

similar in the hygienic codes of ACu with Zn in the first place. In Ket and Arem this element has even the greatest influence among all 10 metals. Unlike ACu, the hygienic codes of ANi differ: not only Cr (Met, Ekr, Av), but also Ni (Arem) and even Mo (Ket) can be on the first place.

The ***southern*** district is the most variable according to pollution types: both maximum metals-pollutants (Pb, Ni and Sn) and MAP-codes (PbCuNi, CuPb(Ni) and NiPbCu) are different. A strong influence of Pb in Pr and Re can be explained by transport activity, Ni in Akl – by the functioning of a galvanic shop, P, Sn and Cu in K – by casting of non-ferrous metals. The elements with the highest percentage of samples exceeding MPC are in different metal associations: Zn and Cu in ACu, Pb in APb and Ni in ANi.

Pollution types estimated on the areas of complex metal anomalies (Z10 > 16) (Table 2) were similar to pollution types estimated on the whole territories (Table 3), but some changes could be observed. The main difference was that part of the main pollutants in complex anomalies (Table 3) was other than in the whole plant (Table 2). Of course, due to the small number of samples taken from the territories of some plants, their complex anomalies could be characterised insufficiently. However, it seems possible that when analysing the whole territories, Pb was masking the peculiarities of metal processing in Arem, DS, Pr and Re. MAP-codes in complex metal-anomalies are mainly the same as in the whole territory, except TM2, where the role of ANi is lower and Re where it is higher. After such adjustment the role of ANi in complex anomalies of the western district is the lowest in LK and Au2, being higher in TM1 and TM2 and the highest in Au1. It is very important that mainly within complex anomalies all 10 metals usually exceed their MPC. When Z10 < 16, only in 7 samples from Ekr and 1 sample from Re Pb exceeds its MPC, also in 1 sample from Av Cr exceeds its MPC and in 1 sample from Av Sn exceeds its MPC. However, in all these cases Z10 > 10. This regularity proves that mainly the areas of complex anomalies must be studied for revealing the geochemical structure, the rest of the territory being less important.

The maps with aureoles of metal associations (Figs. 1–4) show that the overlapping of all three associations is possible only in enterprises of a more complex type, meanwhile in M-type enterprises there are usually only two overlapping aureoles. Besides, ACu usually forms the largest aureole and prevails almost everywhere. This is natural, because it has the greatest number of elements. Exceptions are Ekr, which is most widely polluted by APb, and El, where ANi anomaly is the largest. When there are three overlapping aureoles, ACu is usually followed by ANi and the latter by APb.

To analyse the geochemical structure of complex anomalies, 10 metals can be subdivided into several groups according to their input to these anomalies: 1) very great input (Cu, Zn, Pb); 2) great input (Ni, Mo, Cr); 3) medium input (Sn, Ag); 4) small input (Mn, Co). The elements of the first group most often form wide and contrasting (WC) anomalies in complex anomalies of metal processing plants, *i.e.* they are the main priority pollutants. Metals of the forth group do not form WC anomalies.

Mainly **Cu** has polluted complex anomalies (even 12 of 16) of almost all the investigated plants (Ia = 100%). Its input was lower only in Ekr, Av, Arem and TM2 from the eastern district, either because metal processing is not the main function of the enterprise (Ekr, Arem) or because its territory is large (Av, TM2). In TM1, Lk and Ket even total pollution of the whole territories with Cu is observed. The most contrasting input to anomalies from different districts is observed in K (southern), TM1 (western) and Met (eastern). In 11 plants Cu is a priority pollutant.

Zn forms wide anomalies in all plants and very often also totally contaminates complex anomalies, especially in the eastern and southern districts; however,

Table 2. **Pollution types on the whole territories of metal processing plants in Panevėþys**
2 lentelė. **Tarðos tipai visoje Panevėþio metalo apdorojimo ámoniø teritorijoje**

Code Kodas	Type Tipas	MP	Average CC of association Vidurkinis asociacijos CC			MAP-code MAP-kodas	Hygienic codes of metal associations* Metalų asociacijų higieniniai kodai*			Elements rarely detected by analytical equipment** Elementai retai aptinkami analizės prietaisais**
			ACu	APb	ANi		ACu	APb	ANi	
TM1	GME	Cu	71.8	13.4	14.3	CuNiPb	Cu94Sn85Zn59 Ag3Mn3	Pb53	Cr82Ni71 Mo32Co18	W28Cd2Bi16
LK	M	Cu	42.0	8.14	2.20	CuPbNi	Cu88Sn46Zn38	Pb42	Ni4Mo4Co4	Cd
Au2	CM	Cu	15.7	5.36	3.95	CuPbNi	Cu54Zn54Mn41 Sn37	Pb17	Cr52Mo13Ni7	W16Cd2
Au1	CM	Cu	6.77	4.69	9.33	NiCuPb	Sn40Cu32Zn16 Mn8	Pb8	Cr28Mo24Ni16	W22
TM2	M	Cu	2.61	1.41	2.64	NiCu(Pb)	Cu9Zn6Sn3		Ni15Co6Cr3	W4Cd
Met	GM	Zn	25.7	10.9	16.2	CuNiPb	Zn67Cu59 Sn15Ag4	Pb33	Cr74Ni70Mo48	W15Cd5
Ekr	ME	Pb	4.42	66.5	2.61	PbCuNi	Zn34Sn9Cu7 Mn2Ag1	Pb91	Cr13Ni8Mo7	W32Cd71 Sb89Ce46Hf2
DS	M	Pb	3.04	9.12	1.47	PbCu(Ni)	Zn40	Pb40	–	–
Ket	CM	Zn	8.02	135	4.54	PbCuNi	Zn41Cu29 Sn24Mn12Ag6	Pb35	Mo35Cr29Ni24	W4CdBi2 GeCe3Sb
Av	GM	Zn	4.07	7.43	1.65	PbCu(Ni)	Zn16Sn12Cu8	Pb20	Cr16	W3Cd9
Arem	M	Pb	6.18	8.43	1.97	PbCu(Ni)	Zn17Cu7Sn7	Pb14	Ni10Cr7Mo3	W3Cd
Pr	CM	Pb	9.36	12.2	4.93	PbCuNi	Zn46Cu35 Sn23Mn8	Pb15	Mo38Cr38 Ni19Co4	W19Cd2
Akl	GM	Ni	7.72	12.1	12.5	NiPbCu	Cu28Zn25 Sn13Mn8	Pb15	Ni40Cr28Mo13Co5	W9Ge
Re	M	Pb	2.12	4.64	2.01	PbCuNi	Zn8	Pb19	Ni4Cr4	Be4
K	CM	P (Sn)	11.3	4.61	1.46	CuPb(Ni)	Cu15Zn11 Sn11Ag4	Pb7	Mo4	W3Cd2
El	ME	Ni	10.4	3.78	9.26	CuNiPb	Cu27Zn27Sn27	Pb18	Ni45Cr27Mo9	W2Ge

Codes and types are given in Table 1. MP – maximum pollutant, i.e. element with highest median CC, MAP-code – metal average pollution code. ACu – association Cu–Zn–Sn–Ag–Mn, ANi – Ni–Mo–Cr–Co, APb – Pb. * – each element is followed by percentage of samples, where its MPC is exceeded. ** – each element is followed by the number of samples where it was detected.
Kodai ir tipai pateikti 1 lentelėje. MP – maksimalus teršalas, t. y. elementas su didžiausia CC (koncentracijos koeficientų) mediana, MAP kodas – metalų vidurkinės taršos kodas. ACu – asociacija Cu–Zn–Sn–Ag–Mn, ANi – Ni–Mo–Cr–Co, APb – Pb. * – po kiekvieno elemento eina mėginių, kuriuose viršyta jo DLK, procentinis kiekis. ** – po kiekvieno elemento eina mėginių, kuriuose jis buvo aptiktas, skaičius.

its pollution does not cover all the territory of plants. Its most contrasting anomalies from different districts are in K (southern), Met (eastern), TM2 (western). In 11 plants it is a priority pollutant.

Pb also forms wide anomalies (except TM2) and often totally contaminates complex anomalies. Ekr, Ket and DS are characterised by the total contamination of the whole territory with Pb. The Pb anomalies from three main districts are most contrasting in Ekr (eastern), K (southern) and TM1 (western). In 8 plants it is a priority pollutant.

Elements of **great** (Ni, Mo, Cr) and **medium** (Sn, Ag) input are also sometimes priority pollutants. However, their wide anomalies are observed not so often, total contamination of complex anomalies is rare and usually related to some technological processes: Ni in

Table 3. **Pollution types and geochemical structure of complex metal anomalies in topsoil of metal processing plants in Panevëþys**
3 lentelė. **Metalø kompleksiniø anomalijø dirvoþemyje tarðos tipai ir geocheminë struktûra Panevëþio metalo apdorojimo ámonëse**

Code Kodas	N an.	Type Tipas	MP an.	MAP-code	Aureoles Aureolės	Cu		Zn		Pb		Ni		Sn		Mo		Ag		Cr		Mn		Co		PP
						Ia	**Ic**	**Ia**	**Ic**	**Ia**	**Ic**	**Ia**	**Ic**	**Ia**	**Ic**	**Ia**	**Ic**	**Ia**	**Ic**	**Ia**	**Ic**	**Ia**	**Ic**	**Ia**	**Ic**	
Eastern district / Rytinis rajonas																										
Ekr	76	ME	Pb	PbCuNi	Pb>Cu>Ni	M	**M**	W	**M**	**W***	**C**	M	**M**	S	**M**	S	**M**	S	**M**	S	*	S	*	*	*	**Pb**
Met	22	GM	Zn	CuNiPb	Cu>Ni>Pb	W*	**C**	W*	**C**	W*	**M**	W*	**C**	W	*	W	**C**	M	**M**	W*	**C**	S	*	S	*	**CuZnNi**Mo**Cr**
Ket	12	CM	Zn	PbCuNi	Cu>Ni>Pb	W*	**C**	W*	**C**	W*	**C**	W*	**M**	W	**M**	W	**C**	W	**C**	W	*	M	*	S	*	**CuZnPb**MoAg
Av	9	GM	Zn	PbCuNi	Cu>Pb	W	**M**	W*	**M**	W*	**M**	S	*	W	**M**	M	*	W	*	S	*	S	*	S	*	
Arem	8	M	Zn	PbCuNi	Cu>Pb	M	**M**	W*	**C**	W*	**C**	W	*	W	**C**	M	*	S	*	S	*	*	*	*	*	**ZnPb**Sn
DS	3	M	Zn	PbCu(Ni)	–	W*	*	W*	**C**	W*	**C**	M	*	M	*	*	*	W*	*	*	*	*	*	*	*	**ZnPb**
Western district / Vakarinis rajonas																										
Au2	36	CM	Cu	CuPbNi	Cu>Ni>Pb	W*	**C**	W*	**C**	W	**M**	W	**M**	W*	**M**	W*	*	M	**M**	W	**M**	W	**M**	*	*	**CuZn**
TM1	32	GME	Cu	CuNiPb	Cu>Ni>Pb	W*	**C**	W	**C**	W*	**C**	W	**C**	W*	**C**	W	**M**	M	**M**	W	**C**	S	*	W	**M**	**Cu**Zn**Pb**Ni**SnCr**
LK	24	M	Cu	CuPbNi	Cu>Pb	W*	**C**	W*	**M**	W	**M**	M	*	W	**M**	M	*	M	**M**	S	*	S	*	*	*	**Cu**
Au1	17	CM	Cu	NiCuPb	Cu>Ni>Pb	W*	**C**	W	**M**	W	**M**	W	**M**	W*	**M**	W*	**M**	W	*	W	**C**	S	*	S	*	**Cu**Cr
TM2	6	M	Ni	CuNiPb	Cu>Ni	W	**C**	W	**C**	S	*	W*	**C**	M	**C**	S	*	*	*	S	*	*	*	S	**C**	CuZn**Ni**
Southern district / Pietinis rajonas																										
Akl	19	GM	Ni	NiPbCu	Cu>Ni>Pb	W*	**C**	W	**C**	W	**C**	W*	**C**	M	**M**	M	**C**	M	**M**	W	**M**	S	**C**	S	*	**Cu**ZnPb**Ni**
Pr	18	CM	Cu	PbCuNi	Cu>Ni>Pb	W*	**C**	W*	**C**	W	**C**	W	**M**	W	*	W	**C**	S	*	W	*	M	*	S	*	**CuZn**PbMo
Re	7	M	Zn	PbNiCu	Cu>Ni	W*	*	W	**M**	W*	**C**	M	**C**	M	*	S	*	S	*	M	*	S	*	S	*	**Pb**
K	4	CM	Cu	CuPbNi	Cu>Pb	W*	**C**	W*	**C**	W	**C**	W*	*	W*	**C**	W*	*	W	**C**	S	*	S	*	S	*	**CuZn**Pb**Sn**Ag
Central district / Centrinis rajonas																										
El	5	ME	Ni	CuNiPb	Ni>Cu	W*	**C**	W*	**C**	W*	*	W*	**C**	W	*	W	**C**	M	*	W	**C**	S	*	S	*	**CuZnNi**MoCr

N an. – number of samples in complex anomaly. MP an. – maximum pollutant in anomaly (greatest median CC from 10 metals). MAP-code – metal average pollution code computed for anomaly. Aureoles – visual ranking of associations (ACu – Cu, ANi – Ni, APb – Pb) according to descending area of their aureoles (zones where their partial contamination index exceeds the allowable level in Fig. 1–4). Ia – area index: W – wide monoelement anomaly (W* – **Ia** = 100%), M – medium, S – small, * – insignificant anomaly. Ic – contrast index: C – contrasting anomaly, M – medium contrasting, * – not contrasting. PP – priority pollutants, *i.e.* metals forming their own wide and contrasting (WC) anomalies within complex anomaly (bolded elements have **Ia** = 100%, *i.e.* contaminate all area of anomaly)

N an. – mėginių skaičius kompleksinėje anomalijoje. MP an. – maksimalus teršalas anomalijoje (didžiausia CC mediana iš 10 metalų). MAP kodas – metalų vidurkinės taršos kodas, apskaičiuotas anomalijai. Aureolės – vizualus asociacijų (ACu – Cu, ANi – Ni, APb – Pb) išrikiavimas pagal jų aureolių (zonų, kur jų dalinis užterštumo rodiklis viršija leistiną lygį, 1–4 pav.) mažėjantį plotą. Ia – ploto indeksas: W – plati monoelementinė anomalija (W* – **Ia** = 100%), M – vidutinė, S – maža, * – nereikšminga anomalija. Ic – kontrastingumo indeksas: C – kontrastinga anomalija, M – vidutinio kontrastingumo, * – nekontrastinga. PP – prioritetiniai teršalai, t. y. metalai, kompleksinės anomalijos viduje formuojantys plačias ir kontrastingas (WC) anomalijas (paryškintų elementų **Ia** = 100%, t. y. jie užteršia visą anomalijos plotą).

Akl, Met (galvanic shops), El (electrical engineering), Ket, K (casting) and TM2, Mo in Au2, Au1, K (casting), Cr in Met (galvanic shop), Sn in TM1 (galvanic shop), Au1, Au2, K (casting), Ag in DS. Total contamination of the whole territory is even more rare: only Ni has polluted the whole territory of El.

The elements of **small** input (Mn and Co) are never priority pollutants, they form mostly small anomalies. However, in some enterprises they are large (Mn in Au2, Co in TM1) or contrasting (Mn in Akl, Co in TM2). The elements of these three groups are useful for revealing the peculiarities of each enterprise. This can be done analysing groups of priority pollutants. Some of them include only one element (Pb in Ekr and Re, Cu in Lk), others even 5 or 6 (usually where the technological type is more complex). Plants of the same technological type can have a different number of priority pollutants. The number of priority pollutants is not related to total contamination level. Great polluters can have only one priority pollutant while small polluters much more. The aviation repair plant Av has even no priority pollutants.

CONCLUSIONS

On the territories of metal processing plants it is expedient to analyse complex anomalies formed by 10 metals: Cu, Zn, Pb, Ag, Sn, Mn, Cr, Ni, Co, Mo. Their subdivision into three paragenetic associations enables to characterise each anomaly not only by a maximum pollutant, but also by metal average pollution code showing the relative importance of each association. The most hazardous are priority pollutants, *i.e.* metals forming wide and contrasting anomalies: most often these are at least one of Cu, Zn, Pb, not so often Ni, Mo, Cr, Sn, Ag, while Mn and Co never. Complex anomalies of metal processing plants are different according to priority pollutants, so the listing of these elements perfectly indicates the geochemical structure of each complex metal anomaly. No direct relationship exists between the number of priority pollutants and contamination level, however, more complex technological types of metal processing usually result in their greater number. These elements should be taken into account when planning means of pollution reduction.

References

Kadūnas V., Katinas V., Radzevičius A., Taraškevičius R., Zinkutė R. 1995. Metalo apdirbimo įmonių teritorijų grunto užterštumo ekologinis-geocheminis įvertinimas. *Geologijos mokslo pasiekimai gamtosaugai*. Vilnius, Geologijos institutas. 13–15.

Lietuvos higienos norma HN 60:2004 „Pavojingų cheminių medžiagų didžiausios leidžiamos koncentracijos dirvožemyje". 2004. *Valstybës þinios*. ***4***. 2004 m. kovo 17 4 d. 107–113.

Radzevičius A., Budavičius R., Kadūnas V., Katinas V., Tverkutė Z., Zinkutė R. 1997. Geochemical atlas of Panevėžys. Panevėžio miesto geocheminis atlasas. M 1:25000. Vilnius–Panevėžys. 18 p.

Taraškevičius R., Šiaudinienė A. 2001. Vilniaus miesto Žirmūnų seniūnijos pramonės rajono pedogeocheminės kaupimosi ir paragenetinės asociacijos. *Aplinkos inþinerija*. ***9***(*3*). Vilnius: Technika. 176–183.

Zinkutė R. 1999. Subdivision of the territory of "Ekranas" plant according to dangerous point summary pollution codes. *Environment. Technology. Resources. Proceedings of the 2nd International Conference. Rezekne, June 25–27, 1999*. Rezekne. 255–263.

Zinkutė R. 2000. Paragenetinių asociacijų bei taršos kodų taikymas ekologiniuose-geocheminiuose tyrimuose. *Geologija*. ***31***. Vilnius. 15–24.

Zinkutė R., Radzevičius A. 2001. Metal processing enterprises as the main threat to environmental quality in Panevėžys. *Environment. Technology. Resources. Proceedings of the 3rd International Conference. June 19–21, 2001*. Rezekne. 236–242.

Zinkutė R., Tverkutė Z. 2001. The structure of technogenous geochemical anomalies in topsoil of Panevėžys metal processing enterprises. *Metals in the Environment. II International Conference, Lithuania. Vilnius, Lithuania, September, 23–26, 2001. Book of abstracts*. Vilnius, Lithuanian Metalecology Society, Institute of Geology. 161–162.

Zinkutė R., Taraškevičius R., Radzevičius A. 2002. Heavy metal associations in topsoil of metal-working plants. *Aplinkos inþinerija*. ***10***(*3*). Vilnius, Vilniaus Gedimino technikos universitetas. 130–139.

Zinkutė R. 2002. Trace element technogenous associations in topsoil of urbanised territories of Lithuania. Vilnius, Institute of Geology and Geography. 200 p.

Зинкуте Р. 1999. Оценка фоновых значений микроэлементов в почвах методом последовательного исключения аномалий. *Геологія и геохімія горючих копалин*. ***1***(*106*). Львів. 91–106.

Rimantë Zinkutë

PANEVËÞIO METALO APDOROJIMO ÁMONIØ PAVIRÐINIAME DIRVOÞEMYJE SUFORMUOTØ TECHNOGENINIØ GEOCHEMINIØ ANOMALIJØ STRUKTÛRA

S a n t r a u k a

Remiantis mikroelementų kiekiais, nustatytais paviršiniame dirvožemio sluoksnyje atominės emisinės spektrofotometrinės (B, Ga, P, Mn, Ti, V, Cr, Co, Ni, Cu, Zn, Pb, Mo, Ag, Sn, Zr, Y, Sc, Ba) bei rentgeno fluorescencinės (Sr, As, U) analizės metodais Panevėžio geocheminio kartografavimo metu, aptariamas šešiolikos šio miesto metalo apdirbimo įmonių užterštumo lygis bei ypatumai, tiriami kompleksinių anomalijų, išskirtų pagal 10 metalų (Cu, Zn, Pb, Ag, Sn, Mn, Cr, Ni, Co, Mo) bendrą užterštumo rodiklį, užterštumo tipai ir geocheminė struktūra. Užterštumo tipai pateikiami apibendrintai, kiekviename iš jų išskiriant maksimalius teršalus (dažniausiai Cu, Zn, Ni, o „Ekrane" – Pb) ir metalų vidurkinės taršos kodus. Geocheminė kompleksinių anomalijų struktūra nagrinėjama pagal prioritetinius teršalus – metalus, kurie šiose zonose formuoja plačias ir kontras-

tingas anomalijas (dažniausiai Cu, Zn, Pb, rečiau – Ni, Mo, Cr, Sn, Ag). Šiam tikslui skaičiuojami du rodikliai: ploto indeksas **Ia** – užterštų (koncentracijos koeficientas viršija 2) mėginių procentas ir kontrastingumo indeksas **Ic** – neleistinai užterštų (koncentracijos koeficientas viršija 16) mėginių procentas tarp užterštų mėginių. Elemento anomalija laikoma plačia (W), kai Ia ≥ 75%, vidutine (M), kai 50 ≤ Ia < 75 (%), maža (S), kai 10 ≤ Ia < 50 (%), ir nereikšminga (*), kai Ia < 10 (%). Elemento anomalija laikoma kontrastinga (C), kai Ic ≥ 25 (%), vidutiniškai kontrastinga (M), kai 0 < Ic < 25 (%), ir nekontrastinga (*), kai Ic = 0 (%).

Erdvinį struktūros vaizdą iš dalies atspindi trijų asociacijų – ACu (Cu–Zn–Sn–Ag–Mn), ANi (Ni–Mo–Cr–Co) ir APb (Pb) – aureolių plotas ir tarpusavio padėtis, taip pat vyraujanti asociacija. Ši informacija gali būti naudinga planuojant neleistinai užterštų plotų rekultivaciją ar įvertinant, kurie teršiantys metalai gali kelti didžiausią pavojų.

Риманте Зинкуте

СТРУКТУРА ТЕХНОГЕННЫХ ГЕОХИМИЧЕСКИХ АНОМАЛИЙ, СФОРМИРОВАВШИХСЯ В ПОВЕРХНОСТНОМ СЛОЕ ПОЧВ МЕТАЛЛООБРАБАТЫВАЮЩИХ ПРЕДПРИЯТИЙ Г. ПАНЯВЕЖИСА

Резюме

На основании содержания в поверхностном слое почвы микроэлементов, при геохимическом картировании г. Панявежиса определенных методами атомного эмиссионного спектрофотометрического (B, Ga, P, Mn, Ti, V, Cr, Co, Ni, Cu, Zn, Pb, Mo, Ag, Sn, Zr, Y, Sc, Ba) и рентгенофлуоресцентного (Sr, As, U) анализа, обсуждаются степень и особенности загрязнения шестнадцати металлообрабатывающих предприятий этого города, исследуются типы загрязнения и геохимическая структура комплексных аномалий, выделенных по суммарному показателю загрязнения 10 металлами (Cu, Zn, Pb, Ag, Sn, Mn, Cr, Ni, Co, Mo). Типы загрязнения представляются обобщенно, с указанными для каждого предприятия преобладающим загрязняющим элементом (чаще всего Cu, Zn, Ni, а на территории «Экранас» – Pb) и кодом среднего загрязнения металлами. Геохимическая структура комплексных аномалий рассматривается по приоритетным загрязняющим элементам – металлам, которые внутри этих зон формируют широкие и контрастные аномалии (чаще всего Cu, Zn, Pb, реже – Ni, Mo, Cr, Sn, Ag).

С этой целью рассчитываются два показателя загрязненных образцов: индекс площади ***Ia*** – процент загрязненных образцов (коэффициент концентрации превышает 2), а также индекс контрастности ***Ic*** – процент недопустимо загрязненных образцов (коэффициент концентрации превышает 16). Аномалия элемента считается широкой (W), если Ia ≥ 75%, средней (M), если 50 ≤ Ia < 75%, малой (S), если 10 ≤ Ia < 50%, и незначительной (*), если Ia < 10%. Аномалия элемента считается контрастной (C), если Ic ≥ 25%, среднеконтрастной (M), если 0 < Ic < 25%, и неконтрастной (*), если Ic = 0%. Пространственный образ структуры частично отражают площади ареалов трех ассоциаций ACu (Cu–Zn–Sn–Ag–Mn), ANi (Ni–Mo–Cr–Co) и APb (Pb), их взаимное расположение, а также преобладающая ассоциация. Эта информация может быть полезна при планировании рекультивации площадей с недопустимым уровнем загрязнения или при выявлении загрязняющих элементов, которые могут представлять наибольшую опасность.