CHEMICAL COMPOSITION OF TILE GLAZE AS POTENTIAL SOURCE OF SOIL CONTAMINATION

GLAZĒTO FLĪŽU ĶĪMISKAIS SASTĀVS KĀ POTENCIĀLAIS GRUNTS PIESĀRŅOJUMA AVOTS

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Abstract. *The paper deals with the chemical composition of coloured glaze of 16 tiles from restored furnace of Biržai castle. It demonstrates that glaze is enriched with different elements compared to soil and therefore can be one of the multiple contamination sources of soil, especially in the old urban quarters. High variability of element contents in glaze is predetermined by its colour. However, Bi, Sb, Ag, Pb, Sn, Cu are elements-indicators of coloured glaze chemical composition. 1 g of coloured glaze added to 1 kg of soil causes at least medium level of local contamination.*

Keywords: *colour, contamination indices, glazed tiles, heavy metals, historical quarters, urban soil*

Introduction

Intensive anomalies of heavy metals and (or) other toxic chemical elements are often found in the old urban quarters, e.g. in Senamiestis and Naujamiestis districts of Vilnius [1]. Some anomalies there can be explained by historical development, when the old constructions are ruined and their debris becomes soil constituent. The breakage of coloured glazed ceramics is a frequent ingredient of old cultural layers. The aim of research was to determine the elements-indicators of the coloured glaze of tiles and to find out if coloured glaze can be the source of local anomalies of heavy metals and other toxic chemical elements in urban soil.

Materials and methods

The analytical results of glaze of 16 tiles from restored furnace of Biržai castle were used for evaluation. There were 10 different colours of glaze: sky blue (2 samples), white (3 samples), black (4 samples), blue, turquoise, green, yellow, brown, purple and colourless (1 sample of each). AES analysis was done in laboratory the Institute of Geology and Geography (Lithuania). The real total contents of the following elements were determined: Ag, As, B, Ba, Bi, Co, Cr, Cu, Ga, Mn, Mo, Ni, P, Pb, Sb, Sn, Ti, V, Y, Zn, Zr, and W. Quality control of laboratory is assured by its participation (since 1997) in "International Soil-analytical exchange" program organised by WEPAL. For evaluation of the relative enrichment of chemical elements in glaze compared to soil, the coefficients of concentration (Kk) were calculated. Their values for most elements were computed in comparison with Lithuanian soil background values [2], except for Sb, Bi and W, the soil background values of which (1 mg/kg, 0.2 mg/kg and 1.7 mg/kg, respectively) were based on investigations in other countries. Mean values of Kk were calculated for sky blue, white and black glaze in order to compare with glaze of other colours. Only 13 elements, i.e. Ag, As, Bi, Co, Cu, Mn, Mo, Ni, Pb, Sb, Sn, Zn, W were chosen for characterization of glaze, because their Kk (or mean Kk) were higher than 10 in at least one glaze colour. For each colour the elements were subdivided into groups according to the following intervals of Kk (or mean Kk): I ($Kk \geq 10000$); II ($10000 > Kk \geq 1000$); III ($1000 > Kk \geq 100$); IV ($100 > Kk \geq 10$). In each group the elements were listed according to descending values of their Kk (As and W were mentioned only when their content was above the detection limit). Also additive accumulation indices Za were calculated for each colour by summing up Kk of 11 elements (except for As, W). For each of these elements and each glaze colour the mass of this glaze added to 1 kg of soil and resulting in the element content in contaminated soil higher than maximum permitted concentration (MPC) was calculated. Possible contamination level of 1 kg of soil by 1 g of each glaze colour was also estimated according to the same 11 elements.

Results and discussion

According to Za the glaze of different colour can be arranged in the following way: blue > purple > white > yellow > brown > black > sky blue > turquoise > colourless > green (Fig. 1).

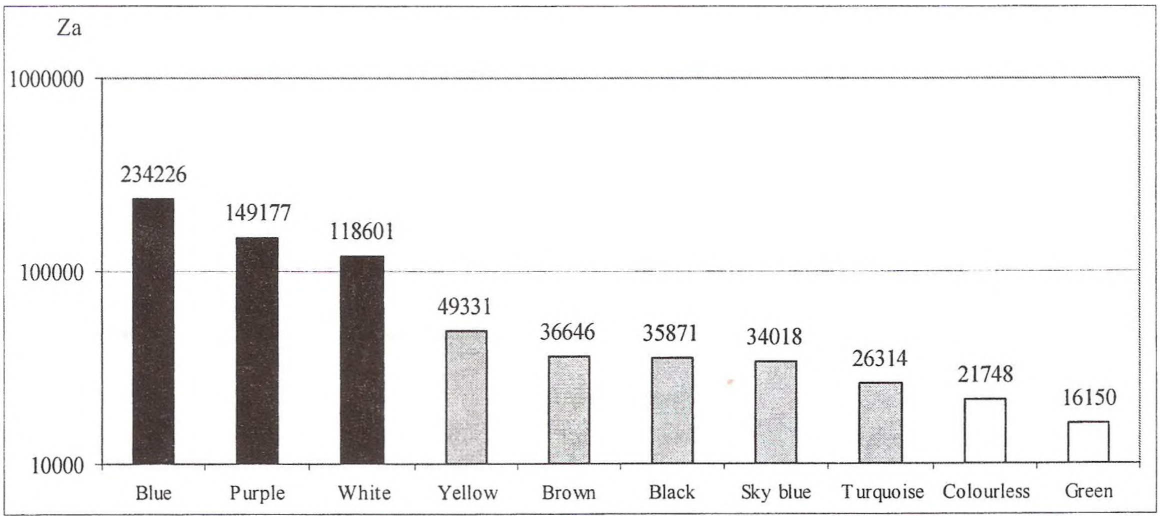

Fig.1. **Average additive accumulation indices (Za) of various colour glaze**

Enrichment in Bi, Sb, Ag, Pb, Sn, Cu is observed in glaze of all colours (Table 1). Therefore these 6 elements are indicators of glaze. Arsenic is also found in almost all glazes, except for colourless, green and brown. Besides, some colours are characterised by specific elements: blue glaze by Co(Kk=20380), Ni(327), Mo(149), purple by W(441), Mn(64) and Zn(12), brown by W(403), Mn(110), Co(31), Zn(19), black by W(155) and Mn(110).

Table 1.

Distribution of elements among groups in glaze of different colour

Glaze	I (Kk≥10000)	II (10000>Kk>1000)	III (1000>Kk>100)	IV (100>Kk>10).
Blue	Bi>Co>Pb	Ag>Sn>Sb>*As*	Cu>Ni>Mo	–
Purple	Bi>Sn	Pb	Ag>Sb>W>*As*>Cu	Mn>Zn
White	Bi, Sn, Ag	Pb	Sb, *As*	Cu
Yellow	Sb, Pb	Sn	Ag, Bi, *As*	Cu
Brown	Pb, Ag	Bi	Sb, W, Sn, Mn	Co, Cu, Zn
Black	Bi	Pb, Ag, Cu, Sb	Sn, W, *As*, Mn	–
Sky blue	Sn, Pb	Sb, Ag	Bi, Cu, *As*	–
Turquoise	Sn	Pb, Cu, Ag, Bi	Sb, *As*	–
Colourlessc	Pb	Ag	Sb, Sn	Bi, Cu
Green	–	Pb, Ag, Cu, Bi	Sb	Sn

The group of coloured glaze with Za>100000 is predetermined by the highest enrichment (Kk>50000) in Bi, followed by Sn, Pb (Kk>5000) (Fig. 2), the group with Za from 25000 to 50000 is – by high enrichment (Kk>5000) in Pb in different combinations with Sb, Sn, Bi, Ag depending on the colour (Fig. 3) and the group with Za<25000 – by the highest accumulation (Kk>5000) of Pb and Ag, for green colour also with high Kk (>1000) of Cu and Bi (Fig. 4).

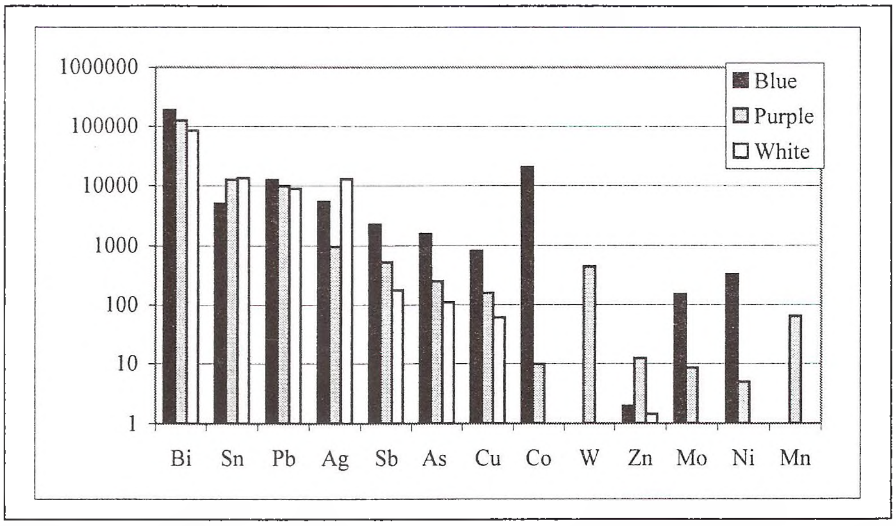

Fig.2. **Enrichment of elements in coloured glaze group with highest (>100000) Za**

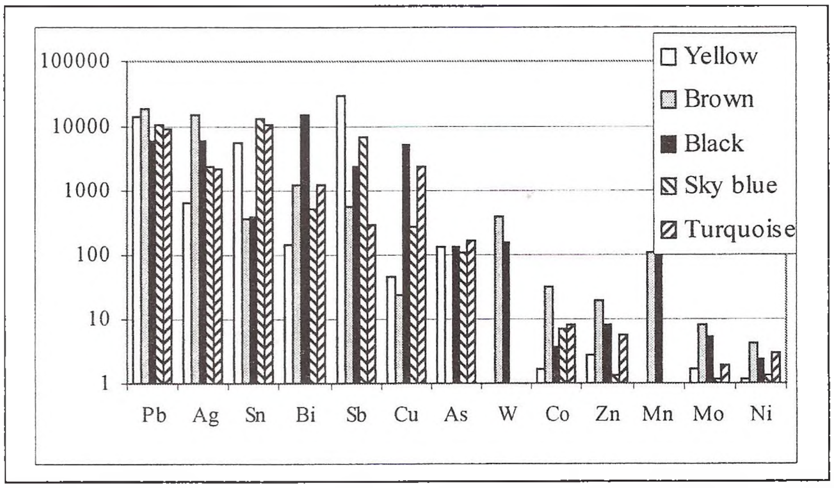

Fig.3. **Enrichment of elements in coloured glaze group with medium (25000-50000) Za**

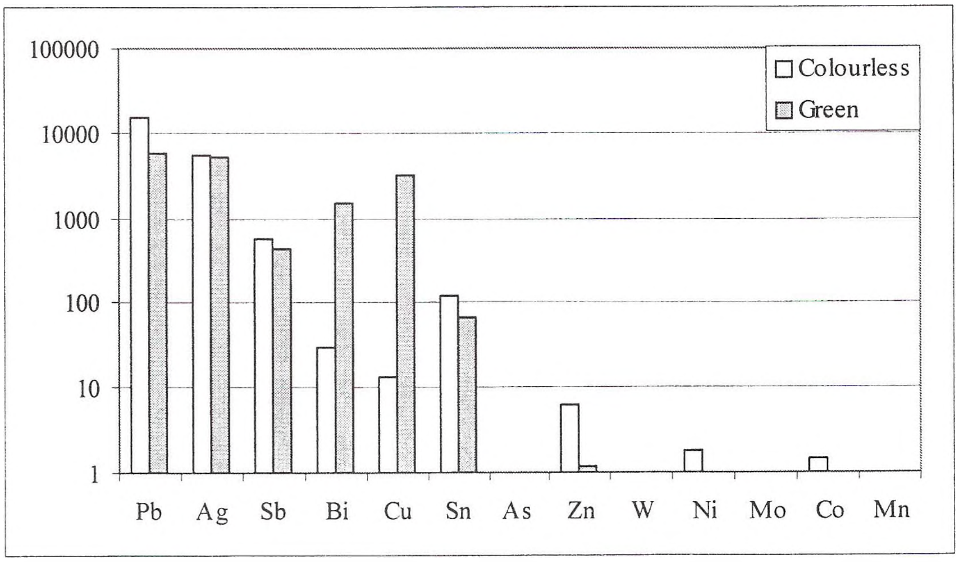

Fig.4. **Enrichment of elements in coloured glaze group with lowest (<25000) Za**

There is distinct grouping of white and black graze samples, but not sky blue samples according to 6 elements-indicators (Fig. 5). Also the group of the colours with the highest enrichment in 11 elements (blue, purple and white glaze) is well separated from other colours.

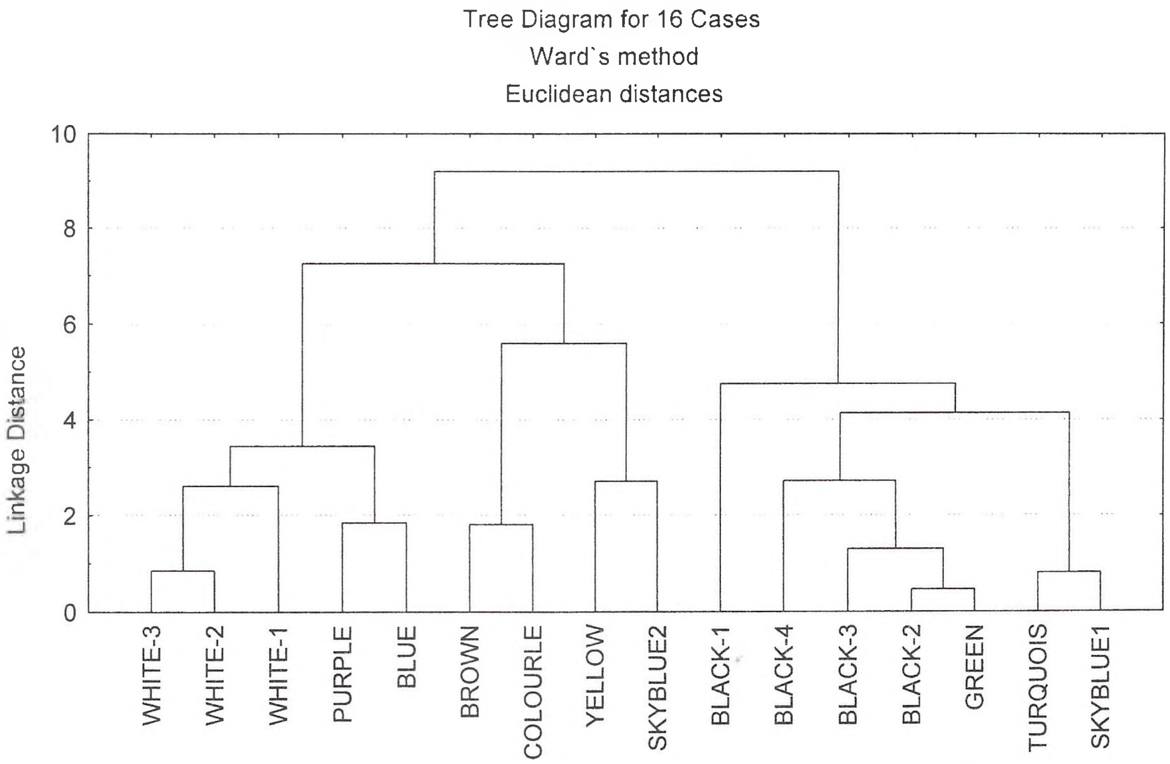

Fig.5. **Cluster analysis results of glazes according to enrichment of Bi, Sb, Ag, Pb, Sn, Cu**
Explanation: “turquois” – turquoise, “skyblue” – sky blue, “colourle” – colourless, the colour is followed by the number.

For most of the above-mentioned 11 elements (except for Mn), the median concentration coefficients in all analysed glazes are higher than 1, indicating enrichment of glaze in these elements (Fig. 6). Six elements-indicators of glaze (Pb>Sn>Ag>Bi>Sb>Cu) have much higher median enrichment compared Zn, Co, Ni and Mo.

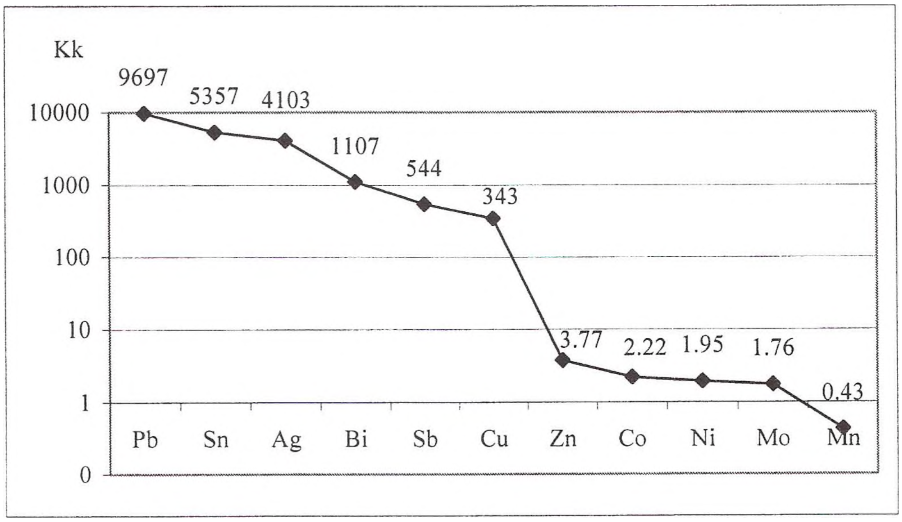

Fig.6. **Median enrichment of elements in all investigated glaze**

Two indices are used in Lithuania for evaluation of soil quality in residential districts: *coefficient of danger* K_0 and *total (additive) contamination index* Zd [3]. The first one is calculated as a ratio of element content in soil to maximum permitted concentrations (MPC) in soil. The index Zd depends on the number of contaminants and sum of their concentration coefficients, which are calculated by dividing the element concentration in soil by its background value. Investigations in Russia [4] and later in Vilnius [5] have shown that Zd index is related to sick children rate. The same four categories of danger can be determined according to each index: allowable (A), medium dangerous (MD), dangerous (D) and extremely dangerous (ED). Soil quality is estimated by choosing the more dangerous category from two different categories (according to K_0 and according to Zd). Medium dangerous, dangerous or extremely dangerous categories of soil contamination will be called hazardous contamination.

To show the possibility of the above-mentioned 11 elements to form anomalies in urban soil contaminated with breakage of glazed tile, the following estimation has been done. For each element and each glaze colour the minimum mass of glaze, the addition of which to 1 kg of soil results in element soil content higher than its MPC, was calculated (Table 2). When element content exceeds MPC, soil contamination is hazardous. While Bi has no MPC, the limit of its 16 background values was chosen instead of MPC. This is because when the concentration coefficient of an element exceeds 16, the element alone causes hazardous soil contamination. The limit of 16 background values was chosen also for W, as it has no defined MPC values. The following classification of masses was chosen: <1 g extremely low mass, 1-10 g – low mass, 10–100 g – medium mass, 100–500 g – high mass, >500 g – not realistic mass.

It is obvious that the elements-indicators of glaze pollution (Pb, Sn, Ag, Bi, Sb and Cu) can create hazardous soil contamination. Very low mass of whatever glaze colour added to 1 kg of soil creates hazardous soil contamination by Pb (Table 2). Hazardous soil contamination by Sn can be created by very low mass of most glaze colours (except for brown, black, colourless and green) or medium mass of whatever glaze colour. Hazardous soil contamination by Ag can be formed by low mass of most glaze colours (except for yellow, purple, sky blue and turquoise) or medium mass of whatever glaze colour. Hazardous soil contamination by Bi can appear due to very low mass of blue, purple, white or black glaze, medium mass of most glaze colours (except for yellow and colourless) or high mass of yellow glaze. Hazardous soil contamination by Bi from colourless glaze is not realistic. Hazardous soil contamination by Sb can be caused by very low mass of yellow glaze, low mass of blue, black or sky blue glaze or medium mass of whatever glaze colour. Hazardous soil contamination by Cu can be caused by low mass of black, turquoise or green glaze, medium mass of blue, purple or sky blue glaze or high mass of white or yellow glaze. Hazardous soil contamination by Cu from brown and colourless glaze is not realistic.

Hazardous soil contamination by other 5 elements (Zn, Co, Ni, Mo and Mn) is either not realistic at all (Zn) or can be formed only by some colours of glaze (Co – by very low mass of blue glaze or high mass of brown glaze, Ni and Mo – by medium mass of blue glaze, Mn – by medium mass of purple, brown or black glaze).

Some glaze colours are enriched with As or W. Medium mass of purple or brown glaze will result in hazardous soil contamination by W. Low mass of blue, medium mass of purple, yellow, sky blue or turquoise glaze result in hazardous soil contamination by As.

While each colour of glaze is enriched with many elements, even very low mass of glaze can create hazardous soil contamination. The theoretical contamination levels were calculated for 1 kg of soil contaminated by 1 g of different colour glaze (Table 3). It is obvious that even very small mass (1 g) of each glaze colour creates at least medium dangerous category of contamination. This is because in all cases at least one element (Pb) exceeds its MPC. The MPC values of Sn are also often exceeded, in blue glaze – of Co and in yellow glaze – of Sb. The categories of soil contamination due to exceeding MPC values are usually medium dangerous (except for Co in blue glaze and Pb in brown glaze, which cause dangerous category of soil contamination). The final category of soil contamination is predetermined by Zd index, which ranges from 17 for green glaze to 235 for blue glaze. Blue or purple glaze causes extremely dangerous category of soil contamination, white, yellow, brown, black or sky blue – dangerous and turquoise, colourless or green – medium dangerous. All this proves that chemical composition of tile glaze is potential source of soil contamination.

Table 2.

Estimation of the mass of different colour glaze to be added to 1 kg of soil for creating hazardous soil contamination

	Pb	Sn	Ag	Bi	Sb	Cu	Zn	Co	Ni	Mo	Mn
Soil background (mg/kg)	15.1	2	0.065	0.2	1	8.9	28.1	4.6	12.6	0.67	390
Soil MPC (mg/kg)	100	10	2		10	100	300	30	75	5	1500
16 background values (mg/kg)	242	32	1	3	16	142	450	74	202	11	6240
	Element content (mg/kg) in glaze										
Glaze colour	**Pb**	**Sn**	**Ag**	**Bi**	**Sb**	**Cu**	**Zn**	**Co**	**Ni**	**Mo**	**Mn**
Blue	187500	10000	350	37500	2250	7250	55	93750	4125	100	213
Purple	150000	25000	63	25000	525	1400	350	45.0	62.5	5.8	25000
White	133333	26667	833	16675	177	540	40	2.2	8.5	0.5	93
Yellow	214286	11429	43	29	28571	400	74	7.4	14.3	1.1	34
Brown	285714	714	1000	243	571	214	543	142.9	52.9	5.4	42857
Black	93533	803	384	3149	2377	45580	219	17.2	30.1	3.4	42763
Sky blue	162500	26667	150	106	6797	2457	37	32.7	17.1	0.8	94
Turquoise	142857	21429	143	243	300	21429	157	37.1	37.1	1.3	271
Colourless	235294	235	353	6	565	118	176	6.8	22.4	0.6	71
Green	88889	133	333	300	444	27778	33	1.4	10.4	0.6	89
Mass of glaze (grams) to be added to 1 kg of soil in order to exceed soil MPC or limit value											
Glaze colour	**Pb**	**Sn**	**Ag**	**Bi**	**Sb**	**Cu**	**Zn**	**Co**	**Ni**	**Mo**	**Mn**
Blue	0.45	0.80	5.56	0.1	4.02	12.7		0.27	15.4	45.6	
Purple	0.57	0.32	32.0	0.1	17.5	70.1	**5438**	**1693**		**5773**	47.2
White	0.64	0.30	2.33	0.2	54.0	207					
Yellow	0.40	0.70	47.4	118	0.32	304					
Brown	0.30	11.4	1.94	12.5	16.0	**797**	**1120**	225		**10103**	26.8
Black	0.91	10.1	5.07	1.0	3.80	2.00					26.9
Sky blue	0.52	0.30	13.1	29.1	1.33	38.7		**9525**			
Turquoise	0.59	0.37	13.7	12.5	31.0	4.27		**3556**			
Colourless	0.36	35.5	5.51	**1118**	16.2	**5162**					
Green	0.96	64.9	5.84	10.1	20.7	3.29					

Explanation: not realistic mass of glaze, which is necessary to add to 1 kg of soil for creating its hazardous contamination is indicated in bold. As Bi has no defined MPC values, the value equal to its 16 background values was used as a limit value for determination of hazardous soil contamination.

Of course the mobility of contaminants in glaze should be studied. It is only known that elements in overglaze-decoration are mobile, because acid leaching 24-h tests with 4% acetic acid applied to overglaze-decorated porcelain dinnerware manufactured in European and Asian countries before the mid-1970s showed that half of the samples released lead in concentrations exceeding the US allowable maximum of 3.0 μg/ml and that there were dishes, which released Cd, Zn, Co, Cu and Cr [6].

Table 3.

Estimation of soil contamination level, when 1 g of glaze is added to 1 kg of soil

Colour	Element Kk in contaminated soil											Zd	Contamination categories according to		
	Pb	Sn	Ag	Bi	Sb	Cu	Zn	Co	Ni	Mo	Mn		Zd	K_0	Both
Blue	13.4	6.0	6.4	188	3.2	1.8	1.0	21.4	1.3	1.1	1.0	235	ED	D(Co),MD(Pb, Sn)	ED
Purple	10.9	13.5	2.0	126	1.5	1.2	1.0	1.0	1.0	1.0	1.1	150	ED	MD(Pb,Sn)	ED
White	9.8	14.3	13.8	84.3	1.2	1.1	1.0	1.0	1.0	1.0	1.0	119	D	MD(Pb,Sn)	D
Yellow	15.2	6.7	1.7	1.1	29.5	1.0	1.0	1.0	1.0	1.0	1.0	50	D	MD(Pb,Sn, Sb)	D
Brown	19.9	1.4	16.4	2.2	1.6	1.0	1.0	1.0	1.0	1.0	1.1	38	D	D(Pb)	D
Black	7.2	1.4	6.9	16.7	3.4	6.1	1.0	1.0	1.0	1.0	1.1	37	D	MD(Pb)	D
Sky blue	11.7	14.3	3.3	1.5	7.8	1.3	1.0	1.0	1.0	1.0	1.0	35	D	MD(Pb,Sn)	D
Turquoise	10.5	11.7	3.2	2.2	1.3	3.4	1.0	1.0	1.0	1.0	1.0	27	MD	MD(Pb,Sn)	MD
Colourless	16.6	1.1	6.4	1.0	1.6	1.0	1.0	1.0	1.0	1.0	1.0	23	MD	MD(Pb)	MD
Green	6.9	1.1	6.1	2.5	1.4	4.1	1.0	1.0	1.0	1.0	1.0	17	MD	MD(Pb)	MD

Possible categories of danger according to K_0: A – allowable ($K_0 \leq 1$), MD – medium dangerous ($1 < K_0 \leq 3$), D – dangerous ($3 < K_0 \leq 10$), ED – extremely dangerous ($K_0 > 10$). Possible categories of danger according to Zd: A – allowable (Zd<16), MD – medium dangerous (16<Zd≤32), D – dangerous (32<Zd≤128), ED – extremely dangerous (Zd>128).

Conclusion

The elements with the highest median accumulation in the coloured glaze of tiles compared to soil background are Pb>Sn>Ag>Bi>Sb>Cu. They are indicators of chemical composition of all colours of glaze. High enrichment of glaze in As is also usual. The contents of the elements in glaze are related to their colour, so high enrichment in Co, W, Ni, Mn, Mo, Zn is characteristic of some colours. Different glaze colours can cause unequal level of soil contamination. For some elements (especially Pb and Sn, in some of glaze colours also Bi, Sb, Co), even 1 g of glaze added to 1 kg of soil can create hazardous soil contamination by this element. While each colour of glaze is enriched with many elements, this mass of glaze always creates hazardous soil contamination. So it is obvious that glazed tile breakage can form local heavy metal anomalies in urban soil. Such anomalies can also be found in the sites of manufacturing of ceramics. For explanation of anthropogenic anomalies in soil it is recommended to take interest in urban history. It is not recommended to bury the breakage of glazed multicolor ceramics in the ground of the garden, especially if it is used for vegetable-growing, horticulture or other agrarian purposes.

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