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Article

Magnetic and Geochemical Properties of Zagreb City Area Soils

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Abstract: The study was performed to get the first insight of distribution of the low field volume magnetic susceptibility (MS) throughout the Zagreb city area, based on in-situ field measurements. Most interesting locations were selected for soil sampling and geochemical content was determined using ICP-OES. A geostatistical approach was applied on MS and geochemical results. Median value of 0.245 x 10^{-3} SI units is proposed to be used as relevant average MS value in Zagreb area. Mean concentrations of heavy metals in Zagreb soils (in µg/g) are: Pb (36.82), Zn (87.77), Cu (30.84), Cd (0.66), Cr (29.04), Co (11.89) and Ni (28.40), being relatively low in comparison with Croatian legislation and with European and world average. Boxplot analyses showed that 45% of studied elements do not show any anomaly, while the rest of elements mostly show only one weak anomaly and they are located at the same sites as MS anomalies. Statistical analysis found significant correlations between MS and following elements: Cd, Co, Fe, Mn, Na, Pb, Sb and Zn. In-situ MS measurements proved to be an efficient tool for initial screening of large areas in terms of elevated heavy elements concentrations, enabling cheap and fast assessment of state of environment.

Keywords: magnetic susceptibility; geochemistry; Zagreb urban area (Croatia); soils; anthropogenic influence; geological background

1. Introduction

Magnetic susceptibility (MS) is a degree of magnetization of some material as respond to applied magnetic field. The method of determining volume susceptibility is a cheap and fast method and it is possible to use it as an indicator of anthropogenic contamination with some heavy metals. Development of application of magnetic measurements in environmental research begun inchoate in the second half of 8th and in 9th decades of 20th century. Investigation of application of this method to sediments was initiated by Thompson and Oldfield in 1986 [1] and the whole series of authors is using it for different investigations in geosciences. Shortly after that one of the main research themes became application of magnetic measurements as a replacement for expensive and complicated chemical analyses in contamination research [2–7].

More investigations have shown that a significant correlation exists between distribution of magnetic particles and distribution of heavy metals around the industrial areas [4,8,9]. Those investigations, performed in industrial areas of Poland, have also shown that distribution of magnetic susceptibility is closely connected with sedimentation of industrial dust and that magnetic measurements could be used as a method for detection of presence of heavy metals in soils. In the area of Leoben (Austria) a similar investigation was performed by [10]. The most detailed overview of magnetic monitoring methods in pollutant research was given by Petrovský and Ellwood in 1999 [11].

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Several studies in other parts of the world (China, Morocco) also investigated connections of MS with particular heavy metals and with mineral content of samples [12–15]: Wang and Qin (2005); Lu and Bai (2008); Lu et al. (2010); El Baghdadi et al. (2012).

The majority of authors are in accordance with the conclusion that this method is promising and confident for identification of polluted areas. Because this method is fast and cheap, it is possible to handle a dense network of sampling points and later the basis of constructed MS maps to determine most important points on which chemical analyses will also be performed.

Until recently, MS measurements have not been used in Croatia with the purpose of environmental quality assessment. First such measurements in Croatia were performed by Frančišković-Bilinski in 2008 on the samples from Kupa River watershed [16]. As the area with highest values of MS lower flow of Mrežnica River showed and this anomaly originates from uncareful coal burning products disposal. Preliminary measurements have also shown increased values of MS in the upper flow of Dobra River and preliminary results point to a possible impactite [17].

As was discovered by Frančišković-Bilinski [16], the Mrežnica River near Duga Resa (Croatia), contaminated by discharge of coal slag and ash from a former textile factory serves as an ideal „natural laboratory" for studying downstream transport of material in river systems. So, this study was expanded in collaboration with scientists from Germany and was published in 2017 [18].

Hasan et al. performed the first attempt of mapping of spatial variability of soil MS across Croatia in 2018 [19]. Their maps of soil MS in Croatia show two clearly differentiated distributions – Pannonian region versus karst area of Croatia and soils developed on carbonate rocks have higher values of MS and Xfd compared to soils of Pannonian region.

There are few geochemical investigations of soil pollution in Croatia, of which only one could be of interest for our current research: Sollitto et al. investigated heavy metal contamination in soils of the Zagreb region in 2010 using multivariate geostatistics [20]. They found that variation in the metal concentrations in the topsoil of Zagreb region has both natural and anthropogenic origin.

One of the most important issues in the subject of environmental magnetism is determination of connections between MS of soils and sediments vs. their heavy metal content, as well as their mineralogical composition. There are few such studies in the world which are trying to establish such relations.

Urban soils of city of Zagreb, the capital of Croatia, are not yet investigated in terms of their MS and poorly investigated in terms of their geochemistry and heavy metal pollution assessment. Therefore, **the aim of the work** is to perform such study, which will give the first insight of distribution of the low field volume MS throughout the largest part of territory of the City of Zagreb, based on in-situ field measurements. Also based on those data, the average MS value for the City of Zagreb will be proposed. Then, the most interesting locations will be selected, and soil sampling will be performed there, and geochemical content determined using ICP-OES method. Using a geostatistical approach, we will achieve the goal to determine the correlations between values of MS and particular chemical elements, respectively minerals, which are valid in the investigated region. Knowledge about these ratios will enable fast and cheap assessment of the state of environment in the broader area, without performing of complicated and expensive chemical and mineralogical analyses. Also, the final aim of our research is to evaluate and explain in detail the origin of all important anomalies of MS with respect to their anthropogenic or geogenic origin. We hope that our research will improve the overall knowledge on environmental magnetism, and will contribute to worldwide promotion of this method.

2. Study area

Zagreb is capital of the Republic of Croatia and largest city in Croatia (Figure 1).

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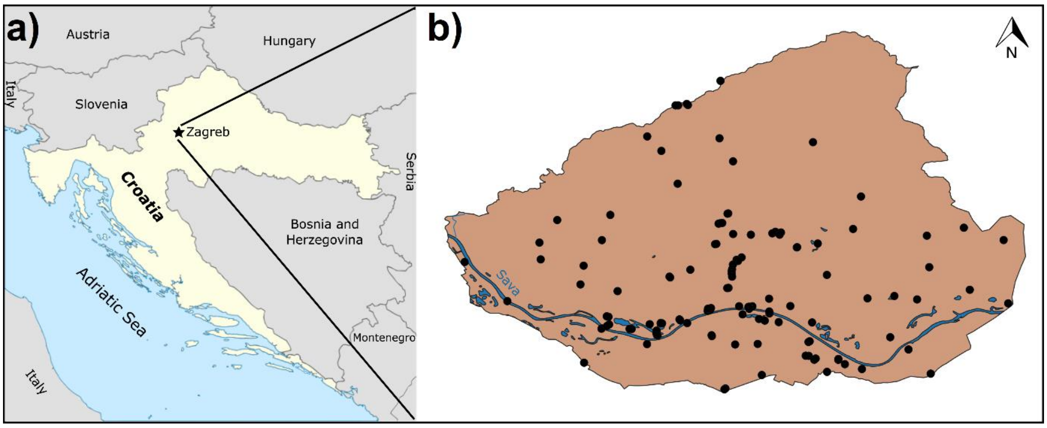

Figure 1. Overview of the study area. a) Geographical position of the Republic of Croatia and Zagreb city research area (indicated with the black star); b) Enlarged view of the Zagreb city research area with the black dots indicating sampling spots.

It has 809,268 inhabitants living on surface of 641 km^2, with the population density of 1200.56 inhab./km^2, while population of Zagreb urban agglomeration is 1,071,150 [21]. Vertically it extends from 122 m a.s.l. in the Sava River plains until 1,035 m at the top of Medvednica Mountain (Sljeme peak). Zagreb is a large traffic hub and crossroads of several highways connecting Middle Europe and Adriatic coastand a large industrial center, especially it was during the past and different anthropogenic influences are present.

The geology of the Zagreb area is various. A major part of the city is influenced by Sava River with Holocene alluvial sediments and the slopes of Medvednica Mountain by Miocene sediment cover while the core of the mountain consists of metamorphic rocks. There are parametamorphic and ortometamorphic rocks which are often interchanged at small scale area. Such distribution is a consequence of the Upper Jurassic-Lower Cretaceous metamorphism [22] of the Paleozoic-Mesozoic magmatic-sedimentary complex, made of carbonate and clastic rocks and basic magmatic rock varieties [23]. Many streams are flowing from Medvednica Mountain towards the Sava River, transporting geological material from the mountain, therefore this influence should also be considered, as well as influence of the Sava River, bringing material from Slovenian Alps.

The climate of Zagreb is very close to borders between several climate types. According to [24] it is classified as an oceanic climate (Köppen climate classification Cfb) with significant continental influences, very closely bordering on a humid continental climate (Dfa/Dfb), as well as a humid subtropical climate (Cfa). Zagreb has four separate seasons and precipitation is 840 mm yearly.

3. Materials and Methods

3.1. In-situ field measurements

In-situ field measurements, the first step of our research, were performed at 125 locations, which are presented in Figure 1b and Table A1 (see Appendix A). They were performed throughout the city of Zagreb territorial unit (excluding some rural parts like Brezovica and part of Sesvete).

Locations were selected in such a way that all parts of the study area were covered with measurement network. Special attention was given to possible pollution sources in the way that many locations were selected to be near industrial objects, around the large landfill Jakuševec, near the highways with heavy traffic, in densely populated parts of the city, etc.

Work in the field was like following: The most suitable micro-location was selected. Precise geographic coordinates were determined using GPS and each location was photographed from different angles. Within the perimeter of 5 m, 11 measurements using SM-30 instrument were performed and mean value was used as result of MS measurement for each location. On each point of measurement grass cover (or leaves cover on forested locations) was removed prior to performing of measurements.

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3.2. Sampling and sample preparation

After detailed statistical evaluation of in-situ measurements, the most interesting 25 (20% of in-situ studied locations) were selected for sampling of soil for geochemical analysis of elements using ICP-OES method. They are presented also in Table A1 (see Appendix A). When selecting those locations, following things were considered: locations with MS statistical anomalies (extremes or outliers), locations near possible pollution sources (landfill Jakuševec, industry, etc.), representative locations from each of three clusters obtained by Q-mode cluster statistical analysis, location with low MS value as representative of anthropogenically unpolluted areas.

During sampling and sample preparation following protocol was followed:

1. On each sampling location first micro-location of previous in-situ measurement was found and exact on this point sample will be taken.
2. Grass or leaves cover was removed until the bare surface of soil was reached. A square with sides of 25 cm was marked with a spade and the soil was sampled to a depth of 2 cm.
3. Soil sample is taken with a spade, packed in PVC bags and transported to the laboratory.
4. Soil samples were dried under 40°C in cardboard boxes in an air-flow. The dried soil is first sieved through 12-mesh (approximately 2 mm) sieve and after that homogenized by grounding in a mechanical mortar.
5. 40 g of each prepared sample was separated and stored in plastic container for ICP-MS analysis, rest of sample was stored separately for archive and for other possible analysis in the future.
6. In each separated prepared sample for ICP-MS analysis MS was measured in laboratory conditions prior to analysis, also using SM30 instrument.

One of the samples, the sample from Mikuševa Street – Dubec in the eastern part of the city, was sampled in two layers: upper from 0 – 2 cm and lower from 2 – 4 cm depth. Each of the sampled layers was handled as a separate sample. This location was chosen due to its lowest MS value among all studied locations and because most probably it is completely anthropogenically unpolluted. On another location, Novi Jelkovec, where MS value is also very low, two layers were also sampled – upper from 0 – 2 cm and deep from 15 – 25 cm, with the aim to investigate if there is some heavy metal migration towards deeper layers and if there are significant differences in MS value and in element concentrations between surface and deeper layer. In the case of the existence of significant differences between two observed layers, this could be thematic of a new study.

3.3. Magnetic susceptibility measurements

For determination of MS (expressed as SI units) a SM30 instrument, manufactured by ZH Instruments, Brno, Czech Republic, was used. It is a sensitive and accurate tool for both field and laboratory measurements of MS of outcropping rocks, soils, drill cores or rock samples.

The sensitivity of SM30 is 1×10^{-7} SI Units and the results are displayed in $1\text{x}10^{-3}$ SI UNITS. The sensor design enables to get 90% of its signal from the first 20 mm of the rock.

Each studied sample was measured eleven times in the field and three times in laboratory and mean value of measurements was taken as measurement result.

3.4. Determination of geochemical composition using ICP-OES

Soil samples were analyzed by the optimized BCR three-step sequential extraction procedure. The modifcation of the original protocol included the use of aqua-regia for a residual fraction (fourth step). The detailed sequential extraction method used in this research has been described in [25,26]. This manuscript considered results for the total amounts of the extracted elements, defined as the sum of the element contents in the three fractions plus aqua-regia extractable content of the residue.

Element concentrations in the water and extracts obtained at each of BCR extraction step were determined using techniques of Inductively Coupled Plasma - Optical Emission spectrometry (Thermo Scientific ICP-OES iCap 6500 Duo). The analytical data quality was controlled by using laboratory quality assurance and quality control methods, including the use of standard operating procedures, calibration with standards, and analysis of both, reagent blanks and replicates [26].

The accuracy and precision of the obtained results were checked by analyzing sediment reference material (BCR 701) for three-step sequential extraction. Acceptable accuracy (80–120%) and precision (≤ 20%) of metals was achieved for all steps of sequential extraction. Soil data in this study are reported on a dry weight mg kg^{-1} basis.

3.5. Statistical analyses

All statistical analyses were obtained using program Statistica 6.0 [27]. The following analyses were performed:

a) Determination of basic statistical parameters: N (number of cases), Mean, Geometric mean, Median, Mode, Frequency, Minimum, Maximum, Standard deviation, Skewness, Kurtosis. They were determined to present a closer view to the experimentally determined values, without presenting the whole dataset.

b) Correlation analysis was performed by calculating Pearson's correlation coefficient and presented in the form of correlation matrix to determine the strength of linear correlation of mass fractions between researched elements. Obtained values were statistically significant at $p<0.05$.

c) Boxplot method was used to determine anomalies in sediment samples. Normal or lognormal boxplots are constructed based on the empirical cumulative distribution plots. The box length was of interquartile range, where outlier values were defined between 1.5 and 3 box lengths from the upper or lower edge of the box. Extremes are values more than 3 box lengths from the edge of the box [28,29] (Reimann et al., 2005; Tukey, 1977).

d) Cluster analysis of Q-mode, in which clusters of samples are sought, was performed to find groups which contain similar samples. Cluster analysis belongs to multivariate statistics and represents a hierarchical method [30] (Kaufman and Rousseeuw, 1990).

4. Results and discussion

4.1. Distribution of MS within the City of Zagreb based on in-situ measurements

Results of in situ measurements on 125 locations throughout the study area are presented in Table A1 (see Appendix A) and basic statistical parameters are presented in Table 2.

Table 2. Basic statistical parameters (valid N, Mean, Median, Sum, Minimum, Maximum, Range, Variance and Std. deviation) of in-situ MS measurements.

	Valid N	Mean	Median	Sum	Minimum	Maximum	Range	Variance	Std.Dev.
MS	125	0.373680	0.245000	46.71000	0.054000	3.027000	2.973000	0.178747	0.422785

Several statistical analyses (determination of basic statistical parameters, boxplot analysis of anomalies and Q-mode cluster analysis) have been performed to make data more illustrative and to help in interpretation.

From the presented data we can see that Mean value for the whole study area is 0.374 x 10^{-3} SI units. Range (2.973) between minimal (0,054 x 10^{-3} SI units) and maximal (3.027 x 10^{-3} SI units) value is rather high. Minimum value is measured on a meadow in Mikuševa Street in Dubec residential area in eastern part of the city, while maximum is measured on a meadow at the Sljeme peak, 1,035 m high top of Medvednica Mountain, the highest point of the City of Zagreb (Figure 2).

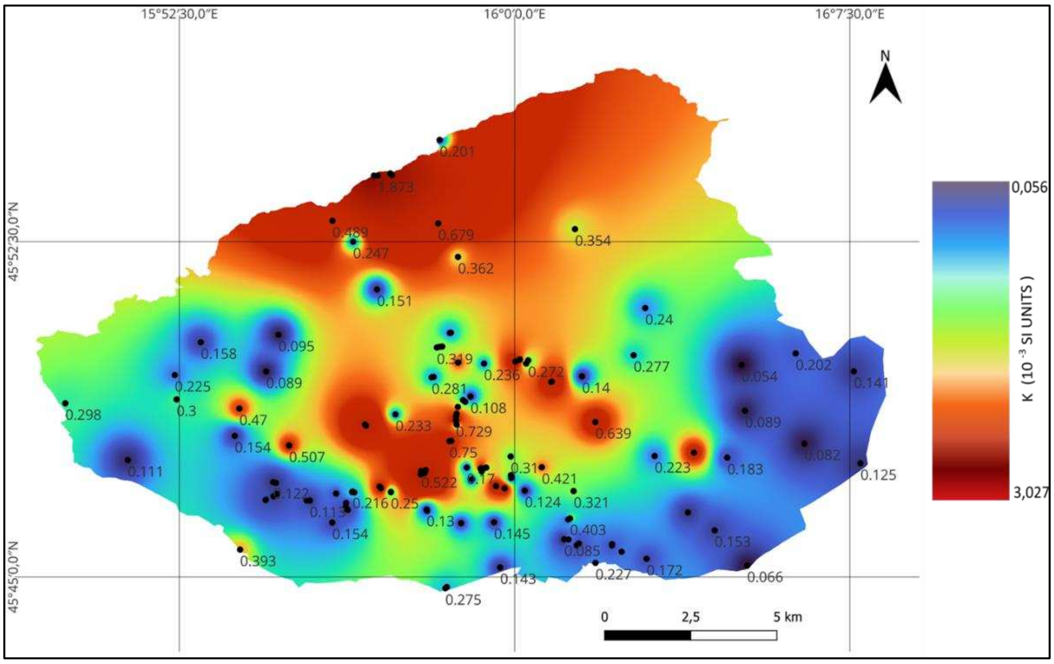

Figure 2. Zagreb city area volume specific MS contour map produced in QGIS software showing range and pattern of MS values in the research area. The highest MS values have been observed in the upper left part of the investigated area while the lowest MS values have been observed in the right and lower left part of the investigated area.

It is important to mention that according to the rather large difference between Mean and Median (0.245 x 10^{-3} SI units) it could be assumed that distribution is rather irregular and larger anomalies could be expected within the dataset.

Next step in statistical evaluation of in-situ measured MS data was boxplot statistical analysis of anomalies, which is presented in Figure 3.

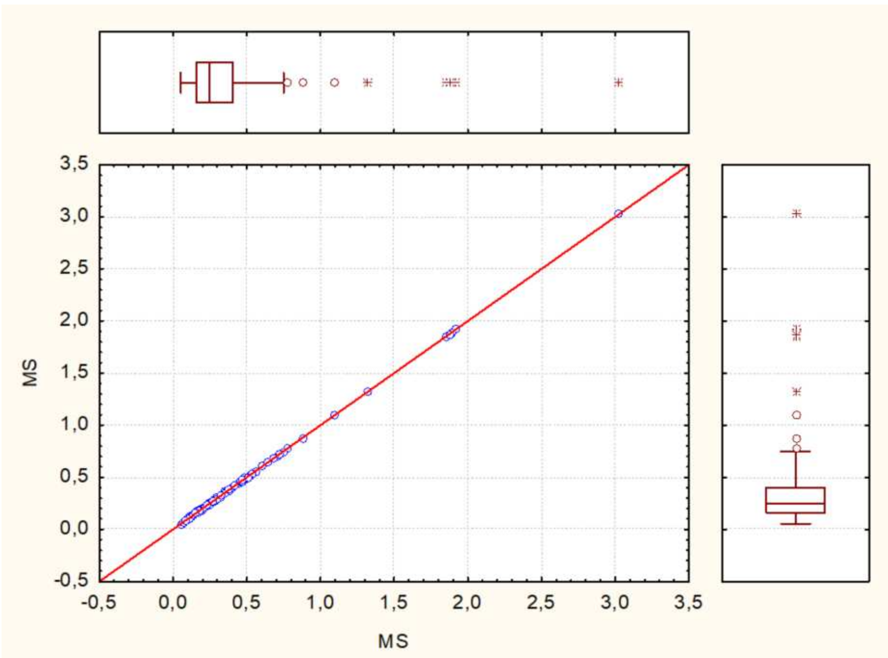

Figure 3. Statistical evaluation of in-situ measured MS data - boxplot statistical analysis of anomalies. Stars present extremes, while circles present outliers.

Boxplot evaluation showed that 6 extremes and 3 outliers are present. Strongest 4 extremes are concentrated around Sljeme, highest peak of Medvednica Mountain and surrounding ski slope. Those extremes originate as result of local geological background. The remaining two extremes are from location Prisavlje (samples 1 and 2 from this location), which are located very close to Sava River, within the inundation area. It could be assumed that those elevated MS values are caused by composition of Sava River overbank sediments, which are being deposited in this area and Sava River is bringing material from Celje old metallurgic region in Slovenia. From outliers, one (Trnjanski nasip 2) is also from area around Sava River, so its influence could be expected. The other possible explanation is that this location is very close to Kunišćak weir, place where there was inflow of Kunišćak stream, which brings material from Medvednica Mt. to Sava River. The remaining two, very weak, outliers are from both locations in The Park Pravednika među narodima, situated exactly 400 m west from the chimney of the city thermal power and heating plant, operating on oil fuel, so these anomalies could be explained as anthropogenic.

A further step in explanation and presentation of distribution of MS within the City of Zagreb was Q-mode cluster statistical analysis, in which three clusters are extracted. Results of Q-mode cluster analysis are presented in following Tables: Table 3 in which cluster means are presented, Table 4 in which Euclidean distances between clusters are presented and Tables A5–A7 (see Appendix B) in which members of each cluster are listed and distances from respective cluster center are given.

Table 3. Q-mode Cluster analysis – cluster means for in situ MS measurements, in 10^{-3} SI units.

	Cluster - No. 1	Cluster - No. 2	Cluster - No. 3
MS	0.638480	2.111600	0.212526

Table 4. Euclidean distances between clusters – in situ MS measurements.

	No. 1	No. 2	No. 3
No. 1	0.000000	2.170083	0.181437
No. 2	1.473120	0.000000	3.606481
No. 3	0.425954	1.899074	0.000000

Q-mode cluster analysis extracted following three clusters:

Cluster 1, with the MS Mean value of 0.638 x 10^{-3} SI units, is composed of 25 locations. In this cluster are present locations from different city parts, which have elevated MS values, what is caused by different factors. Some of those locations are under the Sava River influence and its old branches, some under the influence of industrial pollution, some under the different anthropogenic influences in the central and densely inhabited city parts, while some of them are with naturally elevated MS, because of their locations at the slopes of Medvednica Mountain and local geological composition. On some locations there is also influence from irresponsible waste disposal.

Cluster 2, with the MS Mean value of 2.112 x 10^{-3} SI units is composed of 5 locations, 4 of which are located around the highest Sljeme peak on Medvednica Mountain and under the natural influence of geological composition, while 1 location is at location Prisavlje in the Sava River inundation area, connected with river sediment influence.

Cluster 3, with the MS Mean value of 0.213 x 10^{-3} SI units is composed of the majority of measured locations (95 locations). In this cluster anthropogenic influence is not significantly present, despite some of locations are located right next to Jakuševec landfill, next to highways with heavy traffic, next to sewage purification plant, or next to the warehouse of the cleaning company, etc. Also, localities from this cluster are located further away from strong influences of local geology from Medvednica Mountain. Also, Mean MS value of this cluster of 0.213 x 10^{-3} SI units, which is very close to Median value of the total dataset (0.245 x 10^{-3} SI units), could be used as average MS value for the whole City of Zagreb area.

4.2. Distribution of MS within the City of Zagreb, based on laboratory measurements of selected samples

MS was measured in laboratory for collected samples on 25 selected locations. Results of laboratory MS measurements of all collected samples (including two deeper layers) are presented in Table A1.

Basic statistical parameters of samples measured in laboratory are presented in Table 8.

Table 8. Euclidean distances between clusters – in situ MS measurements.

	Valid N	Mean	Median	Sum	Minimum	Maximum	Range	Variance	Std.Dev.
MS-Lab	25	0.442120	0.319000	11.05300	0.052000	2.423000	2.371000	0.272685	0.522193

From the data, the mean value (Mean) of the samples measured in the laboratory (25 samples, only those with a layer of 0-2 cm) is higher than it was for the in-situ measurements of 125 samples and is 0.442 x 10^{-3} SI units. Also, the Median is much higher than it was for in-situ measurements and is 0.319 x 10^{-3} SI units. The range between the minimum and maximum values is slightly smaller for laboratory measured samples, where the minimum is almost the same value and in the same place (Mikuševa Street in Dubec) as in in-situ measurements, and the maximum is also in the same place (Sljeme, top of Medvednica Mt.) as is the maximum for in-situ, however, in laboratory measurements, its value is much lower than in-situ, although still very high.

Regarding these rather large deviations between the Mean/Median values between the data set measured in-situ and in the laboratory, the main cause lies in the fact that the locations of this set measured in the laboratory were selected according to the most interesting locations revealed by in-situ measurements, and one of the main criteria for selection, among other things, was the increased value of MS in the localities that were selected for sampling.

So, we can see that despite the fact that there are still a lot of deviations between results of in-situ and laboratory measurements at the same locations, statistically the data from the field (in-situ) and the laboratory are very well correlated, correlation factor 0.90.

It is interesting to see that all the samples except 2 of them had more and mostly much higher values measured in-situ than in the laboratory. At Park pravednika među narodima, ravine, the values are slightly higher in the laboratory, it can be said to be equal, and only at Jakuševec East (2) is the difference noticeable and the value measured in the laboratory is significantly higher than in the field. It is necessary to see and investigate the causes of this phenomenon. The causes could already be sought in soil moisture, the presence of vegetation, then in the fact that under the device in laboratory conditions there was only 40 g of material, and in nature on the spot an “unlimited amount”, etc. As for humidity, it was certainly present in-situ at least to some extent, while completely dry samples were measured in laboratory conditions.

Statistical analysis of anomalies was performed using the boxplot method and presented in Figure 4.

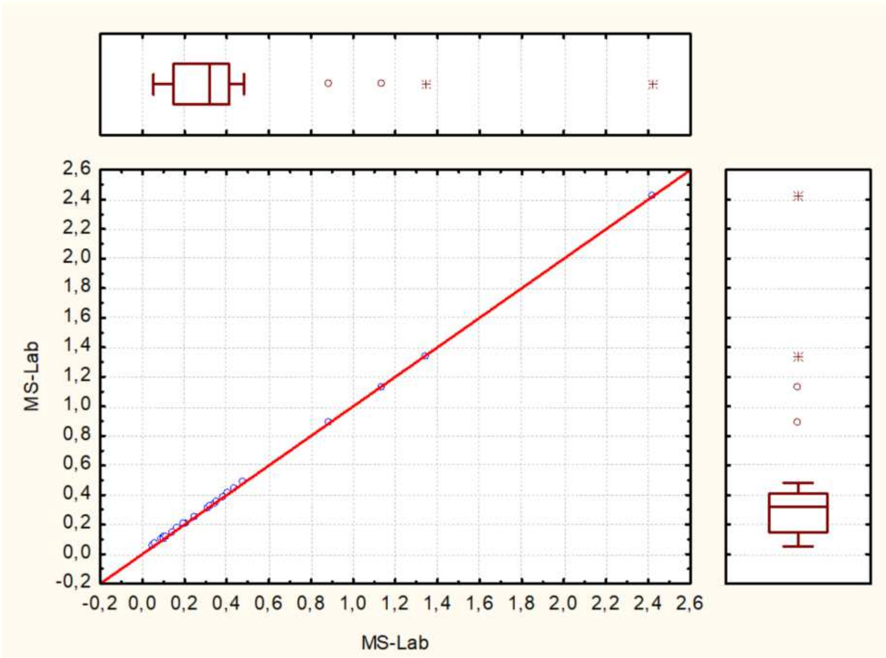

Figure 4. Statistical evaluation of laboratory measured MS data - boxplot statistical analysis of anomalies.

Boxplot analysis of laboratory measured data for 25 samples showed the existence of 2 extremes and 2 outliers. Although this is only 20% of the total number of locations where in-situ measurements were made, the results are very similar to those when as many as 125 samples were measured in the field. Namely, it was shown again that the top part of Medvednica Mt. is extremely anomalous, so that the extremes are present in the samples of Sljeme peak - meadow, and Činovnička meadow - lower part in the forest. And the outliers are present at the Prisavlje location near the Sava River (1) and in the ravine of the Park pravednika među narodima. As already assumed based on in-situ measurements, the extremes at the peak of Medvednica obviously originate from the geological structure of the terrain. The outlier on Prisavlje is probably related to the old alluvium of the Sava, while the one in the ravine in the mentioned park can be attributed to the influence of the nearby heating plant.

Further step in explanation and presentation of distribution of MS within the collected 25 samples from the City of Zagreb was Q-mode cluster statistical analysis, in which three clusters are extracted. Results of Q-mode cluster analysis are presented in following tables: Table 9 in which cluster means are presented, Table 10 in which Euclidean distances between clusters are presented and Tables 11–13 in which members of each clusters are listed and distances from respective cluster center are given.

Table 9. Q-mode Cluster analysis – cluster means for laboratory MS measurements, in 10^{-3} SI units.

	Cluster - No. 1	Cluster - No. 2	Cluster - No. 3
MS-Lab	1.633000	0.422364	0.137091

Table 10. Euclidean distances between clusters – in situ MS measurements.

	No. 1	No. 2	No. 3
No. 1	0.000000	1.465640	2.237744
No. 2	1.210636	0.000000	0.081381
No. 3	1.495909	0.285273	0.000000

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Table 11. Laboratory measurements – Members of Cluster Number 1 and distances from respective cluster center. Cluster contains 3 cases.

Locality	Distance
Činovnička livada - donji dio šuma	0.290000
Prisavlje uz Savu (1)	0.500000
Sljeme vrh - livada	0.790000

Cluster 1, mean MS value 1,633 x 10^{-3} SI units (which is very elevated), consists of 3 samples, two of which (Činovnička livada - lower part in the forest and Sljeme vrh - meadow) are at the top of Medvednica Mt., while one (Prisavlje near the Sava River (1)) is located in the inundation of the Sava in the immediate vicinity of its course. The causes of elevated MS in this cluster are natural - on Medvednica Mt. due to the influence of local geology, and on Prisavlje the influence of old alluvium from the Sava River.

Table 12. Laboratory measurements – Members of Cluster Number 2 and distances from respective cluster center. Cluster contains 11 cases.

Locality	**Distance**
Borongaj cesta-šuma	0.060636
Crkva Sv. Jakov	0.081364
Činovnička livada - dno (2)	0.035364
Poglavarstvo grada Zagreba (2)	0.115364
Jakuševec istok (2)	0.101364
JANAF terminal Žitnjak	0.014636
Jaruga Rebar - Kozjak (1)	0.073364
Maksimir blizu Bukovačke	0.103364
Park pravednika među narodima. jaruga	0.460636
Strossmayerov trg	0.013364
Trnjanski nasip (2)	0.012364

Cluster 2, mean values of MS 0.422 x 10^{-3} SI units (moderately elevated) consists of 11 locations from all parts of the city. A combination of natural and anthropogenic influences can be assumed here. Thus, natural influences (local geology) are likely at the Church of St. Jakov and the bottom of the Činovnička meadow on Medvednica Mt., and it is possible that they are at least partly the cause in the area of Maksimir and the Rebar-Kozjak ravine, perhaps also near Borongaj. On the Trnjanski nasip (2), both anthropogenic and natural influence is possible, and the natural one would be the possible delivery of alluvium by the Kunišćak stream. In the Park Pravednika među narodima (ravine), the anthropogenic impact of the nearby thermal power plant is very likely, at the JANAF oil terminal in Žitnjak, the anthropogenic impact of the said terminal, and in Jakuševac-East, the impact of the waste dump. In the central part of the city (near the City Polgavarstvo, and on Strossmayer Square) there is almost certainly an anthropogenic impact, since it is a very densely populated and built-up area with a lot of traffic.

Table 13. Laboratory measurements – Members of Cluster Number 3 and distances from respective cluster center. Cluster contains 11 cases.

Locality	**Distance**
Autocesta. petlja Hrušćica	0.030091
Bauhaus Buzin	0.043091
Bejzbol klub Jarun uz Savu (3)	0.038091
Bundek istok	0.033909
Grubišnopoljski put - Rudeš	0.110909
Jakuševec sredina (2)	0.025091

Mala Mlaka uz vodocrpilište (1)	0.070909
Mikuševa - Dubec. 0-2 cm	0.085091
Novi Jelkovec 0-2 cm	0.071091
Šire područje oko ustave Kunišćak	0.011909
Tuškanac. livada	0.064909

Cluster 3, mean value 0.137 x 10^{-3} SI units, consists of 11 remaining locations from all parts of the city. It is very interesting that in this cluster, with the lowest MS values, there are also two locations next to the busiest highway in Croatia (Bauhaus Buzin, and the Hrušćica interchange), as well as a location right next to the middle of the Jakuševec landfill, which would preliminarily indicate that these locations are not under strong anthropogenic influence.

4.3. Element distribution in soils of Zagreb area

Results of ICP-OES analysis for 20 elements at 25 selected locations and presented in Table 14. In total there are 27 results, as on two locations additional layer was sampled for comparison (besides layer 0 – 2 cm, on which sampling was performed).

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Table 14. Results of ICP-MS analysis for 20 elements: Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Sb, Sr and Zn (element concetrations are in ppm).

Sample name Element	Al	As	B	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	Pb	Sb	Sr	Zn
Autocesta petlja Hrušćica	7107	3.70	1.95	55.0	63370	0.39	5.76	14.05	17.14	15567	936	13.52	13584	444	22.75	19.37	15.21	1.22	49.46	59.7
Bauhaus Buzin	8865	4.94	3.76	57.3	65982	0.50	8.29	17.28	20.55	19513	1079	18.63	15449	627	17.34	26.98	17.82	1.30	42.32	60.0
Bejzbol Klub Jarun Uz Savu (3)	5561	2.45	2.06	40.7	58844	0.38	4.73	10.75	14.22	13453	946	10.95	13776	442	7.27	14.89	15.45	0.88	32.17	52.1
Borongaj cesta-šuma	14757	9.08	1.34	46.4	6024	0.57	18.97	34.02	44.94	32471	1311	25.97	5125	766	5.65	38.11	20.79	4.20	13.71	73.1
Bundek-istok	11806	3.18	3.14	93.8	24978	0.57	18.27	36.81	34.82	26024	1520	14.28	9175	665	7.06	30.52	21.93	3.86	26.83	73.3
Crkva Sv. Jakov	16895	1.61	0.77	79.4	7073	0.86	23.51	71.53	54.73	25735	626	15.28	6947	861	2.55	41.04	68.82	6.00	18.41	85.4
Činovnička livada - donji dio - šuma	19627	2.42	1.46	53.1	4609	0.93	23.42	49.14	33.31	30134	726	17.93	5051	1334	8.64	26.99	43.93	6.71	16.29	92.5
Činovnička livada - dno (2)	17985	2.84	1.37	70.0	2660	1.16	11.86	24.86	31.13	25659	897	25.61	4984	1519	23.16	18.41	67.00	2.50	9.08	110.7
Poglavarstvo grada Zagreba (2)	8922	4.92	3.24	83.2	49963	0.54	9.09	21.00	28.11	17905	960	15.37	13560	577	28.42	23.81	42.98	1.98	31.97	87.7
Grubišnopoljski put - Rudeš	10857	5.44	4.01	80.8	35585	0.56	9.71	22.55	36.74	22132	992	16.81	10786	587	10.19	28.28	32.56	2.13	23.85	94.5
Jakuševec Istok (2)	6730	3.76	3.85	56.4	60186	0.38	7.68	16.53	18.06	16171	917	10.44	11971	425	20.28	17.33	20.30	1.78	43.66	110.4
Jakuševec Sredina (2)	5147	3.12	1.24	92.8	82694	0.37	4.58	15.37	17.11	12038	787	12.26	14452	331	20.10	14.24	42.99	1.63	42.63	69.0
Janaf Terminal Žitnjak	2929	1.53	0.91	54.5	60634	0.44	9.63	14.25	12.52	9770	325	5.70	12988	211	13.03	46.20	45.20	1.09	32.42	85.8
Jaruga Rebar - Kozjak (1)	15450	4.75	7.35	135.4	9418	0.75	12.14	29.20	45.63	25123	1904	14.31	2789	368	11.56	18.54	39.08	2.28	30.90	130.6
Potok u Maksimiru blizu Bukovačke	11748	6.00	2.56	93.1	17372	0.67	19.17	35.01	31.76	27881	1166	12.46	6878	880	8.70	23.57	60.30	3.27	22.39	89.6
Mala Mlaka - uz vodocrpilište (1)	13293	6.71	6.40	84.6	40083	0.74	11.41	23.86	47.76	24904	1542	23.35	10909	825	26.12	35.93	31.09	1.63	29.95	86.1
Mikuševa ulica - Dubec. 0-2 cm	14993	4.98	3.48	91.2	9016	0.64	8.30	30.10	25.85	22960	1308	18.67	3974	285	7.59	32.16	18.25	2.09	47.76	66.2
Novi Jelkovec. 0-2 cm	18496	4.40	2.98	92.2	9744	0.73	7.09	34.85	28.27	26461	1338	20.32	4244	219	6.14	31.48	19.90	1.95	48.48	77.7
Park Pravednika među narodima - jaruga	14292	12.07	8.31	79.1	23999	0.71	14.16	36.19	37.47	25872	2033	19.27	7679	595	21.04	57.11	25.96	2.63	33.78	85.2
Prisavlje - uz Savu (1)	7675	6.20	2.50	203.9	82630	0.72	5.88	25.30	26.37	17616	684	13.24	13279	392	104.63	18.53	34.22	1.96	81.11	127.7
Sljeme Vrh - livada	17470	0.33	0.79	73.6	8048	0.95	26.30	49.14	46.35	35025	1468	17.44	5488	1641	25.19	25.37	65.45	6.75	19.43	153.2
Strossmayerov Trg	9977	6.04	3.80	118.5	46635	0.62	12.48	27.12	43.03	21675	1108	15.09	11520	692	30.36	25.04	58.45	3.25	37.08	100.2
Šire područje oko Ustave Kunišćak	16021	6.31	4.45	114.0	10058	1.02	12.87	28.23	31.47	28312	1328	23.20	5940	849	7.40	37.66	32.25	1.89	14.50	82.7
Trnjanski nasip (2)	9524	4.42	3.48	99.0	33054	0.60	8.09	21.93	26.93	17140	1383	11.80	8040	463	23.80	31.25	36.52	2.15	31.06	108.1
Tuškanac-livada	14391	6.17	0.81	93.6	5075	0.40	10.33	27.00	20.53	22357	652	16.34	3567	355	11.06	17.62	77.83	2.06	9.57	58.7
Mikuševa ulica - Dubec. 2-4 cm	13841	4.81	2.18	92.1	7390	0.65	7.85	27.21	24.75	22314	961	16.74	3727	272	4.73	30.52	19.06	1.50	45.19	64.0
Novi Jelkovec. 15-25 cm	21964	6.01	3.41	104.9	8768	0.90	9.42	40.79	33.25	31012	1474	23.94	4561	329	14.94	35.74	20.89	2.32	49.31	85.7

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Basic statistical parameters of those results are presented in Table 15.

Table 15. Basic statistical parameters and ICP results (Valid N, Mean, Median, Sum, Minimum, Maximum, Range, Variance and Std.Dev.).

	Valid N	Mean	Median	Sum	Minimum	Maximum	Range	Variance	Std.Dev.
Al	27	12456.38	13293.04	336322.3	2929.395	21963.72	19034.33	23708144	4869.10
As	27	4.75	4.81	128.2	0.329	12.07	11.74	6	2.40
B	27	3.02	2.98	81.6	0.774	8.31	7.53	4	1.94
Ba	27	86.60	84.61	2338.3	40.669	203.86	163.19	1073	32.76
Ca	27	30884.88	23999.33	833891.7	2660.019	82693.63	80033.61	687813701	26226.20
Cd	27	0.66	0.64	17.8	0.367	1.16	0.79	0	0.21
Co	27	11.89	9.71	321.0	4.580	26.30	21.72	36	5.97
Cr	27	29.04	27.12	784.1	10.752	71.53	60.78	171	13.08
Cu	27	30.84	31.13	832.8	12.523	54.73	42.21	125	11.17
Fe	27	22786.01	22959.73	615222.2	9770.359	35024.52	25254.16	40204133	6340.67
K	27	1124.87	1078.96	30371.4	324.710	2033.26	1708.55	155497	394.33
Li	27	16.63	16.34	448.9	5.703	25.97	20.27	24	4.92
Mg	27	8534.94	7678.73	230443.4	2788.817	15448.99	12660.17	16525554	4065.16
Mn	27	627.89	576.95	16953.0	211.495	1640.70	1429.21	140427	374.74
Na	27	18.14	13.03	489.7	2.551	104.63	102.08	366	19.12
Ni	27	28.40	26.99	766.7	14.240	57.11	42.87	104	10.19
Pb	27	36.82	32.56	994.2	15.207	77.83	62.62	350	18.70
Sb	27	2.63	2.09	71.0	0.877	6.75	5.87	3	1.60
Sr	27	32.72	31.97	883.3	9.079	81.11	72.03	251	15.85
Zn	27	87.77	85.66	2369.9	52.092	153.21	101.12	578	24.03

To get a better insight about element distribution, boxplot statistical method was applied to ICP-OES results and its results are presented in Figure A5 (see Appendix C).

As one can see from Appendix C, 9 of 20 studied elements (45% of them) do not show any anomaly and most of them have regular normal distribution. Elements without any anomaly are: Al, Ca, Cu, Fe, K, Li, Mg, Ni and Pb. Rest of elements mostly show only one anomaly, among which outliers prevail.

According to boxplot analysis, it is obvious that majority of studied elements show natural distribution and anthropogenic influence is not likely, at least not large, especially when taking into account that maximal concentrations of elements are not high, but this will be discussed later. There are only two extremes, of Ba and of Na, located at Prisavlje near Sava River. All other determined anomalies are outliers, most of them very weak. Also, all elements except one which show anomalies have only one anomaly – only Sb shows three outliers.

Within the whole Zagreb city area only three zones with anomalous concentrations of some elements can be defined:

1. Park pravednika među narodima jaruga: This location is situated within a ravine located very close to thermal powerplant/heating plant, operating on fuel oil. This ravine was surrounded by the fence and during the past it was within the area of this plant and there are signs that fuel oil contaminated soil there. So, this is the most probable reason for anomalies of As and B at this location [31,32].

2. Medvednica Mountain highest part of mountain ridge, represented by several locations: Sljeme vrh livada (just at the top of the mountain), Činovnička livada donji dio šuma, Činovnička livada dno and Crkva Sv. Jakov. On those locations of this mountain zone several outliers of heavy metals are present: Cd, Cr, Mn, Sb, Co and Zn. This area is far away from any pollution source, so it could be assumed that those anomalies are of natural origin, due to geological composition of metamorphic rocks. In this part of research area Pb-Zn ore bodies inside the ortometamorphic rocks are present [23]. Those bodies are usually associated with the afore-mentioned heavy metals.

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Therefore, mentioned outliers in this area are probably connected with the geological background of the area [33].

3. Prisavlje uz Savu – this location is situated within Sava River inundation and soils are partially composed of overbank sediments of Sava River. Only two extremes found within the current research, those of Ba and Na, are found on this location and extreme of Na is extremely high. Besides them outlier of Sr is present too at this location.

4.4. Determination of correlations between MS and elements

Correlations between measured MS in situ and in laboratory and 20 determined elements using ICP-OES are presented in Table 16.

Table 16. Correlation matrix between in situ and laboratory MS measurements (SI units) and elements determined using ICP-OES. Marked correlations (in red) are significant at p < ,05000, N=27.

	Al	As	B	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	Pb	Sb	Sr	Zn
MS in-situ	0,22	-0,25	-0,23	0,15	-0,14	0,52	0,54	0,34	0,32	0,35	-0,01	0,06	-0,13	0,74	0,45	-0,09	0,48	0,63	-0,18	0,75
MS lab	0,21	-0,18	-0,15	0,07	-0,12	0,38	0,60	0,41	0,34	0,39	0,07	-0,01	-0,13	0,63	0,36	0,04	0,37	0,68	-0,12	0,69

Highest correlations are observed between elements and volume specific MS measured in situ, while a bit lower are for those measured in laboratory conditions. Strongest correlations of MS are present for Zn, Mn, Sb, Co and Cd and a bit weaker (but also significant) with Fe, Cr, Pb and Na.

The next step was to compare boxplot results of anomalies determination between magnetic parameters and of elements. So, boxplot determination of anomalies of laboratory measurements using SM-30 device showed the existence of 2 extremes and 2 outliers. It was again shown that the top part of Medvednica Mt. is extremely anomalous, so that the extremes are present in the samples of Sljeme peak - meadow, and Činovnička meadow - lower part in the forest. And the outliers are present at the Prisavlje location near the Sava River (1) and in the ravine of the Park pravednika među narodima. When we compare that with boxplot determination results of 20 determined chemical elements we can see that they have anomalies exact on those locations, plus two more locations (Činovnička livada dno (2) and Crkva Sv. Jakov) within the same zone of Medvednica Mt. ridge, where measured MS values were also a bit elevated.

It can be concluded that measuring MS directly in the field using a small field instrument like SM-30 is really a very effective tool for screening large areas searching for possible heavy metal pollution. In such a way a large number of unnecessary chemical analyses can be avoided and whole process could be speed up.

4.5. Estimation of state of anthropogenic pollution of Zagreb, determination of average MS value of urban soils and recommendations for future

Based on distribution of measured elements concentrations and low number of mostly weak anomalies, as well as on not very high maximal concentrations, it could be estimated that generally in Zagreb city area anthropogenic influence (with respect to heavy metals) is not large. From determined anomalies there is indication of some degree of anthropogenic pollution for two of them: possible fuel oil contamination at Park Pravednika među narodima jaruga (ravine) and some unknown contamination at Prisavlje near Sava River (1). It is very interesting that at locations around the large communal waste landfill Jakuševec MS values and element concentrations do not show anomalies and similar is at locations near the largest highways.

We propose that Median value of 0.245×10^{-3} SI units is used in the future as relevant average value for soils in Zagreb City area. This value is much more realistic than Mean value of 0.374×10^{-3} SI units, as this value is increased under the influence of several present extremes, which significantly increase the Mean value.

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When geochemical data of current research are compared with several selected cities (Palermo, Lisbon and Ljubljana) and with world average, we can see that heavy metal concentrations in Zagreb are not very high (Table 17).

Table 17. Comparison of selected heavy metals concentrations (ppm) between Zagreb, several European cities and world average. Data composed from [34,35].

Element/city	Zagreb – current study	Palermo[34]	Lisbon[35]	Ljubljana[35]	World average (16 cities)[35]
Pb	Min-max: 15.21 – 77.83 Mean: 36.82; Median: 32.56	Min-max: 57 – 2516 Median: 253	Min-max: 0.55–12.2 Mean: 8.5	Min-max: 30 – 57 Mean: 40	Min-max: nd–5469 Mean: 84.1
Zn	Min-max: 52.09 – 153.21 Mean: 87.77; Median: 85.66	Min-max: 52 – 433 Median: 151	-	-	-
Cu	Min-max: 12.52 – 54.73 Mean: 30.84; Median: 31.13	Min-max: 10 – 344 Median: 77	-	-	-
Cd	Min-max: 0.37 – 1.16 Mean: 0.66; Median: 0.64	Min-max: 0.27 – 3.80 Median: 0.84	Min-max: 0.11–1.04 Mean: 0.41	-	Min-max: nd–20.3 Mean: 0.396
Cr	Min-max: 10.75 – 71.53 Mean: 29.04; Median: 27.12	Min-max: 12 – 100 Median: 39	Min-max: 9.61–88.5 Mean: 51.5	Min-max: 24–66 Mean: 41	Min-max: nd–1586 Mean: 55.6
Co	Min-max: 4.58 – 26.30 Mean: 11.89; Median: 9.71	Min-max: 1.5 – 14.8 Median: 6.5	-	-	-
Ni	Min-max: 14.24 – 57.11 Mean: 28.40; Median: 26.99	Min-max: 7.0 – 38.6 Median: 19.1	Min-max: 9.77–120.4 Mean: 62.4	Min-max: 30 – 56 Mean: 39	Min-max: nd–727 Mean: 34.6
V	-	Min-max: 21 – 124 Median: 58	-	-	-

Situation with some heavy metals will be shortly discussed:

Pb concentrations in Zagreb are much lower than in Palermo and slightly lower than in Ljubljana, also more than two times lower than the world average, but they are much higher than in Lisbon.

Zn and Cu concentrations in Zagreb are about 2 times lower than in Palermo, while for other cities and world average data do not exist.

Cd concentrations in Zagreb are lower than in Palermo, but higher than in Lisbon. For Ljubljana data do not exist. And in comparison with the world average Cd concentrations in Zagreb are a bit higher.

Cr concentrations in Zagreb are significantly lower than those in Palermo, Lisbon and Ljubljana, also than world average.

Co concentrations in Zagreb are a bit higher than those in Palermo, while for other cities and world average data do not exist.

Ni concentrations in Zagreb are a bit higher than in Palermo, about 2 times lower than in Lisbon and significantly lower than in Ljubljana and of world average.

V was not measured in Zagreb, so it cannot be compared.

In Croatia a specific legislation about heavy metals in “urban soils” does not exist. But, there is legislation about agricultural soils, with which we can make comparisons (Table 18).

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Table 18. Selected heavy metals concentrations (mg kg-1) allowed in soils according to the Croatian Legislation for protection of agricultural soil from contamination [36].

Soil type/element	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Sandy soil	0.0-0.5	0-40	0-60	0.0-0.5	0-30	0-50	0-60
Powdery - loamy soil	0.5-1.0	40-80	60-90	0.5-1.0	30-50	50-100	60-150
Clay soil	1.0-2.0	80-120	90-120	1.0-1.5	50-75	100-150	150-200

According to this legislation, soils are divided into following categories: Sandy soil, Powdery - loamy soil and Clay soil. Based on our field experience, soils in Zagreb area vary from sandy soils near Sava River to clay soils on some locations. One can say that "in average" Zagreb soils are closest to powdery-loamy soils.

When heavy metal concentrations from our study are compared with Croatian legislation for agricultural soils, we can see that mean concentrations of Pb, Cu, Cr and Ni are within limits of the strictest rule, which is valid for sandy soils. Concentrations of Zn and Cd are within the limits of rule valid for powdery-loamy soils. When we compare maximal values for those elements with legislation for agricultural soils, majority of them show maximal values within the range of allowed concentrations for powdery-loamy soils and no element has maximal value out of range allowed for clay soils. That indicates that studied soils within the City of Zagreb are rather unpolluted regarding heavy metals. Also, we should be aware that soils on studied locations are not used for agriculture, as they are situated in parks and other green areas of mostly urban zones, situation is even better.

Several parts of our research are pointing towards the conclusion that investigated area within Zagreb is rather unpolluted due to heavy metal concentrations and that known pollution sources, e.g., road traffic, Jakuševec landfill and some industrial objects do not influence significantly on heavy metal concentrations in their surroundings. However, there are some exceptions, e.g., thermo-power and heating plant. But, in each case regular monitoring should be advised and besides heavy metals also organic pollutants should be included.

A very important finding of our research is that in-situ MS measurements were proved to be a very efficient tool for initial screening of a large area in the terms of searching for possible heavy element contamination.

5. Conclusions

Our research lead to the following conclusions:

- This study was performed to get the first insight of distribution of MS in the City of Zagreb and to establish correlations between magnetic parameters and concentrations of heavy metals.
- The median value of 0.245 x 10-3 SI units, obtained by in-situ measurements is proposed to be used in the future as relevant average value of MS in Zagreb City area.
- Mean concentrations of most heavy metals measured in Zagreb: Pb (36.82 μg/g), Zn (87.77 μg/g), Cu (30.84 μg/g), Cd (0.66 μg/g), Cr (29.04), Co (11.89) and Ni (28.40) are relatively low in comparison with Croatian legislation for agricultural soils, also with values reported for several other cities in Europe and with world average.
- Boxplot analysis showed that 9 of 20 studied elements (45% of them) do not show any anomaly and most of them have regular normal distribution. Elements without any anomaly are Al, Ca, Cu, Fe, K, Li, Mg, Ni and Pb. The rest of the other elements mostly show only one anomaly, among which outliers prevail.
- Boxplot analysis confirmed that heavy metal anomalies are located at the same sampling points where MS anomalies are located.
- Correlation analysis between measured magnetic parameters and analyzed chemical elements showed that very good correlations exist, especially with in-situ measurements: Cd (0.52), Co (0.54), Fe (0.35), Mn (0.74), Na (0.45), Pb (0.48), Sb (0.63) and Zn (0.75).
- Based on the in-situ MS measurements, it can be assumed that there is no contamination in some areas where one could expect it (close to industrial areas, landfill etc.). In the Zagreb city area, one can say that there is mostly geogenic influence driving the MS changes.

• In-situ MS measurements were proved to be a very efficient tool for initial screening of a large area in the terms of searching for possible heavy element contamination, what can enable cheap and fast assessment of state of environment in the area of the whole Croatia.

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Appendix A

In this Appendix, the sample list for Zagreb study area was provided followed with geographical coordinates and MS in situ/laboratory measurements values for each sampling location.

Appendix B

In this Appendix, the part of the results of Q-mode cluster analysis is presented in 3 tables in which members of each cluster are listed and distances from respective cluster center are given.

Appendix C

In this Appendix, the results of boxplot statistical method applied to ICP-MS results – element distribution are shown.

References

1. Thompson, R.; Oldfield, F. *Environmental Magnetism*; Allen & Unwin: London, UK, 1986.
2. Oldfield, F.; Hunt, A.; Jones, M.D.H.; Chester, R.; Dearing, J.A.; Olsson, L.; Prospero, J.M. (1985) Magnetic differentiation of atmospheric dusts. *Nature* **1985**; pp. *317*, 516–518. https://doi.org/10.1038/317516a0
3. Hay, K.L.; Dearing, J.A.; Baban, S.M.J.; Loveland, P. A preliminary attempt to identify atmospherically derived pollution particles in English topsoils from magnetic susceptibility measurements. *Phys Chem Earth* **1997**; *22(1–2)*, pp. 207–210. https://doi.org/10.1016/S0079-1946(97)00104-3
4. Heller, F., Strzyszcz, Z., Magiera, T. Magnetic record of industrial pollution in forest soils of Upper Silesia, Poland. *J Geophys Res* **1998**; *103(B8)*, pp. 17767–17774. https://doi.org/10.1029/98JB01667
5. Scholger, R. Heavy metal pollution monitoring by magnetic susceptibility measurements applied to sediments of the river Mur (Styria, Austria). *Eur J Environ Eng Geophys* **1998**; *3*, pp. 25–37.
6. Plater, A.J.; Ridgeway, J.; Appleby, P.G.; Berry, A.; Wright, M.R. (1998) Historical contaminant fluxes in the Tees estuary, UK. *Mar Pollut Bull* **1998**; *37*, pp. 343–360. https://doi.org/10.1016/S0025-326X(99)00052-1
7. Kapička, A.; Petrovský, E.; Ustjak, S.; Macháčková, K. Proxy mapping of fly ash pollution of soils around a coal-burning power plant. *J Geochem Explor* **1999**; *66*, pp. 291–297. https://doi.org/10.1016/S0375-6742(99)00008-4
8. Strzyszcz, Z. (1993) *Magnetic susceptibility of soils in the areas influenced by industrial emissions*. In: Schulin R. (ed.) Soil Monitoring, Birkhäuser Verlag, Basel, Switzerland **1993**; pp. 255–269.
9. Strzyszcz, Z.; Magiera, T.; Heller, F. The influence of industrial emissions on the magnetic susceptibility of soils in Upper Silesia. *Stud Geophys Geod* **1996**; *40*, pp. 276–286. https://doi.org/10.1007/BF02300743
10. Hanesch, M.; Scholger, R. Monitoring of heavy metal loadings in soils by means of magnetic susceptibility measurements. *Env Geol* **2002**; *42*, pp. 857–870. https://doi.org/10.1007/s00254-002-0604-1

11. Petrovský, E.; Ellwood, B. *Magnetic monitoring of air- land- and water-pollution.* In: Maher B, Thompson R (eds) Quaternary Climates, Environments and Magnetism, Cambridge University Press, Cambridge, UK **1999**; pp 279–322.
12. Wang, X.S.; Qin, Y. Correlation between magnetic susceptibility and heavy metals in urban topsoil: a case study from the city of Xuzhou, China. *Environ Geol* **2005**; *49*, pp. 10–18. https://doi.org/10.1007/s00254-005-0015-1
13. Lu, S.G.; Bai, S.Q. Magnetic characterization and magnetic mineralogy of the Hangzhou urban soils and its environmental implications. *Chin J Geophys* **2008**; *51(3)*, pp. 549–557. https://doi.org/10.1002/cjg2.1245
14. Lu, S.G.; Wang, H.; Guo, J. Magnetic response of heavy metals pollution in urban soils: magnetic proxy parameters as an indicator of heavy metals pollution. 19th World Congress of Soil Science, Soil Solutions for a Changing World. **1 – 6 August 2010**, Brisbane, Australia.
15. El Baghdadi, M.; Barakat, A.; Sajieddine, M.; Nadem, S. Heavy metal pollution and soil magnetic susceptibility in urban soil of Beni Mellal City (Morocco). *Environ Earth Sci* **2012**; *66*, pp. 141–155. https://doi.org/10.1007/s12665-011-1215-5
16. Frančišković-Bilinski, S. Detection of coal combustion products in stream sediments by chemical analysis and magnetic susceptibility measurements. *Min Mag* **2008**; *72*, pp. 43–48. https://doi.org/10.1180/minmag.2008.072.1.43
17. Frančišković-Bilinski, S.; Bilinski, H.; Scholger, R.; Tomašić, N.; Maldini, K. Magnetic spherules in sediments of the sinking karstic Dobra River (Croatia). *J Soils Sediments* **2014**; *14*, pp. 600–614. https://doi.org/10.1007/s11368-013-0808-x
18. Frančišković-Bilinski, S.; Bilinski, H.; Maldini, K.; Milović, S.; Zhang, Qi; Appel, E. Chemical and magnetic tracing of coal slag pollutants in karstic river sediments. *Environ Earth Sci* **2017**; *76*, pp. 476. https://doi.org/10.1007/s12665-017-6792-5
19. Hasan, O.; Miko, S.; Ilijanić, N.; Ivkić Filipović, I.; Steinberger, A.; Marjanović, H.; Grahovac, B. Spatial variability of soil magnetic susceptibility across Croatia. 13. KONGRES HRVATSKOG TLOZNANSTVENOG DRUŠTVA **10 –14 September 2018**, Vukovar, Croatia.
20. Sollitto, D.; Romić, M.; Castrignanò, A.; Romić, D.; Bakić, H. Assessing heavy metal contamination in soils of the Zagreb region (Northwest Croatia) using multivariate geostatistics. *Catena* **2010**; *80*, pp. 182–194. https://doi.org/10.1016/j.catena.2009.11.005
21. Wikipedia (2023a) Zagreb. Wikimedia Foundation. Last modified June 28, 2023, 21:28. https://hr.wikipedia.org/wiki/Zagreb. Accessed 04 July 2023
22. Mišur, I.; Balen, D.; Klötzli, U.; Belak, M.; Massonne, H.-J.; Brlek, M.; Brčić, V. Petrochronological study of chloritoid schist from Medvednica Mountain (Zagorje Mid-Transdanubian zone, Croatia). *Geol Croat* **2023**; *76(1)*, pp. 13–36. https://doi.org/10.4154/gc.2023.02
23. Šikić, K. *Geološki vodič Medvednice*. Institut za geološka istraživanja, INA-industrija nafte, Zagreb, Croatia, **1995**.
24. Wikipedia (2023b) Zagreb climate. Wikimedia Foundation. Last modified June 26, 2023, 20:59. https://en.wikipedia.org/wiki/Zagreb#Climate. Accessed 04 July 2023
25. Passos, E. de A.; Alves, J.C.; Santos, I.S. dos; Alves, J. do P.H.; Garcia, C.A.B.; Costa, A.C.S. Assessment of trace metals contamination in estuarine sediments using a sequential extraction technique and principal component analysis. *Microchem* **2010**; *96*, pp. 50–57. https://doi.org/10.1016/j.microc.2010.01.018
26. Sakan, S.; Popović, A.; Anđelković, I.; Đorđević, D. Aquatic Sediments Pollution Estimate Using the Metal Fractionation, Secondary Phase Enrichment Factor Calculation, and Used Statistical Methods. *Environ. Geochem. Health* **2016**; *38*, pp. 855–867. https://doi.org/10.1007/s10653-015-9766-0
27. StatSoft. Statistica, Data analysis software system, Version 6, **2001**
28. Reimann, C.; Filzmoser, P.; Garrett, R.G. Background and threshold: critical comparison of methods of determination. *Sci Total Environ* **2005**; *346*, pp. 1–16. https://doi.org/10.1016/j.scitotenv.2004.11.023
29. Tukey, J.W. *Exploratory data analysis*, Addison-Wesley, Reading, MA, USA, **1977**.
30. Kaufman, L.; Rousseeuw, P.J. *Finding Groups in Data: An Introduction to Cluster Analysis*. Wiley Series in Probability and Statistics, New Jersey, USA, **1990**.
31. WHO. *World Health Organization & International Programme on Chemical Safety Boron*. World Health Organization, **1998**. https://apps.who.int/iris/handle/10665/42046 . Accessed 22 June 2023
32. Schreiber, M.E.; Cozzarelli, I.M. Arsenic release to the environment from hydrocarbon production, storage, transportation, use and waste management. *J Hazard Mater* **2021**; *411*, pp. 1–16. https://doi.org/10.1016/j.jhazmat.2020.125013
33. Sun, G.T.; Zhou, J.X. Application of Machine Learning Algorithms to Classification of Pb–Zn Deposit Types Using LA–ICP–MS Data of Sphalerite. *Minerals* **2022**; *12(10)*, pp. 1293. https://doi.org/10.3390/min12101293
34. Manta, D.S.; Angelone, M.; Bellanca, A.; Neri, R.; Sprovieri, M. Heavy metals in urban soils: a case study from the city of Palermo (Sicily), Italy. *Sci Total Environ* **2002**; *300(1-3)*, pp. 229-243. https://doi.org/10.1016/s0048-9697(02)00273-5.

35. Silva, H.F.; Silva, N.F.; Oliveira, C.M.; Matos, M.J. Heavy Metals Contamination of Urban Soils-A Decade Study in the City of Lisbon, Portugal. *Soil Syst* **2021**; *5*, pp. 1–27. https://doi.org/10.3390/soilsystems5020027
36. NN. *Pravilnik o zaštiti poljoprivrednog zemljišta od onečišćenja*. Narodne novine, **2014**. https://narodne-novine.nn.hr/clanci/sluzbeni/full/2014_01_9_167.html. Accessed 22 June 2023