

METAL PROCESSING ENTERPRISES AS THE MAIN THREAT TO ENVIRONMENTAL QUALITY IN PANEVĖŽYS METĀLAPSTRĀDES UZNĒMUMI KĀ GALVENAIS VIDES KVALITĀTES RISKA FAKTORS PANEVĖŽĀ

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Abstract. The purpose of the article was to demonstrate the threat of metal processing to urban environmental quality and to reveal the peculiarities of this kind of pollution. Geochemical data of topsoil mapping in Panevėžys were used for this aim. There has been analysed the input of 16 enterprises involved in this activity to pollution of Panevėžys by Cu, Zn, Pb, Sn, Mo, Ni, Mn, Cr, Ag, Co, as well as Ba, Sr, As, P, U, B, Ga, Ti, V, Zr, Y, Sc. The content of most elements was determined by DC Arc ES in topsoil fraction <1 mm after mineralisation at 450⁰C, while Sr, As, U – by XRF. In many analysed objects W was detected by DC Arc ES, in some of them – also more rare pollutants: Ce, Cd, Sb and elevated content of La and Y (TV-tubes plant “Ekranas”), Bi (Precise mechanics plant). According to total contamination indices these objects were compared among themselves, as well as with enterprises of other type production. Accumulation and good correlation of Cu, Zn, Pb, Sn, Mo, Ni, Mn, Cr, Ag, Co caused many problems in classification of the enterprises. It can be done according to object pollution codes or maximum pollutant.

Introduction

Urban environmental quality can be evaluated according to topsoil total contamination level by dangerous chemical elements. This is usually done during geochemical mapping. The aim of the article was to analyse the input of enterprises involved in metal processing to general urban environmental quality. The geochemical data for comparison and analysis were taken from material of geochemical mapping of Panevėžys [1]. Besides the town territory, 52 objects were analysed in Panevėžys in more detail: water-intake territory – for element local background determination after consecutive elimination of anomalies [2], 6 non-industrial objects – for comprehensive investigation of contamination level danger on their territories and 45 objects involved in industrial activity – for ascertaining of their input as potential pollution sources to general contamination of the city. The latter were conditionally subdivided into 6 groups, the greatest part of them (16 enterprises) was attributed to metal processing, the other 29 enterprises – to transport (10), energetics (2), food (9), light (3), building (5) industries.

Methods

Samples on the territories of the objects were collected more or less evenly from 1*1 m areas of the upper layer of soil (depth 0–10 cm) by the principle of envelope mainly in green planting zones. All samples were air-dried, sieved through nylon sieves taking fraction <1 mm. After organic matter mineralisation at 450⁰ C they were pulverised. Then they were analysed by DC arc emission spectrometry for determination of B, Ga, P, Mn, Ti, V, Cr, Co, Ni, Cu, Zn, Pb, Mo, Ag, Sn, Zr, Y, Sc, Ba content and by XRF – for Sr, As, U (22 elements at all). International reference materials OOKO 153 and OOKO 151 have been used for quality control of spectral analysis results. In some of the samples it was possible to detect W, Cd, Sb, As, Bi by

DC arc ES due to their elevated content. Soil general contamination was evaluated on the basis of total contamination index (Z_s) using the recommended levels [3]. It was calculated by summing up concentration coefficients (CC) of 22 elements, analysed in all Panevėžys (Z22), or only of 10 metals – Cu, Zn, Pb, Sn, Ag, Cr, Ni, Co, Mn, Mo, which were most often polluting (Z10). CC were computed dividing the amount, determined in each sample, by local background values. Median values of CC (CCmed) or total contamination index (Z22med and Z10med) were used for comparison of the objects. Elements with CCmed>1,3 were included to accumulating associations. Distinguishing of element paragenetic associations was based on correlation matrix and sorted factor loading matrix obtained by principal component analysis and rotated by varimax method with the help of corresponding SPSS program. Supposing lognormal distribution of microelements, the logarithms of data recalculated to air-dry material were taken. Surfer software was used for compiling of maps. Geohygienic state was evaluated in comparison with the highest allowable element concentrations in soil HAC_s [4] or average highest allowable level HAL values [5].

Results and discussion

More than 1/3 topsoil samples collected in Panevėžys are unallowably (Z22>16) polluted, most of all on the territories of industrial enterprises, mainly metal processing (Table 1). Besides, in all other types of industries the main part of unallowably polluted samples is of medium, while in metal processing plants – of dangerous level. The greatest part of extremely dangerous pollution level (even 22,3%) and the highest percentage of samples exceeding HACs or HAL for all elements, except V and Mn+V, is also on their territories.

Table 1. Comparison of pollution level and danger in different objects of Panevėžys

Group (number of objects)	Number of samples	Total contamination levels					Per cent of samples exceeding HACs (mg/kg) or HAL (mg/kg)							
		Z22<16	Z22>16	16– 32	32– 128	>128	Cu 50	Cr 50	Ni 40	Zn 160	Pb 32	Mn 1500	Mn+ V 1000 +100	V 150
Whole Panevėžys	2516	68,0	32,0	14,1	12,3	5,6	12,8	16,1	8,0	21,2	41,4	1,5	0,1	0,2
Industrial enterprises	1058	53,7	46,3	14,0	20,4	11,9	26,0	30,0	17,1	29,1	54,9	3,4	0,2	0,5
Town territory	1278	76,3	23,7	15,8	6,9	1,0	3,3	6,5	1,6	17,0	33,6	0,1	0,1	0,0
Non-industrial objects	92	90,2	9,8	4,3	4,3	1,1	4,3	4,3	0,0	8,7	31,5	0,0	0,0	0,0
Water-intake territory	88	97,7	2,3	1,1	1,1	0,0	1,1	2,3	1,1	0,0	2,3	0,0	0,0	0,0
Metal processing (16)	489	34,8	65,2	12,9	30,1	22,3	42,3	45,4	31,1	43,6	64,4	6,3	0,0	0,0
Transport objects (10)	249	63,9	36,1	15,7	15,3	5,2	18,1	13,7	4,8	18,9	58,2	0,8	0,4	0,0
Building industry (5)	98	66,3	33,7	20,4	11,2	2,0	10,2	34,7	5,1	12,2	48,0	0,0	1,0	1,0
Energetics (2)	34	67,6	32,4	17,6	14,7	0,0	5,9	38,2	17,6	26,5	23,5	2,9	0,0	5,9
Light industry (3)	47	70,2	29,8	14,9	12,8	2,1	8,5	17,0	8,5	19,1	68,1	2,1	0,0	0,0
Food industry (9)	141	83,7	16,3	9,2	6,4	0,7	5,0	4,3	1,4	12,8	24,1	0,7	0,0	1,4

Samples with unallowable level of pollution are observed in all 16 enterprises involved in metal processing, in most of them the greatest part of such samples belongs to dangerous level (Table 2). Though total contamination of various objects is different, their main part (even 10) is unallowably polluted ($Z_{22}med > 16$), while in other types of potential pollution sources this limit is exceeded not so often (from 29 objects only in 7, besides, in 3 of them – service station, motor transport enterprise, locomotive depot – metal processing is also sometimes used, while other 3 – plant of furniture, regional heating nets and plant of spirit – are situated near metal processing plants and might have been affected by their pollution). This shows that the leading role in unallowable pollution level in Panevėžys belongs to enterprises involved in metal processing. The territories of the analysed objects are of different area, therefore the number of taken samples was unequal. The type of production is also various, therefore different metal processing methods are used. The allowable level of contamination is usually exceeded in those plants, where metal casting (C), galvanic processing (G) or electrical engineering (E) is used besides mechanical processing (M), the only exceptions are Plk and Pds. The highest Z22 is observed in Ptm1, where even three methods of metal processing are used (type GME). Metal processing enterprises are situated in 4 industrial districts of the city: western (W), eastern (E), southern (S) and central (C), most of them in W (5), E(6) and S (4). The greatest number of unallowably polluted enterprises is observed in W (4) and E (4) districts.

Table 2. Description and contamination level of metal processing plants in Panevėžys

Dist -rikt	Code	Title	N	Type	Production	Z22	Z10	Z10 per cent of Z22	Per cent of samples where Z22 is:			
									>16	16-32	32- 128	
W	Ptm1	"Tiksloji me- chanika" (I site)	34	GME	Electronic devices	314,42	311,90	99,2	94,1	5,9	17,6	
W	Plk	"Lietkabelis"	26	M	Cables	122,30	120,26	98,3	96,2	19,2	30,8	
E	Pme	"Metalistas"	27	GM	Locks	114,67	111,19	97,0	81,5	11,1	25,9	
E	Pek	"Ekranas"	91	ME	TV-tubes, crystal	71,66	50,47	70,4	92,3	13,2		31,9
W	Pau2	"Aurida" (II site)	46	CM	Autocompressors	53,15	50,15	94,4	78,3	13,0		13,0
S	Pr	"Praktika"	26	CM	Portative boring machine-tools	46,07	42,83	93,0	69,2	3,8		11,5
E	Pds	Gas-main construction	5	M	Bituminisation of pipes	31,38	28,85	91,9	60,0	20,0		0,0
E	Pket	"Panevėžio ketus"	17	CM	Cast iron production	29,73	27,00	90,8	82,4		17,6	29,4
W	Pau1	"Aurida" (I site)	25	CM	Autocompressors	26,15	22,82	87,3	80,0	32,0		12,0
S	Akl	Blind society plant	40	GM	Consumer goods	16,07	13,56	84,4	50,0	12,5		17,5
C	Pel	"Elektro- technika"	11	ME	Desk lamps	15,62	12,73	81,5	45,5	0,0		18,2
E	Pav	Aviation repair plant	25	GM	Aircraft repair	13,89	11,68	84,1	44,0			4,0
S	Pre	"Remeksta"	26	M	Domestic applian- ces repair	10,23	7,86	76,8	30,8			0,0
E	Arem	Automobile repair enterprise	29	M	Automobile repair	9,29	5,63	60,6	27,6	6,9		3,4
S	Pk	Deaf society plant	27	CM	Consumer goods	9,22	5,92	64,2	18,5	3,7	3,7	
W	Ptm2	"Tiksloji me- chanika" (II site)	34	M	Precise mecha- nical devices	8,72	5,03	57,7	23,5	5,9		2,9

The accumulating associations of unallowably contaminated plants usually include the following 10 metals, which are typical to alloys: Cu, Zn, Pb, Sn, Mo, Ni, Mn, Cr, Ag, Co, only the last 4 elements (especially Co) are sometimes absent (Table 3). Therefore in unallowably contaminated enterprises the input of Z10 (calculated according to these 10 metals) to Z22 exceeds 80% (Table 2). In less contaminated enterprises more of these 10 metals may be absent in accumulating associations. However, correlation among them is usually significant, some separation of Pb may be explained by transport activity, of Mn, Co – by lower pollution level (Table 4). The other reasons of insignificant correlation among some elements or their groups may be different shops, large territory, short time of functioning or end of industrial activity. Besides the above mentioned 10 metals, some other elements, mainly As, Sr, Ba, P, V, B may belong to accumulating associations, the last 3 elements – usually in plants with metal casting (Table 3). In most of these plants (especially with casting) W and Cd are detected. Sometimes CCmed>1,3 even for Y, U, Sc and Zr (Y and U in “Ekranas” are undoubtedly due to contamination caused by production and polishing of special glass). Plants of G or E types usually have the most multielement accumulating associations, the second type is also characterised by the greatest number of additional elements: La, Ce, Sb, Hf (“Ekranas”), Bi (Ptm1). Therefore total Zs including the additional elements for “Ekranas” is the largest in Panevėžys. Be and Ge are very rare (Ge is found where Ni is the main contaminant).

Table 3. Comparison of accumulating rows (CCmed) of metal processing plants in Panevėžys

E	Pme	E	Pket	E	Pav	E	Pek	E	Pds	S	Pre	E	Arem	S	Akl	C	Pel
Zn	24,74	Zn	7,97	Zn	3,13	Pb	34,41	Pb	7,61	Pb	2,22	Pb	2,59	Ni	4,84	Ni	2,92
Ni	18,21	Pb	6,92	Pb	2,81	Sr	6,54	Ag	3,88	Cu	1,96	Ni	1,92	Cu	2,50	Pb	2,28
Cu	15,90	Ni	4,10	Ag	1,87	Ba	5,18	Zn	2,58	Zn	1,77	Zn	1,78	Zn	2,41	Cu	2,25
Cr	13,31	Cu	3,81	Sn	1,84	Zn	4,82	Cu	2,31	Ba	1,75	Ba	1,65	Pb	2,01	Zn	2,22
Mo	8,15	Mo	3,40	Cu	1,71	Ni	2,26	Sr	2,02	Ni	1,62	Cr	1,59	Cr	1,60	Ag	1,95
Pb	5,07	Ag	2,79	P	1,56	Cu	2,18	Ni	1,92	Mn	1,56	Sn	1,48	Mo	1,53	Sn	1,87
Ag	3,59	Cr	2,20	Mo	1,45	Mo	1,75	Sn	1,83	Cr	1,30	Cu	1,36	Sn	1,42	Cr	1,76
Sn	2,51	Sn	2,01	U	1,44	Y	1,72	Mo	1,61			Sr	1,32	Zr	1,41	Mo	1,50
As	1,80	Mn	1,72	Mn	1,38	Sn	1,57	Cr	1,31	Z22	10,23	Co	1,30			Ba	1,42
Mn	1,69	V	1,58	GM		Ag	1,53	M		Be4		M		Z22	16,07	Sc	1,41
Sc	1,38	P	1,52	Z22	13,89	Cr	1,46	Z22	31,38			Z22	9,29	W3Ge		Mn	1,36
Zr	1,37	Co	1,32	GMV3		U	1,46					W3Cr					
Ba	1,34	GM				Mn	1,41									Z22	15,62
Co	1,32	Z22	29,73			As	1,38										
GM				W4Ce3Bi2				GM				VIE					
Z22	114,67							Z22	71,66								
W15Cd5								W9Sb89				Cd71 Ce46 W32 H2					
W	Ptm1	W	Plk	W	Pau2	S	Pr	W	Paul	W	Ptm2	S	Pk				
Cu	169,67	Cu	77,74	Cu	14,37	Cu	9,81	Cu	7,50	Cu	1,74	P	1,66				
Ni	23,39	Zn	8,14	Zn	10,44	Zn	8,43	Sn	4,63	Ni	1,72	Sn	1,63				
Sn	20,22	Sn	4,76	Mo	4,44	Ni	4,81	Mo	4,08	Sn	1,59	Mo	1,57				
Zn	11,20	Pb	4,72	Mn	4,34	Mo	4,44	Pb	3,68	Ba	1,45	Pb	1,55				
Cr	9,49	Mo	3,07	Sn	3,90	Sn	3,60	Cr	2,75	Cr	1,43	Cu	1,54				
Pb	8,26	Ag	2,66	Cr	3,85	Pb	2,89	Zn	2,65	Sr	1,41	B	1,46				
Mo	6,98	Ni	2,11	Pb	3,27	Cr	2,67	Ag	2,42	Sc	1,32	Mn	1,34				
Co	3,72	Sr	1,42	Ni	3,16	Mn	1,80	Ni	2,35	As	1,30	GM					
Ag	2,78	Mn	1,41	Ag	1,78	Ag	1,59	P	2,34			Z22	9,22				
Mn	1,83	Ba	1,40	P	1,60	P	1,56	Co	1,45	Z22	8,72	W3Cd2					
Ba	1,58	As	1,32	GM		As	1,49	Mn	1,43	W4Ca							
As	1,57	M		Z22	53,15	Co	1,45	Sr	1,31								
Sr	1,37	Z22	122,30	W16Cd2		GM		GM									
GM				GM				Z22 46,07				Z22 26,15					
Z22	314,42							W19Cd2				W22					
W23Bi6Cd12																	

Notes: above the row is the district and code of the enterprise, below – the type, Z22 and additional detected elements with number of samples, in which they have been found.

According to main polluting element metal processing plants (except Pk) can be subdivided into 4 groups: Cu-type (most of the plants, including all from W district), Zn-type (all from E district), Pb-type (E and S districts) Ni-type (S and C districts). Some of the elements (usually from 10 typical metals) even alone exceed the allowable level of pollution. Codes of unallowable contamination are additional characteristic of the enterprise (Table 5). Object average pollution codes (OAP-codes) can be used besides them. They are determined according to ranking of average values of CC for members of 3 associations in each enterprise (usually the same codes are in anomalous part of the enterprise). These associations are determined with the help of cluster analysis. 10 metals on the basis of correlation of their content in all 16 objects can be subdivided into 3 associations Cu–Sn–Zn–Ag–Mn (ACu), Ni–Cr–Mo–Co (ANi) and Pb (APb), while 12 main pollutants of Panevėžys – into similar groups: Cu–Sn–Zn–Ag (ACu), Ni–Cr–Mo–Co–Mn (ANi) and Pb–Sr–Ba (APb). Full information about metal processing plants can be useful for decision making (Fig.1).

Table 4. Analysis of correlation among 10 characteristic elements in metal processing plants

Code	Territory	Type	Number of factor in factor loading matrix										Not significant correlation	Explanation	
			Cu	Zn	Pb	Sn	Ag	Mo	Ni	Cr	Co	Mn			
Ptm1	S	GME	1	1	1	1	1	1	1	1	1	1	1	–	–
Plk	M	M	1	1	1	1	1	1	1	1	5	1	Co	LPL	
Pme	S	GM	1	1	1	1	1	3	1	1	3	1	Mo, Co	DS	
Pek	L	ME	1	1	2(1)	1	1	1	1	1	1	1	–	LT, DS	
Pau2	L	CM	1	1	1	1	1	1	1	1	1	1	Co	LT, LPL	
Pr	S	CM	1	3(1)	5	1	4	1	1	1	1	1	Pb, Ag	TA (bus depot)	
Pds	S	M	Small sample size										Prevails	Small sample size	
Pket	M	CM	1	1	4	1	1	1	1	1	1	1	2 gr.	TA (railway)	
Paul	M	CM	1	1	1	1	1	1	1	1	1	1	Pb	TA	
Akl	S	GM	1	1	1	1	1	1	1	1	1	1	–	–	
Pel	S	ME	1	1	1	1	1	1	1	1	1	1	–	–	
Pav	L	GM	1	1	1	1	1	1	2	6(1)	2	2	Mn, Co, Ni	LT, EF, LPL	
Pre	M	M	1	1	3	1	3	1	1	1	1	1	Pb	TA	
Arem	M	M	1	1	1	1	3(1)	1	1	1	2	2(1)	Mn, Co	LPL	
Pk	S	CM	1	1	1	1	1	1	1	1	1	1	Pb	TA	
Ptm2	L	M	3	2	2	5	3	3	2(3)	3(2)	2	2(3)	Cu, Mo, Sn, Ag	LT, DS, LPL, ST	

Explanation: TA – transport activity, LT – large territory, LPL – low pollution level, DS – different shops, ST – short time of exploitation, EF – end of functioning, 2 gr. – two groups, the elements of which are most often not significantly correlated. Territory: S – small, M – medium, L – large.

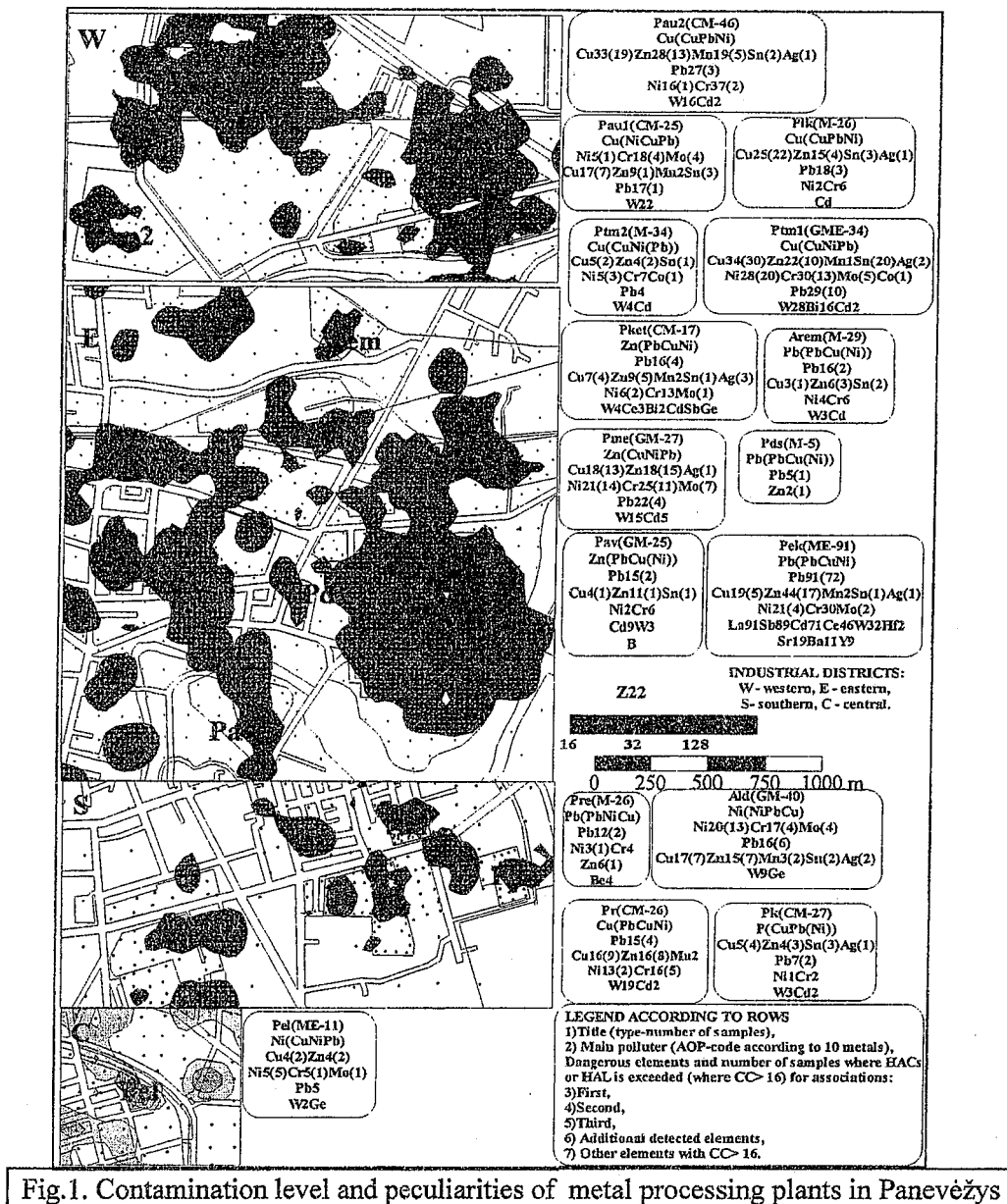


Fig.1. Contamination level and peculiarities of metal processing plants in Panevėžys

Table 5. Comparative analysis of metal processing plants of Panevėžys

Code	Type	Average CC of asso-ciation in plant			Average CC of asso-ciation in anomaly			Main pollutant	OAP-codes		Unallowable level pollutants:	
		ACu	APb	ANi	Acu	Apb	ANi		10 metals	12 elements	Number	Code (element and CC>16 sample number)
Ptm1	GME	71,85	13,45	14,33	76,16	14,16	15,14	Cu	CuNiPb	CuNiPb	9	Cu30NiSn20Cr13Pb10 Zn10Mo5Ag2Co
Pme	GM	25,70	10,90	16,18	31,21	12,89	19,39	Zn	CuNiPb	CuNiPb	7	Zn15Ni14Cu13Cr11 Mo7Pb4Ag
Pel	ME	10,45	3,78	9,26	21,04	5,93	18,41	Ni	CuNiPb	CuNiPb	5	Ni5CuZn2CrMo
Ptm2	M	2,61	1,41	2,64	6,87	2,47	6,62	Cu	CuNi(Pb)	CuNi(Pb)	5	Ni3CuZn2SnCo
Plk	M	41,95	8,14	2,20	43,55	8,42	2,23	Cu	CuPbNi	CuPbNi	5	Cu22Zn4PbSn3Ag
Pau2	CM	15,68	5,36	3,95	19,61	6,48	4,62	Cu	CuPbNi	CuNiPb	8	Cu19Zn13Mn5Pb3 SnCr2NiAg
Pk	CM	11,30	4,61	1,46	55,02	15,82	3,02	P	CuPb(Ni)	CuPb(Ni)	5	Cu4ZnSn3Pb2Ag
Pket	CM	8,02	135,59	4,54	9,37	164,04	5,16	Zn	PbCuNi	PbCuNi	7	Zn5PbCu4MoAg3 Ni2Sn
Pek	ME	4,42	66,47	2,61	4,68	71,57	2,73	Pb	PbCuNi	PbCuNi	10	Pb72Sr19Zn17Ba11Y9 Cu5Ni4Mo2SnAg
Pr	CM	9,36	12,18	4,93	12,86	16,84	6,50	Pb	PbCuNi	CuPbNi	5	Cu9Zn8Cr5Pb4Ni2
Pds	M	3,04	9,12	1,47	4,37	11,74	1,70	Pb	PbCu(Ni)	PbCu(Ni)	2	PbZn
Arem	M	6,18	8,43	1,97	19,04	24,78	3,50	Pb	PbCu(Ni)	CuPbNi	4	Zn3PbSn2Cu
Pav	GM	4,07	7,43	1,65	7,02	14,02	2,19	Zn	PbCu(Ni)	PbCu(Ni)	5	Pb2CuZnSnB
Pre	M	2,12	4,64	2,01	3,51	10,19	3,63	Pb	PbNiCu	PbCuNi	3	Pb2ZnNi
Akl	GM	7,72	12,11	12,47	14,30	22,78	23,74	Ni	NiPbCu	NiCuPb	9	Ni13CuZn7Pb6CrMo4 SnAgMn2
Pau1	CM	6,77	4,69	9,33	8,06	5,37	11,26	Cu	NiCuPb	CuNiPb	7	Cu7CrMo4Sn3PbZnNi

Conclusions

According to topsoil geochemical investigation data the main threat to environmental quality in Panevėžys among different type industry is caused by metal processing enterprises, which form the most contrastic anomalies. Most heavily polluted are western and eastern industrial districts. Their main and usually well correlated pollutants are 10 metals: Cu, Zn, Pb, Sn, Mo, Ni, Mn, Cr, Ag, Co, often detected are also W and Cd. The type of pollution of these enterprises is similar. The differences can be found according to additional pollutants, main pollutant or various object pollution codes. Such information may be useful for decision making, preparation of remediation plans of extremely heavily polluted territories.

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