Urban geochemistry : Sisak in Croatia, a long-lasting historical, urban and industrial city

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URBAN GEOCHEMISTRY: SISAK IN CROATIA, A LONG-LASTING HISTORICAL, URBAN AND INDUSTRIAL CITY

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Introduction

The investigation of the urban soils in different cities is often conducted using various approaches: type of sampling (single or composite), depth of samples, quality control of the field work and analytics, analytical methods and interpretation and presentation of the data. It is difficult or even impossible to compare results and potential soil pollution among different cities due to these differences. The EuroGeoSurveys Geochemistry Expert Group initiated in 2008 the project "Urban Geochemistry in Europe (URGE) – soil, children, health" with the main aim to standardize geochemical studies in the urban areas. Thirteen cities were interested in participating in the project. Some cities dropped out due to financial problems and some did not completely follow the defined manual. The investigations up to 2014 finished in Hämeenlinna (Finland), Karlstad (Sweden), Aschersleben (Germany), Prague (Czech Republic), Hamar (Norway) and Sisak (Croatia).

The Sisak city is located at 45°29' N and 16°20' E, 57 km towards southeast from Zagreb, the capital city of Croatia (Fig. 1.). Sisak is an ancient city, dated from 4th century BC when the Celts founded the settlement Segestica. In the 1st century BC, the Romans set up the town Siscia (Slukan Altić, 2004). Siscia was an important town in the Roman Empire (Fig. 2.). Namely, the city had military function and important mints were located in it for more than 140 years. During the Middle Ages the settlement was more village than town. The biggest development of Sisak was after the World War II in the former Yugoslavia. In this period Sisak became one of the most important industrial towns in the former state with heavy industry like steelworks, a thermoelectric power plant, refinery, chemical industry, etc. However, due to the war in the 1990s and economic difficulties, in the last two decades almost all industry collapsed.

The area of Sisak is situated at the alluvial sediments of rivers Kupa, Odra and Sava (Fig. 3.). The terrain is lowland at about 100 m above the see level. The level of underground waters is high, mostly between 2 and 4 m below surface. Fine-grained Quaternary deposits (silts, sands, clays, loess) cover 99% of the investigated area (Pikija, 1987a, b). The floodplain sediments of the Sava river are composed of carbonates while those of rivers Kupa and Odra are dominated by siliciclastics. The great meander of the river Kupa is covered by loess.

In the rural part of the investigated area hydromorphic soils prevail, dominated by different types of gley soils, while in the urban part technogenic soils (urban soils) predominate (Husnjak, 2012). The climate in the Sisak area is moderately warm and rainy without significantly dray periods.

In this paper we present a part of the results we obtained in the frame of urban geochemical study of the Sisak city. We present the use of multivariate statistics for clarifying the element sources in the area of the Sisak city.

Figure 1. Geographic position of the Sisak area

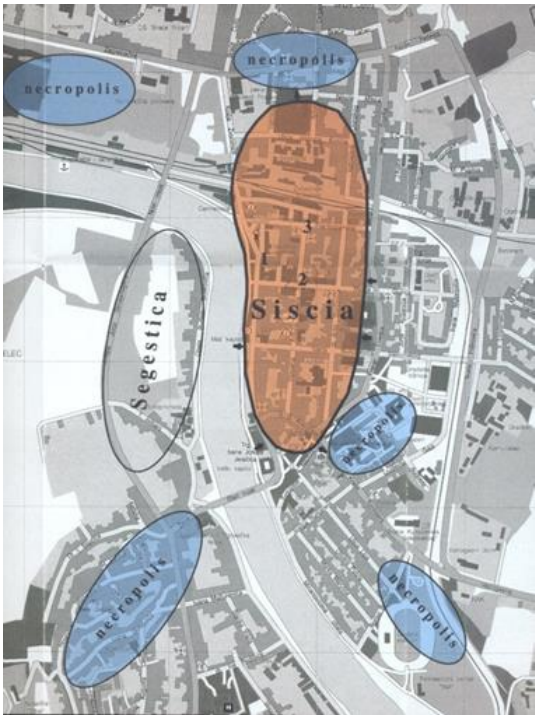

Figure 2. Reconstruction of antique Siscia (1 – thermae, 2 – forum, 3 – basilica, the arrows mark the locations of the gates of the city); after Slukan Altić, 2004

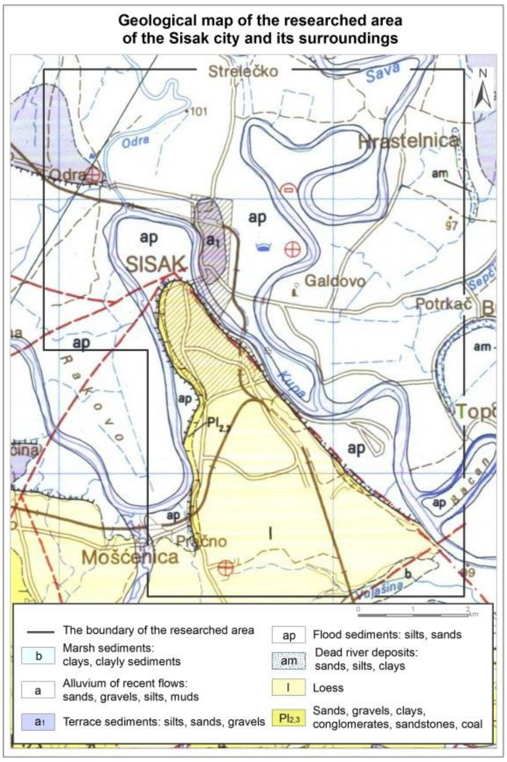

Figure 3. Geological map of the investigated area

Methodology

The field research in the Sisak area was conducted during the summer and autumn 2010. The analyses were made in 2011. The soils were sampled and analysed according to URGE instructions of EuroGeoSurves' Geochemical Expert Group (Ottesen, 2008). In the URGE field manual a single sample method has been proposed. In our investigation both single samples and composite samples were taken at each sampling location. In this paper we present the results based on the analysis of composite samples.

Field research

Composite samples were taken in the topsoil layer from a depth of 0 – 10 cm with a sampling density of 4 samples/km^2 in the urban area and 1 sample/km^2 in the rural area around the city (Fig. 4.). The sampling grid was regular and squared. One composite sample consisted of five subsamples which were taken at the corners of the square 2 x 2 m and in the middle of it. It was not possible to cover a larger area south and southwest of the industrial facilities because of the existing mine field. During the last war in Croatia (Croatian War for Independence, 1991-1995) this area was mined. The area is still not cleared of mines. The total surface of the researched area was 65.18 km^2 at which 144 samples were taken.

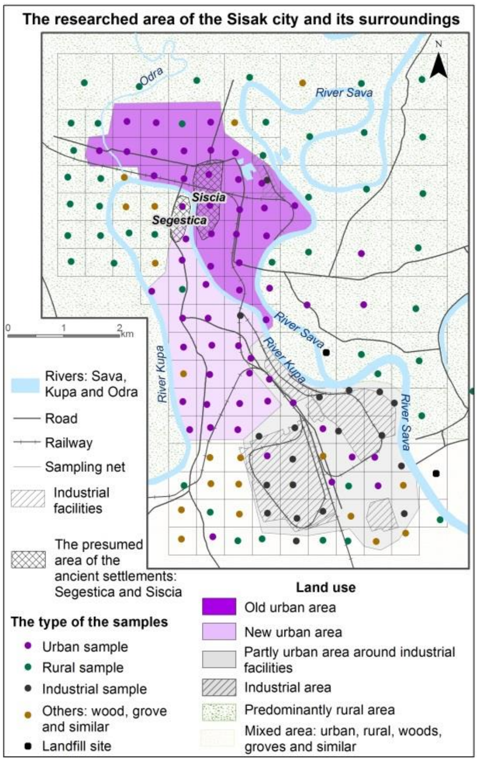

Figure 4. Location of samples and land use of the investigated area

Laboratory research

The samples were air dried at the room temperature, powdered, homogenised and sieved to <2 mm. Samples were digested in the 90 ml of aqua regia, then heated and boiled for one hour in the bath (95°C). After the cooling, up to 300 ml of 5% HCl was added to the solution. Chemical analyses were performed by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) for the set of 53 chemical elements in the ACME Analytical Laboratories, Vancouver, Canada. Soil pH in H_2O was determined according to HRN ISO 10390 (2005).

Quality control (QC)

Quality control was maintained during sampling and analysis. One field duplicate was taken at every 20th sampling location. The location of the field duplicate sample was within 0.5 m of the original sampling site. Seven field duplicates were collected (4.9% of total number of samples), which is generally in accordance with the recommendation of Reimann et al. (2008). Precision and accuracy were evaluated as part of the QC process. The precision was obtained by the analysis of 18 duplicate samples. The coefficient of variation (CV) of precision was computed according to the formula CV (%) = (SD / X) * 100, where SD is standard deviation and X is mean. In order to determinate the accuracy, 27 samples of geochemical standards were also analyzed (STD DS7 - 7 samples, STD OREAS45PA - 8 samples, STD DS8 - 8 samples and SO-2 - 4 samples).

Multivariate statistics (factor analysis) and geochemical maps of factors

Factor analysis (FA) of the data was carried out to reduce the observed variables in order to obtain a better understanding and to simplify its interpretation. Using this approach, the geogenic and/or anthropogenic sources of the factorized geochemical data were evaluated. In order to perform multivariate statistical analyses the analytical data was screened.

Results below the detection limit (DL) of the instrument and method employed were converted to half of the DL value for the particular element (e.g. obtained value was <DL, and DL of the element was 0.02, than half of the DL is 0.01). In some cases were results above the upper detection limit (UDL). For example, the UDL for Zn was 10,000 mg/kg and the obtained values >10,000 mg/kg were increased by 1 unit. In this particular case it means that for the statistical purposes was used value 10,001 mg/kg.

The analytical data, except the pH value, were log-transformed to base 10 logarithms (log10) to approach a normal distribution of the data (Reimann et al., 2008). The factor analysis (FA) was carried out using the statistical software IBM SPSS. The Kaiser-Meyer-Olkin test (KMO) and Bartlett's test of sphericity were used for assessing the strength of the relationships between variables. The Kaiser's recommendation of eigenvalues over 1 was selected (Kaiser, 1960). The retained factor loadings were rotated by Varimax rotation to simplify the interpretation of factors. The obtained factor scores were stored as a new variable and used for generating geochemical maps in GIS software ArcGIS™, using the extension Geostatistical Analyst. After variogram analyses, the geochemical maps of factors were generated using kriging method. The factor scores at the factor maps were classified to emphasize the highest and lowest values.

Results

The data were adequate for factorization since the results of the KMO test is 0.763 and Bartlett's test of sphericity < 0.001. The 8 factors were retained (those with eigenvalues >1) which explain 84.07 of the variance. More detailed description about yielded factors is given in Table 1. The elements with factor loadings of over 0.5 have the biggest influence of the factor. Some additional explanation about individual factor were given also by elements with lower factor loadings and for that reason in the "brackets" elements with factor loadings 0.4 – 0.5 were retained (Šorša, 2014).

Quality control

The QC of the field duplicates showed great variability, this was expected since the urban geochemical data are very variable. The highest CV (%) were obtained for Cu, Hg and Pb while other trace elements showed significantly lower values. Coefficient of variation of the precision of chemical analyses was low for all elements, except for Hg. The reason for the low precision in the Hg analyses was likely due to its low detection limit (5 µg/kg). The accuracy of the reference material STD DS7, STD OREAS45PA and STD DS8 was good with the variation varying from 0 to 10.5 %. Standard SO-2 showed low accuracy. The low accuracy of this reference material was probably low due to its low content of trace elements.

Discussion

Factor analysis yielded 8 factors: 2 geogenic factors (FA 3 and 5), 4 anthropogenic factors (FA 1, 6, 7 and 8), 1 anthropogenic and partly geogenic (FA 4) and 1 geogenic and partially anthropogenic factor (FA 2). The geogenic factors (Figs. 5. and 6.; Tab. 1.) were dominantly influenced by the lithological composition of the investigated area. The composition of elements in the alluvium of rivers Kupa, Odra and Sava was visible in the FA 3 (Fig. 5.). The western part of the investigated area is composed of siliciclastic alluvium of Kupa and Odra rivers rich in Ce, Ga, La, Nb, Rb and Tl. The eastern part of the investigated area is covered by carbonate alluvial sediments of the Sava river with elevated values of Ca, Sr, Mg, higher pH, S and Na (Šorša and Halamić, 2014). In the middle of the map is the transition zone between siliciclastic and carbonate alluviums which is additionally influenced by the urban and industrial activities. It has to be stressed that the geological map of the investigated area (Fig. 3.) is chronostranigraphic and not lithostratigraphic and, therefore, this difference between alluviums is not noticeable.

The big meander of the Kupa river is covered by loess deposits which are continued by terrace sediments (silts, sands, gravels) towards northwest (Fig. 3.). Obviously, loess and terrace sediments have similar elements composition which is presented on the geochemical map of the factor 5 (Fig. 6.). These deposits are enriched in Ti, U, Na and Ba. The rest of the map has very low factor values of these elements.

Table 1. Main geogenic and anthropogenic influences to the factors

Factor	Designation	Sources of the elements	Association of elements in the factor
Anthropogenic factors			
FA 1	Heavy industry	*The south-zone industry, chemical industry, heating on coal, household waste, traffic. Small contribution of the parent material of the siliciclastic alluvium of river Kupa.	Mo - Zn - W - Sn - Sb - Cd - Mn - Cu - Pb - Cr - Fe - Ba - Ni - Ti - Na - Bi - S - Ag - (In - As - U - Hg - V)
FA 6	Roman mints	Smelters and mints of antique time, *the south-zone industry.	Au - Ag - Hg - (Pb - Bi - P)
FA 7	Craft	Chemical and others industry from the end of the 19th century and the beginning of the 20th century.	Re - (As - Nb)
FA 8	Residential	Waste waters and mud, fertilizers.	P - (K - Rb - **–**In)
Geogenic factors			
FA 3	Rivers Kupa and Odra – River Sava	Geogenic material of the alluvium of the rivers Kupa, Odra and Sava. Small anthropogenic influence along the routes, from * the south-zone industry.	**–**Ca - **–**Sr - **–**Mg - **–**pH - Ce - Ga - La - Nb - **–**S - Rb - **–**Na - Tl (Al - **–**Hf - **–**Zr - **–**V)
FA 5	Loess	Loess and terrace sediments of the river Kupa. Minor anthropogenic contribution of *the south-zone industry.	Ti - U - Na - Ba - (**–**Co - La - Ce)
Anthropogenic – geogenic factor			
FA 4	Industry – flood plain	Siliciclastic alluvium of river Kupa and loess. Small anthropogenic influences of *the south-zone industry, chemical industry and pesticide.	Cs - Li - Se - Tl - Rb - In - Al - (Bi)
Geogenic – anthropogenic factor			
FA 2	Alluvial - industrial	Geogenic influences of the alluvium of the rivers Kupa and Odra. Anthropogenic influences of *the south-zone industry, chemical industry, pesticide, fertilizers.	Sc - Y - Th - Zr - Be - Co - Hf - K - Al - Ni - As - Li - Ga - Fe - Ce - (V - La - Bi)

*The south-zone industry includes: thermoelectric power plant, steelworks and oil refinery.

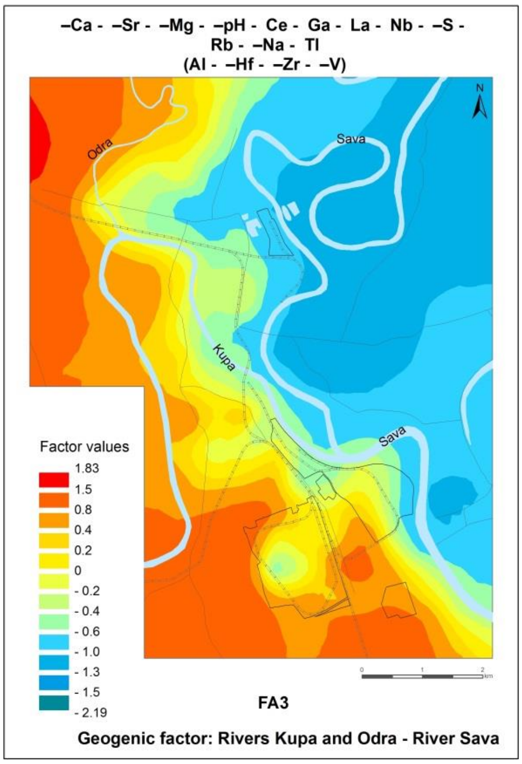

Figure 5. Geogenic factor 3

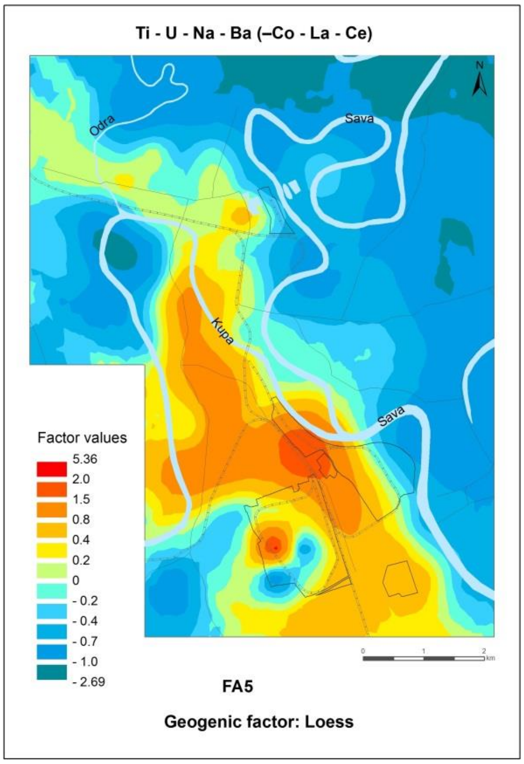

Figure 6. Geogenic factor 5

Anthropogenic factors (FA 1, 6, 7 and 8) indicate important contribution of the urban and industrial development of the region (Fig. 4.). Factor 1 comprised numerous elements (Fig. 7.), connected with different anthropogenic influences. The highest factor values at the south of the investigated area represent the influence of heavy industry and cover the area with industrial facilities, neighborhood settlements and agricultural land across the Sava river, both influenced by the heavy industry due to dispersion of pollutans by wind. At the end of the 19th century and beginning of the 20th century along the river Kupa industry as well as traffic infrastructure (regional railway and roads) developed. This is represented by high factor values alongside this river. The antique part of Sisak at the north, also influenced by industry and long-lasting urban development has also elevated factor loadings.

Elevated factor values for Au, Ag and Hg in the anthropogenic factor 6 were influenced by industry at the south of the investigated area and Roman influence at the north (Figs. 2.; 4. and 8.). The highest factor values were observed at the location of antique settlements Segestica and Siscia. During the Roman period these settlements were joined in one, Siscia. The Siscia was big and important city at the crossroads from eastern part of Roman Empire and its western part. The most significant reason for the elevated content of those elements in the soils are the remains of Roman mints. They were active more than 140 years and used Hg for coating copper coins with Au and Ag (Buzov, 2005; Ingo et al., 2006).

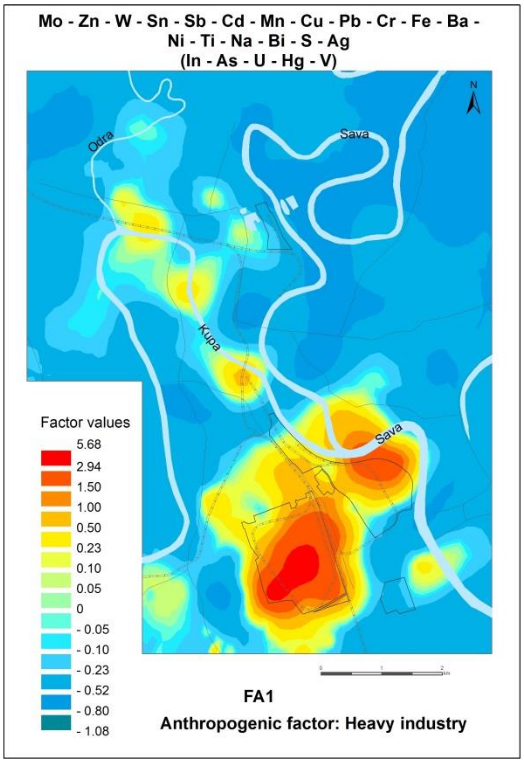

Figure 7. Anthropogenic factor 1

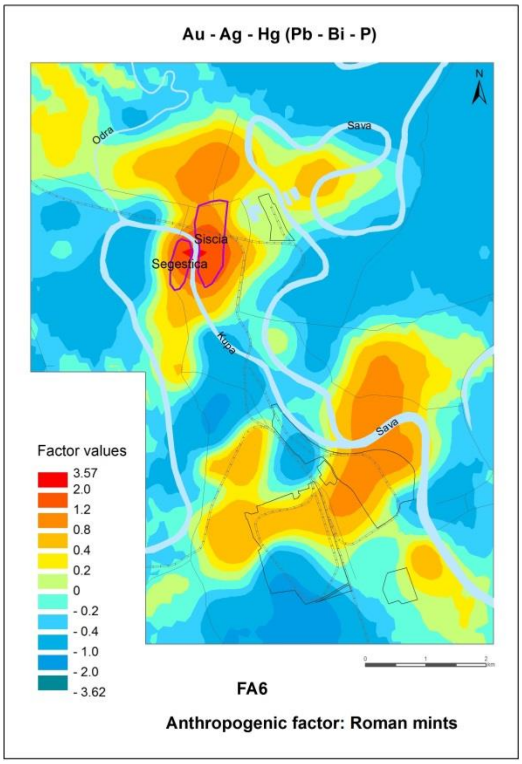

Figure 8. Anthropogenic factor 6

Conclusions

The sources of trace elements in the topsoil layer of the Sisak city primarily depend on the lithological composition and anthropogenic input. According to the results of the factor analysis of 8 yielded factors, 4 are anthropogenic, 2 mixed and only 2 geogenic. The different lithology of the alluvial deposits of Sava, Kupa and Odra rivers, loess at slightly higher terrain in the big meander of the Kupa river and terrace sediments along the Kupa river were clearly visible in the geogenic and partially geogenic factors. The elevated values of the most trace elements, especially of heavy metals, in the topsoil were predominantly due to anthropogenic input. Elevated factor values in the anthropogenic and partially anthropogenic factors were observed in the antique part of Sisak, at some agricultural parcels, along frequent roads and in the industrial zones, from which they were dispersed by wind to the neighboring residential areas and agricultural land. The results pointed out that soils are very good sink for collecting and accumulating trace elements in the long-lasting urban and industrial areas.

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