1. Introduction

The content of trace elements in natural soils depends on many parameters, including fine granulometric fraction, organic matter, oxides and hydroxides (mainly Fe, Mn and Al) [1]. This means that in natural soil, trace elements are closely related to such major elements as Fe, Mn and Al. Of course, this relationship is largely determined by soil clay content on which many major and trace elements depend. For instance, geochemical investigations of natural soil in Lithuania [2] and Poland [3] have shown that the content of most trace elements increases as soil texture becomes more enriched in clay fraction, in Poland also the content of the major element Fe also increases. Aluminium is especially enriched in clay minerals and is often used as a proxy for grain size [4]. Clay and silt-size fractions, on which the sorption properties of the mineral part of soil depend, are mixtures of several aluminosilicate clay minerals with lower amounts of quartz, feldspars and various oxides and hydroxides, sometimes carbonate and phosphate minerals, sulfides or sulfates [1], so that trace element contents in natural soils may be related to Al, K, Ca, Mg, P, S.

In urban territories, investigation of the major elements is even more important, first of all due to possible influence of parent rocks. For example, such influence was observed in the Galway roadside sports ground, where Ca and Na distribution was related to granite or limestone areas [5]. The second reason to analyze major elements in urban soil is that anomalies of some of them might be caused by pollution sources. For example, investigations in Poland have shown common enrichment of urban surface soils not only with Cu, Pb, Zn, Hg, but also with S primarily as a result of industrial activities, because this increase is observed on different parent rocks: igneous, metamorphic or sedimentary, including post-glacial rocks [6]. Sulphur is a known atmospheric pollutant arising from the combustion of fossil fuels, industrial processes, biomass burning, agricultural activities, waste incineration and the use of explosives [7]. The increased content of Ca in urban soil may be due its emissions to the atmosphere from point sources: in Europe mainly cement plants followed by coal combustion (domestic and small boilers dominating) and iron and steel plants [8]. Industrial facilities producing building materials (e.g. grout) as well as erosion of...
buildings and roads can also be the anthropogenic sources of Ca increase in urban soil. Anomalies of Fe are often caused by metal processing plants and the iron-rich clay coatings in illuvial pores of deeper horizons which are enriched in many trace elements – Cu, Co, Cr, Zn [9].

When investigating contaminated territories, the determination of major elements in soil is very helpful, because it can explain trace element anomalies. For example, joint analysis of four major elements (Ca, Mg, Fe and Na) and a group of trace elements (Cu, Mn, Cr, Ni, Zn, Pb, Cd) during investigations of heavily polluted soil in the surroundings of an industrial complex in Germany distinguished four different industrial factors [10]. In the urban soil of Poland, besides the ten trace elements As, Ba, Cd, Cr, Cu, Hg, Ni, Pb, Sr, Zn, the three major elements S, Ca and Mg were also analysed [6]. Their elevated contents can be caused by anthropogenic factors, primarily industrial and traffic sources involving fuel combustion.

The diffuse pollution of urban soil depends on the chemical composition of urban particulate matter. Its PM10 fraction, which contains toxic elements, has negative effects on human health and depends on their origin and season [11], is often analysed not only for trace, but also for major elements [12], especially Ca [13]. Road dust is also analysed for major elements [14]. More sophisticated analyses, such as iron isotopic fractionation, SEM-EDX, are presently applied for the investigation of industrial and urban aerosols and knowledge of their major element and mineral composition is very important [15]. On urban territories, the physical and chemical properties of the soil which determine the binding ability of trace elements may change not only due to climate change, but mainly due to anthropogenic impact [16]. Major element contents in soil can reflect these changes. All the above-mentioned arguments emphasize that it is very important to analyze major elements in urban soil.

As the capital of Lithuania, Vilnius has historically been highly industrialized. Many industrial operations were located in the central part of the city. In Lithuania, geochemical investigations for environmental purposes were started in the 1980s by geochemists from the Institute of Geology (now Institute of Geology and Geography, IGG). The first topsoil sampling in Vilnius was done in 1985 and the results were discussed by R. Taraškevičius [17]. Repeated topsoil sampling in 1995-1998 in six central districts of Vilnius revealed that two of them (Naujamiestis and Senamiestis) were most contaminated [18]. In Naujamiestis, drill works were and still remain the most dangerous pollution source. Other works investigated in this district are the following: former radio engineering, electrical engineering, grinding-machine, turning lathe and consumables [19]. The locomotive depot, wagon depot, hosiery and furniture trade have also been investigated as pollution sources in Naujamiestis [18]. Additionally, the railway station and bus terminal are also located in this district. Žirmūnai, one of the northern districts sampled in 1995-1998, was also abundant in pollution sources [20]. The following three works are among the sources investigated: fuel equipment, former motor transport repair shop and ferro-concrete construction materials. Many transport related operations were analysed in Žirmūnai: two motor transport depots, a bus depot and a former motorised military unit. During the period from 1985 to 2002, the total topsoil contamination index has mainly increased in Vilnius, indicating that this medium is accumulating pollutants over a long period of time [21]. Though many industrial polluting sources are now closed, historical contamination of soil still remains. Geochemical investigations of topsoil in different towns of Lithuania have shown that the contamination level is greatly influenced by land-use [22], which is a very important anthropogenic factor [23]. It has been also revealed that the highest percentage of contaminated and pollution-sensitive sites is in industrial, infrastructural, old town public, old town residential and centre functional zones [24].

However, all above-mentioned investigations were based on real total contents of only trace elements and did not take into account the major element composition of soil, which is also an important factor in trace element anomalies. The goal of this research was to reveal with the help of usual statistical methods the relationship among the 10 major elements Na, Mg, Al, Si, P, S, K, Ca, Ti, Fe and the 17 potentially toxic trace elements Ag, As, B, Ba, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Sn, V, U, Zn found in topsoil in the central part of Vilnius. These trace elements are listed in the Lithuanian hygienic norm together with their maximum permitted concentrations in soil [25]. The novelty of this research is the joint analysis of major and trace element contents and possible overlap of their anomalies in urban soil. The scope of the study is restricted to one city, but the methods used might be useful for seeking analogies with other urban territories. The relationship between major and trace elements can also be analysed using PLS (Projection on Latent Structures or Partial Least Squares), which is a group of chemometric methods for modelling the association between blocks of observed variables by means of latent variables. PLS, developed by Herman Wold in the 1970’s, has many variants, some of which are used for both modeling and prediction [26]. PLS has already been used for geochemical data, e.g. for aerosols where
four latent variables explained the relationship between number concentrations and the measured PM2.5 concentrations of chemical species [27], and to search for possible factors of preschool topsoil contamination variability [28]. PLS regression was performed to predict which metals or PAH in airborne particulate matter contributed to the biological endpoints [29] or to predict potentially harmful element concentrations according to spectrally active soil constituents, i.e., reflectance spectroscopy data [30].

2. Experimental Procedure

2.1. Study area, sampling and primary sample preparation

Vilnius is located in southeastern part of Lithuania. The central part is at the inflow of the Vilnia tributary into the Neris River. The climate is transitional, with a mean January temperature of -5°C, and a mean July temperature of +17°C, and the average amount of precipitation is 664 mm. The city was first mentioned in 1323. Now it has a population of about 550,000 and an area of 402 km². The entire surface of Lithuania is covered by Quaternary deposits which were formed during the advance and retreat of glaciers. Stratigraphy of Quaternary deposits is complicated [31]. From a geomorphological point of view, the environs of Vilnius belong to the domain of continental accumulation and the surface cover was formed during the advance and retreat of glaciers. Stratigraphy of Quaternary deposits is complicated [31]. From a geomorphological point of view, the environs of Vilnius belong to the domain of continental accumulation and the surface cover was formed during the advance and retreat of glaciers. Stratigraphy of Quaternary deposits is complicated [31]. From a geomorphological point of view, the environs of Vilnius belong to the domain of continental accumulation and the surface cover was formed during the advance and retreat of glaciers. Stratigraphy of Quaternary deposits is complicated [31]. From a geomorphological point of view, the environs of Vilnius belong to the domain of continental accumulation and the surface cover was formed during the advance and retreat of glaciers. Stratigraphy of Quaternary deposits is complicated [31]. From a geomorphological point of view, the environs of Vilnius belong to the domain of continental accumulation and the surface cover was formed during the advance and retreat of glaciers. Stratigraphy of Quaternary deposits is complicated [31]. From a geomorphological point of view, the environs of Vilnius belong to the domain of continental accumulation and the surface cover was formed during the advance and retreat of glaciers. Stratigraphy of Quaternary deposits is complicated [31]. From a geomorphological point of view, the environs of Vilnius belong to the domain of continental accumulation and the surface cover was formed during the advance and retreat of glaciers. Stratigraphy of Quaternary deposits is complicated [31].

Figure 1. Approximate scheme of prevailing Quaternary deposits in the central part of Vilnius: 1 – alluvial deposits (Holocene), fine sand; 2 – alluvial deposits (Late Glacial), various, fine or middle sand; 3 – glaciofluvial deposits (Upper Pleistocene), various sand; 4 – marginal glaciofluvial deposits (Middle Pleistocene), various sand.

Topsoil sampling for this research was done in 2006. Composite samples were taken from 141 sites (Fig. 1) by zigzag crossing each site with an area of 200-400 m² and collecting 20-25 increments. After homogenization, a composite sample was reduced and brought to the laboratory of IGG, where the samples were air-dried and sieved to obtain a fraction <1 mm.

2.2. Further sample preparation and analyses

In the first quarter of 2010, the real total contents of 10 major elements Na, Mg, Al, Si, P, S, K, Ca, Ti, Fe and 16 trace elements Ag, As, Ba, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Sn, V, U, Zn were determined by energy-dispersive X-ray fluorescence (EDXRF). Sample preparation for this analysis included milling with MM 400, homogenisation with Licowax (4 g of sample and 0.9 g of wax) and pressing with a PP15 press into 32 mm pressed pellets. Two pellets were prepared for each sample. The primary content of these 26 chemical
elements was determined by EDXRF using SPECTRO XEPOS equipment and the TURBOQUANT calibration method for pressed pellets.

The contents of all major elements and the 9 trace elements Ba, Cr, Cu, Mn, Ni, Pb, Sn, V, Zn were above their detection limits (DL) in all pellets, while 5 elements were sometimes or often below their DL: Sb in 8.2% of samples, U in 41.3%, Se in 45.9%, As in 46.6% and Mo in 74.4% of samples. The following conditional values were used for these elements when their content was below the DL: As, Se – 0.05 mg kg\(^{-1}\), Sb – 2 mg kg\(^{-1}\), U – 0.3 mg kg\(^{-1}\), Mo – 0.1 mg kg\(^{-1}\). Median content of each of these elements was calculated according to two pellets of each sample. The results were recalibrated using 44 ISE reference samples, CRM 2709 and CRM 2711. In most cases, except for Si and Al, linear regression was used for this aim with a coefficient of determination higher than 0.9 (higher than 0.8 for Na and Sb).

The amounts of Ag and Co were too often (in more than 80% of samples) below the DL. Therefore the real total contents of Ag, Co and B (its determination by EDXRF is impossible) determined in 2007 by optical atomic emission spectrophotometry (OAES) were used in this research. Their determination was in a fraction <1 mm. Samples before this analysis were ashed at 350°C and milled.

To ensure quality control, since 1997 the IGG laboratory has been participating with OAES in the “International Soil-analytical exchange” (ISE) program organised by Wageningen University [36]. Since the end of 2007 it started to participate in ISE with EDXRF [37]. The relative standard measurement uncertainties (%) for the mean contents of 24 chemical elements determined by EDXRF according to 56 repeated measurements of CRM 2709 during the first quarter of 2010 (55 for Sb and 46 for Mo) are lower than 5%. For individual measurements, relative standard uncertainties (%) are higher: Fe(0.37), Si(0.56), Al(0.57), Ca(0.58), K(0.59), Zn(0.71), Mn(0.85), Mg, Ti (1.00), Ni(1.14), S(1.20), P(1.52), Pb(2.10), Ba(2.34), Na(2.80), Cr(3.73), Cu(3.75), As(4.38), V(6.07), Se(12.2), Sn(12.4), Sb(24.6), U(28.7), Mo(33.6). Joint uncertainty (sample preparation and measurement) RSD\(_{sp+m}\) was also determined based on two pressed pellets of each sample analysed by EDXRF. This uncertainty is determined not only by measurement but also by the differences between chemical element contents in pressed pellets due to insufficient homogenisation of the sample. For this aim, when possible, the variation coefficients VK were determined in each sample according to its two pressed pellets and divided by square root of 2. Then median values of these ratios MRSD\(_{sp+m}\) (%) were calculated. The result is that for 11 out of 18 chemical elements, the MRSD\(_{sp+m}\) values are lower than 10% and only for 7 cases are higher than 10%. According to MRSD\(_{sp+m}\), the latter elements are arranged as follows: Cr(10.3), V(15.0), Sb(20.0), U(25.0), Se(33.3), Mo(66.7), As(78.6). The contents of Sb, U, Se, Mo and As were often close to the DL.

The relative standard measurement uncertainties (%) of individual measurements of chemical elements, the contents of which were determined by OAES, are as follows: Ag – 2.3, B – 2.1, Co – 2.2.

2.3. Data treatment

Groups of major elements (factors) were distinguished by Ward’s method of cluster analysis applied for their standardised contents, taking into account the results of principal component analysis with varimax rotation and Spearman rank correlation coefficients. The relationship between major elements and trace elements was evaluated analysing their Spearman rank correlation coefficients and overlap of anomalies of trace elements (or their groups) with groups of major elements. Groups of trace elements were also distinguished according to the above-mentioned Spearman rank correlation matrix. The contents of major elements exceeding the upper quartile (75\(^{th}\) percentile) were treated as anomalous. Factors were characterized by their indices, which were calculated in each site according to the formula: \( \Sigma R_i > n+1 \), where \( R_i \) is the ratio of major element content to its upper quartile value, summing is for \( R_i > 1 \) and \( n \) is the number of \( R_i > 1 \). This is similar to the calculation of the additive contamination index [25]. Anomalies of trace element groups were distinguished according to indices Z, Z1, Z2, which were calculated according to the same formula, only \( R_i \) were the ratios of trace element amounts to their median values.

3. Results and Discussion

3.1 Groups and subgroups of elements

Cluster analysis revealed two groups of major elements: (Ca-Mg-Fe)-(P-S) and (K-Al-Ti)-(Si-Na), each of them consisting of two subgroups. The same 4 subgroups were distinguished by principal component analysis with varimax rotation. One subgroup has the highest loadings on the first factor: Al(0.964), K(0.951), Ti(0.936). The next one is characterized by the highest loadings on the second factor: Mg(0.942), Ca(0.921), Fe(0.362). The third one has the highest positive loadings on the third factor: S(0.788), P(0.653). The fourth one has the highest negative loadings on the third factor: Na(-0.777), Si(-0.682). All Spearman correlation
Table 1. Spearman rank correlation coefficients between major elements.

|     | Ti   | Al   | K    | Fe   | Ca   | Mg   | S    | P    | Na   | Si   |
|-----|------|------|------|------|------|------|------|------|------|------|
| Ti  | 1.000| 0.829| 0.871| 0.436| -0.180| 0.092| 0.148| -0.016| -0.113| -0.267|
| Al  | 0.829| 1.000| 0.880| 0.387| -0.305| 0.036| -0.026| -0.158| 0.198| 0.086 |
| K   | 0.871| 0.880| 1.000| 0.274| -0.300| 0.029| -0.065| -0.179| 0.100| -0.042|
| Fe  | 0.436| 0.387| 0.274| 1.000| 0.443| 0.534| 0.463| 0.330| -0.021| -0.630|
| Ca  | -0.180| -0.305| -0.300| 0.443| 1.000| 0.848| 0.382| 0.356| -0.113| -0.605|
| Mg  | 0.092| 0.036| 0.029| 0.534| 0.848| 1.000| 0.267| 0.142| 0.003| -0.527|
| S   | 0.148| -0.026| -0.065| 0.463| 0.382| 0.267| 1.000| 0.484| -0.422| -0.872|
| P   | -0.016| -0.158| -0.179| 0.330| 0.356| 0.142| 0.484| 1.000| -0.265| -0.444|
| Na  | -0.113| 0.198| 0.100| -0.021| -0.113| 0.003| -0.422| -0.265| 1.000| 0.435 |
| Si  | -0.267| -0.086| -0.042| -0.630| -0.605| -0.527| -0.872| -0.444| 0.435 | 1.000 |

Significant (p<0.01) correlation coefficients are in regular bold, less significant (p is 0.01-0.05) are in bold italic. Maximum correlation coefficients are underlined.

Figure 2. Areas where the contents of major elements exceed their upper quartile values. A– subgroup Si-Na; B – subgroup T-K-Al, C – subgroup P-S; D – subgroup Mg-Ca-Fe.
coefficients between the elements of each subgroup are positive and significant (p<0.05), indicating that their presence can be accounted for by similar reasons (Table 1).

The elevated amounts of each subgroup of major elements are observed in similar areas (Fig. 2). Almost all members of different subgroups of (Ca-Mg-Fe)-(P-S) are also significantly positively correlated. This means that their sources have much in common. The areas with elevated amounts of these elements are also rather similar (Fig. 2C, D). Meanwhile, different subgroups of (K-Al-Ti)-(Si-Na) have almost nothing in common, because correlation coefficients between their members are either insignificant (p>0.05) or less significant (0.01<p<0.05) or negative significant (between Si and Ti). Therefore, elevated contents of the elements from these different subgroups are in different areas (Fig. 2A, B). Silicon is known to be related mainly to quartz and sandy soil. Na-feldspars are quite weathering resistant and thus even occur in quartz-sand [4]. So the subgroup Si-Na may be interpreted as a sandy factor (S-factor). The members of the subgroup K-Al-Ti are related to clay, because Al is especially enriched in many clay minerals, and both K and Ti once released by mineral weathering are rapidly adsorbed by clay minerals [4]. So this subgroup may be interpreted as a clayey factor (C-factor).

Spearman rank correlation coefficients between major and trace elements enable us to speculate upon the origin of major elements. As concerns the group (Ca-Mg-Fe)-(P-S), there is significant (p<0.05) positive correlation of 8 trace elements Cu, Zn, Pb, Se, Ba, Ni, Co, Cr with all its members (Table 2). Earlier investigations in Vilnius [17-20] have shown that Cu, Zn, Pb, Cr, Ni, Co are typical pollutants. Such strong correlation between typical pollutants and the group (Ca-Mg-Fe)-(P-S) may be due to different reasons: 1) soil enriched with these major elements is a good accumulating medium for polluting trace elements; 2) major elements are themselves of anthropogenic origin. The first reason does not necessarily indicate anthropogenic origin of major elements. For example, S and P in the study area are correlated with loss on ignition LOI: both Spearman rank correlation coefficients (0.835 and 0.367, respectively) are significant (p<0.01). So soil with elevated contents of S and P may be enriched in organic matter, which is known to be a good accumulating medium for many polluting trace elements. Therefore, unlike the anthropogenic origin of trace elements, the origin of S and P in organic soil may be partly natural. In any case, the group (Ca-Mg-Fe)-(P-S) may be called anthropogenic factor (A-factor). This statement is proved by the fact that most of the other 9 trace elements in Table 2, except for Sb, are also significantly (p<0.05) correlated with major elements of A-factor: B (Fe, P, Mg, Ca), V (Fe, Ca, Mg, P), U (S, Fe, Ca, P), Mn (Fe, P, S), Ag, Sn (P, Ca), Mo (Ca, S), As (Fe).

On the contrary, the group of major elements (K-Al-Ti)-(Si-Na) is of natural origin, because there are many significant negative correlation coefficients between its members and polluting trace elements. This is especially true for subgroup Si-Na (S-factor) indicating the poor sorption capacity of sandy soil. Moreover, during the construction of buildings or roads in urban areas, the relocated, uncontaminated (or less contaminated) sandy soil which becomes the cover of these areas acts as a dilution factor of trace element contents. Most probably subgroup K-Al-Ti (clayey factor) is also of natural origin, because there are much more significant negative than significant positive correlation coefficients between its members and polluting trace elements.

Only four trace elements, i.e., B, Mn, Cr, U, are characterized by significant positive correlation with members of the clayey factor, but even they have higher correlation coefficients with members of the A-factor. Significant positive correlation with both the A-factor and the C-factor enables us to distinguish these four elements into a separate group (Gr1), indicating that their anomalies are of natural origin, and in rare cases of anthropogenic origin. Most trace elements, which correlate only with A-factor, are distinguished into the second group (Gr2), indicating that their anomalies are of anthropogenic origin.

In agricultural soil, the number of trace elements correlating with the clayey factor is greater: many positive correlation coefficients with members of the subgroup K-Al-Ti exceed 0.5: Ba(Al, K, Ti), V, Co (Ti, Al), Cr(Ti), Zn(Al) [4]. Besides, more major elements, i.e., Fe, Mg and Na, are related to K, Ti, Al and there is no negative correlation of trace elements with K, Al or Ti. Negative correlation between polluting trace elements and C-factor in the study area (Table 2) does not mean that soil enriched in clay does not accumulate pollutants. It exists because a majority of pollution sources are located on the areas where sandy soil prevails.

The low range of variation of Ti, Al, K as well as of Na and Si (the maximum value divided by the minimum value does not exceed 2.5) and their low (<20%) coefficients of variation (Table 3) confirm the natural origin of both subgroups and distinguish this group from members of the anthropogenic factor. The median amounts of Ca, Mg, P and S are higher than in the agricultural soil of Lithuania and ten European countries, confirming the anthropogenic origin of these major elements. Unlike them, major elements of C-factor are characterized by much lower contents in comparison with agricultural
soil. The low contents of these major elements may be because the main part of the study area is located in the valleys of the rivers, where sandy sediments prevail; in contrast, agricultural soil is often enriched in clay fraction. The same reason explains the much lower content of Fe in the study area, because it largely depends on clay content (significant positive correlation coefficients with Ti, K and Al confirm this relationship) (Table 1).

3.2. Two important major elements for investigation of urban trace element anomalies

The highest correlation coefficients of Cu, Zn, Pb, Se, Ba, Mo in the study area are with Ca; of Ni, Co, V, As, B, Mn, Cr with Fe; of Ag, Sn with P; of U with S. Antimony is not significantly related to major elements. Mainly chalcophiles correlate with Ca and mainly siderophiles and lithophiles with Fe. In agricultural soil, on the contrary, there are only several chemical elements which positively correlate with Ca: Sr, Mg, Sc, P, Ba and Cu [4]. Trace elements, which in the topsoil of the central part of Vilnius are mostly related to Ca, in the agricultural soil of European countries have the highest correlation coefficients with different other major elements: Cu and Se with S, Zn with Fe, Pb with Ti, Ba with Al [4]. As concerns trace elements which in the study area are mostly related to Fe, some of them (V, Mn, As) also have the highest correlation with Fe in agricultural soil, but some of them (Cr, Co, Ni) with Mg [4]. So an increase of trace element correlation with Ca and Fe is a characteristic feature of topsoil in the centre of Vilnius. Investigations in Poland have shown an increase of Ca in urban soil; fly ash containing CaSO₄, CaO, CaCl₂, CaCO₃ from thermo-electric power stations was mentioned as the main reason [6].

3.3 Relationship between anomalies of trace elements and major elements

As there is a close relationship between the contents of most trace elements with the A-factor, their anomalies are expected on the territories with elevated content of members of this factor. Urban research in Poland has shown that dust particles from fuel combustion and industrial emissions are the source of Cu, Hg, Ca, Mg and Sr [6], confirming the anthropogenic origin of Ca and Mg and overlap of their anomalies with polluting trace elements. However, not only anthropogenic, but also natural anomalies of trace elements are possible in urban soil, e.g. in areas with elevated content of clay. Such areas can be related to soil parent material. However, the areas with elevated contents of members of the C-factor (Fig. 2B) largely differ from the generalized

Table 2. Spearman correlation coefficients between major elements and trace elements and groups of elements.

| Groups of trace elements | Anthropogenic factor (A) | Clayey factor (C) | Sandy factor (S) |
|--------------------------|--------------------------|------------------|-----------------|
|                          | Ca, Mg, Fe, P, S         | Ti, Al, K        | Si, Na          |
| Gr2 Cu                   | 0.599 0.434 0.373 0.403 0.266 | -0.217 -0.321 -0.264 | -0.336 0.026 |
| Gr2 Zn                   | 0.481 0.296 0.214 0.464 0.212 | -0.344 -0.436 -0.403 | -0.190 0.040 |
| Gr2 Pb                   | 0.547 0.400 0.301 0.429 0.219 | -0.235 -0.310 -0.241 | -0.263 0.032 |
| Gr2 Se                   | 0.549 0.433 0.315 0.307 0.403 | -0.055 -0.212 -0.198 | -0.443 -0.122 |
| Gr2 Ba                   | 0.464 0.420 0.444 0.388 0.195 | 0.104 0.025 0.069 | -0.325 0.084 |
| Gr2 Ni                   | 0.378 0.387 0.682 0.357 0.422 | 0.164 0.102 0.005 | -0.469 -0.073 |
| Gr2 Co                   | 0.394 0.364 0.396 0.184 0.218 | 0.002 -0.027 -0.036 | -0.306 -0.050 |
| Gr2 V                    | 0.290 0.197 0.339 0.185 0.138 | -0.199 -0.189 -0.246 | -0.164 0.021 |
| Gr2 As                   | 0.154 0.111 0.346 0.153 0.133 | 0.117 0.111 0.058 | -0.140 0.067 |
| Gr2 Mo                   | 0.219 0.108 0.137 0.148 0.170 | -0.225 -0.251 -0.289 | -0.137 -0.054 |
| Gr2 Ag                   | 0.356 0.136 0.003 0.386 0.137 | -0.342 -0.474 -0.369 | -0.078 -0.036 |
| Gr2 Sn                   | 0.357 0.137 0.126 0.444 0.099 | -0.285 -0.379 -0.275 | -0.136 -0.029 |
| Gr2 Sb                   | -0.049 -0.061 -0.090 -0.058 -0.129 | -0.179 -0.165 -0.142 | 0.158 0.074 |
| Gr1 B                    | 0.199 0.237 0.368 0.295 0.124 | 0.311 0.171 0.225 | -0.246 -0.062 |
| Gr1 Mn                   | 0.062 0.101 0.611 0.408 0.199 | 0.547 0.489 0.365 | -0.340 -0.077 |
| Gr1 Cr                   | 0.300 0.313 0.644 0.357 0.342 | 0.299 0.186 0.140 | -0.404 -0.069 |
| Gr1 U                    | 0.180 0.161 0.334 0.165 0.556 | 0.202 0.151 0.105 | -0.503 -0.204 |

Significant (p<0.01) correlation coefficients are in bold, less significant (p is 0.01-0.05) are in bold italic. Maximum correlation coefficients are underlined.
Table 3. Characteristics of major element contents in the topsoil of the central part of Vilnius.

| Characteristic | Ti  | Al  | K   | Fe  | Ca  | Mg  | S   | P   | Na  | Si  |
|---------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Min (g kg⁻¹)  | 0.795 | 16.0 | 11.2 | 3.91 | 3.23 | 0.919 | 0.243 | 0.443 | 3.36 | 301 |
| Max (g kg⁻¹)  | 2.00 | 27.3 | 18.1 | 23.8 | 52.0 | 10.1 | 2.52 | 3.00 | 7.29 | 421 |
| Max/Min       | 2.5 | 1.7 | 1.6 | 6.1 | 16.1 | 11.0 | 10.3 | 6.8 | 2.2 | 1.4 |
| CV (%)        | 17.2 | 11.5 | 8.9 | 20.9 | 32.6 | 25.3 | 38.4 | 36.7 | 10.6 | 6.3 |
| Med (g kg⁻¹)  | 1.25 | 20.1 | 14.2 | 8.79 | 20.6 | 4.92 | 0.909 | 1.29 | 4.81 | 359 |
| UQ (g kg⁻¹)   | 1.40 | 21.9 | 15.2 | 9.72 | 25.3 | 5.72 | 1.11 | 1.61 | 5.07 | 376 |
| MedA (g kg⁻¹) | 2.60 | 48.3 | 15.6 | 17.1 | 9.93 | 3.44 | 0.253 | 0.820 | 8.98 | 331 |
| MedAL (g kg⁻¹) | 2.24 | 37.1 | 17.9 | 13.1 | 5.22 | 2.98 | 0.207 | 0.574 | 4.97 | 375 |
| Med/MedA      | 0.48 | 0.42 | 0.91 | 0.51 | 2.07 | 1.43 | 3.59 | 1.58 | 0.54 | 1.08 |
| Med/MedAL     | 0.56 | 0.54 | 0.79 | 0.67 | 3.94 | 1.65 | 4.39 | 2.25 | 0.97 | 0.96 |

Min – minimum, Max – maximum, CV – coefficient of variation, Med – median, UQ – the upper quartile, MedA – median in agricultural soil of ten European countries [4], MedAL – median in agricultural soil of Lithuania [4]. Med/MedA and Med/MedAL of S may be overestimated, as the content of S in agricultural soil was determined in aqua regia and therefore is lower than the actual total.

Figure 3. Relationship between major element factors and trace element anomalies in the topsoil of Vilnius. Pollution sources: DR – drill works, LD – locomotive depot, FE – fuel equipment works, BD – bus depot, GA – garages, TD – trolley-bus depot, EI – former electrical engineering institution, EG – former works of electrical gauges, FU – fur processing works, RE – repair works of electrical equipment, MR – former motor transport repair works.
scheme of Quaternary deposits (Fig. 1). Some of these areas can be related to river clay which was earlier transported by river flow and deposited on the terraces. Erosion of slopes, transfer of erosion products with storm-water flow or re-suspension to the atmosphere and transfer by wind to adjacent areas are other possible reasons for topsoil enrichment in clay particles. This is sometimes also due to new soil cover brought to create lawns. So the origin of anomalies of B, Mn, Cr and U, which are correlated with the C-factor can be due to the influence of the above-mentioned reasons. Some of these anomalies may be of anthropogenic origin. The overlap of the C-factor and the A-factor is also possible. Presumably in such areas the origin of trace element anomalies is anthropogenic. It has already been noticed by many researchers [38] that urban soil is highly disturbed and is not necessarily related directly to its immediate geological materials. Furthermore, due to frequent mixing, the signs of surface soil enrichment with trace elements can be obscured and soil contamination masked.

3.4. Comparison of the influence of the clayey factor and the anthropogenic factor

To find out whether the C-factor in the study area is as important for the increase of trace element contents as the A-factor, all sampling sites were divided into four groups according to the values of the A-index and the C-index (Table 4). The N-group includes sites with no influence of both factors (A=1, C=1), the C-group (A=1, C>1) the sites influenced by only the C-factor, the A-group by only the A-factor (A>1, C=1) and the AC-group by both factors (A>1, C>1). First, the N and C groups, which are not affected by the A-factor were compared. Under these circumstances the median values of Cr, B, Mn, U (Gr1) are higher in sites influenced by the C-factor than in sites not influenced by it (Table 4).

The same tendency for these trace elements is seen when comparing two groups of sites A and AC, i.e., under circumstances of the influence of the A-factor. In both cases, the respective ratios of their medians in topsoil enriched with clay compared to topsoil with lower clay content (clay influence coefficients of trace elements) are higher than 1. So the influence of the C-factor on Gr1 trace elements is well reflected. Some elements from Gr2 are also partly influenced by the C-factor: 1) As, which has the same tendency as Gr1 elements in sites both influenced and uninfluenced by the A-factor; 2) Ni and Ba only in sites uninfluenced by the A-factor. However, for most of these trace elements, clay influence coefficients are higher in topsoil uncontaminated by major elements than in contaminated topsoil. The same concerns the clay influence coefficient of the Z1-index calculated according to members of Gr1 (Cr, B, Mn, U): under the influence of the A-factor it is even slightly

| Variable | Median values (mg kg⁻¹) in groups | Ratios of median values in groups: Clay influence coefficients | Anthropogenic influence coefficients |
|----------|----------------------------------|-------------------------------------------------|-----------------------------------|
|          | All sites (n=141) | M(N) (n=41) | M(C) (n=19) | M(A) (n=51) | M(AC) (n=30) | M(C)/M(N) | M(AC)/M(A) | M(A)/M(N) | M(AC)/M(C) |
| Cr       | 19.6 | 15.5 | 19.6 | 21.8 | 22.6 | 1.26 | 1.04 | 1.40 | 1.15 |
| Pb       | 24.8 | 23.0 | 23.8 | 25.1 | 26.5 | 1.03 | 1.06 | 1.09 | 1.12 |
| Mn       | 300  | 268  | 318  | 299  | 336  | 1.16 | 1.12 | 1.11 | 1.066 |
| U        | 0.70 | 0.55 | 0.75 | 0.75 | 0.91 | 1.38 | 1.21 | 1.38 | 1.21 |
| As       | 2.26 | 2.08 | 2.56 | 2.26 | 2.36 | 1.23 | 1.04 | 1.08 | 0.92 |
| Ni       | 8.3  | 7.5  | 7.6  | 9.2  | 9.0  | 1.01 | 0.97 | 1.23 | 1.19 |
| Ba       | 316  | 296  | 316  | 326  | 321  | 1.07 | 0.99 | 1.10 | 1.02 |
| V        | 14.4 | 12.9 | 9.4  | 17.5 | 16.0 | 0.73 | 0.92 | 1.36 | 1.70 |
| Cu       | 20.9 | 20.0 | 14.1 | 27.4 | 18.2 | 0.70 | 0.66 | 1.37 | 1.29 |
| Zn       | 133  | 128  | 96   | 184  | 114  | 0.75 | 0.62 | 1.44 | 1.19 |
| Sn       | 6.1  | 5.8  | 4.4  | 7.3  | 5.7  | 0.76 | 0.78 | 1.26 | 1.29 |
| Pb       | 43.8 | 36.8 | 30.5 | 57.0 | 40.2 | 0.85 | 0.71 | 1.59 | 1.32 |
| Mo       | 0.61 | 0.61 | 0.79 | 0.61 | 1.00 | 1.00 | 1.00 | 1.00 |
| Ag       | 0.43 | 0.54 | 0.32 | 0.59 | 0.32 | 0.60 | 0.55 | 1.09 | 1.00 |
| Co       | 5.62 | 5.57 | 5.28 | 6.34 | 5.78 | 0.95 | 0.91 | 1.14 | 1.10 |
| Se       | 0.44 | 0.40 | 0.38 | 0.49 | 0.44 | 0.95 | 0.89 | 1.23 | 1.15 |
| Sb       | 1.56 | 1.68 | 1.54 | 1.56 | 1.45 | 0.92 | 0.93 | 0.93 | 0.94 |
| Z        | 4.08 | 2.92 | 2.02 | 7.02 | 3.55 | 0.69 | 0.51 | 2.41 | 1.76 |
| Z1       | 1.50 | 1.05 | 1.55 | 1.66 | 1.63 | 1.47 | 0.98 | 1.58 | 1.05 |
| Z2       | 3.38 | 2.75 | 1.61 | 6.25 | 2.81 | 0.59 | 0.45 | 2.27 | 1.75 |

Groups were distinguished according to the influence of factors C (K, Al, Ti) and A (Ca, Mg, Fe, P, Si). The N-group includes sites with usual content of both factors (A=1, C=1), the C-group with influence of the C factor (A=1, C>1), the A-group with influence of the A factor (A>1, C=1), the AC-group with influence of both factors (A>1, C>1), n is number of samples in the groups. Geochemical indices Z (all 17 trace elements), Z1(Cr, Mn, B, U) and Z2(other 13 trace elements) are dimensionless.
lower than 1. This indicates that when there is no influence of the A-factor, the reflection of the influence of the C-factor on trace element contents in topsoil is more expressed. Moreover, the majority of trace elements from Gr2 (V, Cu, Zn, Sn, Pb, Mo, Ag, Co, Se, Sb) have no clay influence coefficients higher than 1. Therefore the influence of the C-factor on the Z2-index is also not visible. As Gr2 includes more trace elements than Gr1, the influence of the C-factor on the values of the Z-index is also masked. The influence of the A-factor on trace element contents is obviously higher (Table 4). It is observed both comparing sites with low content of clay in topsoil (groups N and A) and with high content of clay (groups C and AC). In both cases, the respective ratios of trace element medians in topsoil contaminated by major elements compared to uncontaminated topsoil (anthropogenic influence coefficients of trace elements) are usually higher than 1. However, anthropogenic influence coefficients are lower in topsoil rich in clay, indicating that main pollution sources of the study area are located on sandy soil. The influence of A-factor on trace element anomalies is also seen according to all the geochemical indices: Z1, Z2 and Z.

Anomalies of trace elements are often observed on the territories affected by the A-factor: 74.6% of Z>4 anomalies (Fig. 3), 100% of Z1>4 anomalies and 75% of Z2 anomalies.

More contrasting anomalies (Z>8) are especially obviously related to the territories influenced by the A-factor: they comprise 83.3% of the total number of such anomalies. Sites affected by the A-factor are in the oldest part of the study area, near the railway or roads with intensive traffic. Some of them are clearly related to point pollution sources, e.g. drills works, former works of fuel equipment, motor transport repair or electrical engineering, locomotive depot, garages, trolley-bus or bus depot sites. Trace element anomalies are also in the same places. Their anomalies correspond to anomalies revealed in earlier investigations [17-20].

These results show that the influence of the A-factor on trace element anomalies in the study area is very high, while the influence of the C-factor is masked and therefore has secondary importance. The lower influence of the C-factor may be determined by the location of pollution sources.

4. Conclusions

Two important factors were distinguished according to major element contents: 1) anthropogenic (A) including Ca, Mg, Fe, P, S; and 2) clayey (C) including K, Al, Ti. Four trace elements, B, Mn, Cr and U, are significantly correlated with members of both factors, Sb with none of them and another 12 trace elements either with all (Cu, Zn, Pb, Se, Ba, Ni, Co) or with separate (V, Ag, Sn, Mo, As) members of the anthropogenic factor. The influence of the clayey factor is well reflected only on the contents of B, Mn, Cr and U (Gr1), partly on the As, Ni and Ba and mainly in the sites not affected by the anthropogenic factor. Another 13 elements, Cu, Zn, Pb, Se, Ba, Ni, Co, V, Ag, Sn, Mo, As, Sb, have a Z2 index of their anomalies mainly affected by the anthropogenic factor, while the Z indices of the anomalies of all 17 trace elements are likewise mainly affected by the anthropogenic factor. The majority of trace element anomalies are related to the sites affected by the anthropogenic factor, while the influence of the clayey factor is secondary.

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