minerals

Article

Magnetic and Geochemical Properties of Zagreb City Area Soils

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Abstract: This study was performed to derive the first insight into the distribution of low-field volume magnetic susceptibility (MS) throughout Zagreb city, based on in situ field measurements. The most interesting locations were selected for soil sampling and their geochemical contents were determined using ICP-OES. A geostatistical approach was applied to the MS and geochemical results. A median of 0.245×10^{-3} SI units was proposed as the average MS value in Zagreb. The mean concentrations of heavy metals in Zagreb's 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), and these measurements are relatively low in comparison to the Croatian legislation and the European and world average. Boxplot analyses demonstrate that 45% of the studied elements do not feature any anomalies, while most of the remaining elements indicate only one weak anomaly located at the same site as the MS anomalies. Our statistical analysis found significant correlations between MS and the following elements: Cd, Co, Fe, Mn, Na, Pb, Sb, and Zn. In situ MS measurements proved to be an efficient tool for the initial screening of large areas with elevated concentrations of heavy elements, enabling the cheap and fast assessment of the state of the environment.

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

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1. Introduction

Magnetic susceptibility (MS) refers to the degree of magnetization of some materials in response to an applied magnetic field. The method used for determining the degree of susceptibility is cheap and fast, and the result can be used as an indicator of anthropogenic contamination with heavy metals. The application of magnetic measurements in environmental research began in the 1980s. Investigations into the application of this method on sediments were initiated by Thompson and Oldfield in 1986 [1], and since then, many authors have used it in different contexts in geosciences. Shortly thereafter, the application of magnetic measurements in place of expensive and complicated chemical analyses in contamination studies became a main research theme [2–7].

Recent investigations have shown that a significant correlation pertains to the distributions of magnetic particles and heavy metals in industrial areas [4,8,9]. These investigations, performed in industrial areas in Poland, have also shown that the distribution of magnetic susceptibility is closely related to sedimentation with industrial dust and that magnetic measurements could be used for the detection of heavy metals in soils. In the area of Leoben (Austria), a similar investigation was performed by [10]. The most comprehensive overview of the magnetic monitoring methods used in pollutant research was presented by Petrovský and Ellwood in 1999 [11].

Several studies undertaken in other parts of the world (China, Morocco) have also examined the relation of MS to specific heavy metals, and the mineralogy of samples [12–15].

Most authors agree that this method is promising for use in the identification of polluted areas. Because this method is fast and cheap, it can be applied to a dense network of sampling points, which can then be used for the construction of MS maps to determine prominent locations for the performance of chemical analyses.

Until recently, MS measurements have not been employed in Croatia in environmental quality assessments. The first such measurements in Croatia were performed by Frančišković-Bilinski in 2008 on samples from the Kupa River watershed [16]. The lower flow of the Mrežnica River proved to be the area with the highest values of MS, and the area where the anomaly is related to the indiscriminate disposal of the products of coal burning. Preliminary measurements have also shown increased values of MS in the upper flow of the Dobra River (this is a sinking river with distinct upper and lower flow before and after sinking) and preliminary results point to a possible presence of impactite [17].

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

Hasan et al. made the first attempt at mapping the spatial variability of soil MS across Croatia in 2018 [19]. Their maps of soil MS in Croatia show two clearly differentiated distributions: the Pannonian region versus the karst area of Croatia. In the latter, the soils developed on carbonate rocks demonstrated higher values of MS and frequency-dependent susceptibility (Xfd) compared to soils in the Pannonian region.

Few geochemical investigations have been undertaken into soil pollution in Croatia and of those few, only one might be of interest to our current research. Sollitto et al. investigated heavy metal contamination in soils in the Zagreb region in 2010 using multivariate geostatistics [20]. They found that variations in the metal concentrations in the topsoil of the Zagreb region have both natural and anthropogenic origins.

Many authors worldwide have been searching for the best methods of tracing pollution in soils, especially seeking those that are fast and cost-effective. Besides magnetic techniques, methods based on infrared spectroscopy are promising [21]. The authors of that study demonstrated that combining soil infrared spectroscopy with compositional data analysis is promising in enabling the cost-effective and reliable quantification of soil properties relevant to SOC stability. Thus, it offers a practical means to assess the role of SOC in global C cycling.

Golik et al. [22] proposed a set of measures for sustainable metal mining that will minimize the anthropogenic impact of mining. These measures can be applied to the process of extracting metal from the off-grade raw materials of technogenic deposits. Such processes present the opportunity for an ecological transition to the recycling of rocks. If such measures could be applied in the historically metallurgic Celje region of Slovenia, an area located on the Savinja River, an important tributary of the Sava River upstream from Zagreb, the influence of its river sediments on Zagreb would be much lower.

Shi et al. [23] studied the sorption behavior of uranium (VI) onto two different kinds of soils: surface soil and undersurface soil (at a depth of 30 m under the surface) taken from a low- and medium-level radioactive waste disposal site in SW China. They showed that the mineral composition of the soils and the speciation of U in the natural groundwater are the two main influencing factors. They found that muscovite and clinochlore, which are two of the main minerals found in the soil samples in their study region, dominate the sorption behavior of uranium onto natural soils showing a weak acidic and near-neutral pH range. Their research contributes to a better understanding of the sorption behavior of uranium onto natural soils, and it gives an in-depth exposition of the influences of aqueous and surface speciation.

One of the most important issues in the context of environmental magnetism is the relationship between the MS of soils and sediments vs. their heavy metal contents, as well as their mineralogical compositions. Few studies from around the world have sought to establish such relations.

Urban soils from Zagreb, the capital of Croatia, had not previously been investigated in terms of their MS and have been poorly investigated in terms of their geochemistry and heavy metal pollution. Therefore, this work aimed to undertake such a study and to give the first insights into the distribution of the low-field MS throughout the territory of the City of Zagreb, via in situ field measurements. Based on these data, the average MS value for the City of Zagreb has also been proposed. Then, the most interesting locations were identified, and soil sampling was performed there, with geochemical contents determined via the ICP-OES method. Using a geostatistical approach, we attempted to determine the correlations between MS values and specific chemical elements in the investigated region, as different regions show differences in these correlations. Knowledge about these ratios will enable fast and cheap assessments of the state of the environment in the broader area, without complicated and expensive chemical and mineralogical analyses having to be performed. The final aim of our research was to evaluate and explain in detail all the most significant anomalies in the MS values, with respect to their anthropogenic or geogenic origins. We hope that our research will improve the overall knowledge base concerning environmental magnetism and will contribute to the worldwide proliferation of this method.

2. Study Area

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

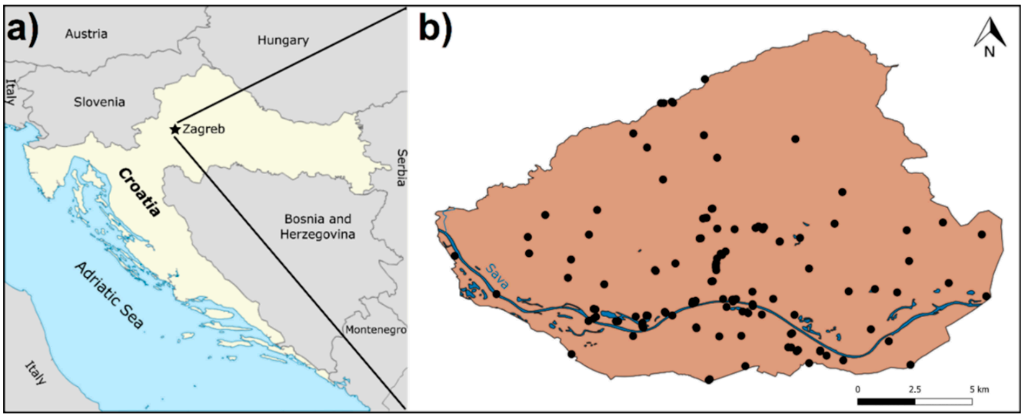

Figure 1. Overview of the study area. (**a**) Geographical position of the Republic of Croatia and the Zagreb research area (indicated with the black star). (**b**) Enlarged view of the Zagreb research area, with black dots indicating sampling spots.

Zagreb has 809,268 inhabitants living within 641 km^2, with a population density of 1200.56 inhab./km^2, while the population of the entire Zagreb urban agglomeration is 1,071,150 [24]. In terms of altitude range, it extends from 122 m a.s.l. in the Sava River plains to 1035 m at the top of Medvednica Mountain (Sljeme peak). Zagreb is a significant traffic hub and crossroad of several highways connecting Central Europe and the Adriatic coast, and it is also a large historic industrial center where many different anthropogenic influences are present.

The geology of the Zagreb area is variable (Figure 2). A major part of the city is characterized by the Holocene alluvial sediments of the Sava River. The slopes of Medvednica Mountain are covered with Miocene sediment deposits, while the core of the mountain consists of metamorphic rocks. There are parametamorphic and ortometamorphic rocks which are often interchanged at small-scale areas. This distributional pattern was produced by the Upper Jurassic–Lower Cretaceous metamorphism [25] of the Paleozoic–Mesozoic magmatic–sedimentary complex, comprising carbonate and clastic rocks and basic magmatic rocks [26]. Many streams flow from Medvednica Mountain towards the Sava River, transporting detrital material from the mountain; this influence should thus also be considered, as should the influence of the Sava River itself, which brings material from the Slovenian Alps.

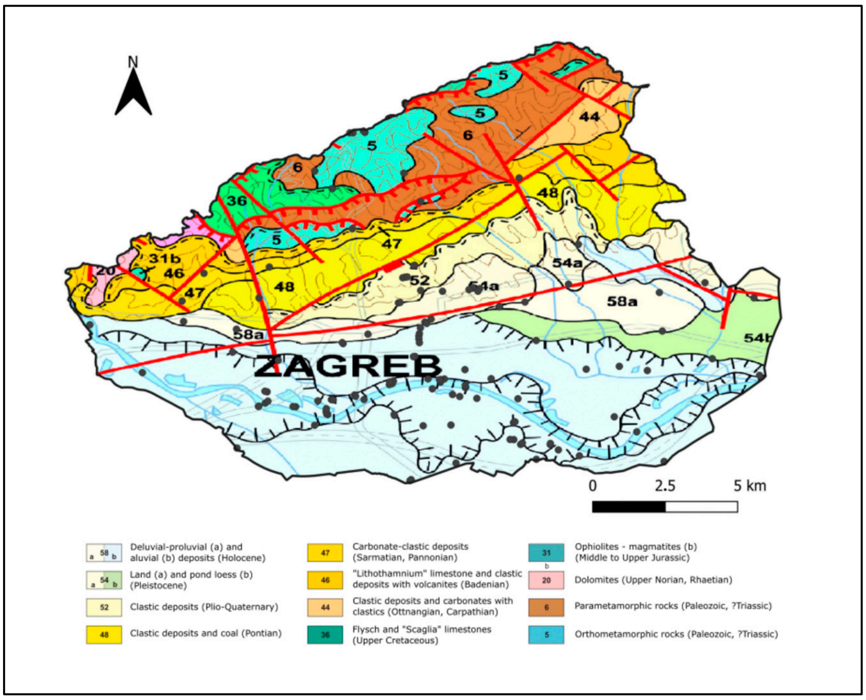

Figure 2. Part of the geological map of Croatia adjusted 1:300,000 to the Zagreb research area. Dark gray circles indicate sampling points. Modified after [27].

The climate of Zagreb comprises several types. According to [28], it is classified as an oceanic climate (Köppen climate classification Cfb) with significant continental influences, showing values very close to those of a humid continental climate (Dfa/Dfb), as well as of a humid subtropical climate (Cfa). Zagreb has four separate seasons, and the level of precipitation is 840 mm yearly [28].

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, as presented in Figure 1b and Appendix A. They were performed throughout the city of Zagreb's territorial unit (excluding some rural parts, such as Brezovica and part of Sesvete). Field campaign, including in situ measurements and sampling, was carried out between September and November of 2022.

The locations were selected in such a way that the entire study area was covered with a network of measurements. Special attention was paid to possible sources of pollution, since many selected locations were near industrial entities, the large landfill at Jakuševec, highways with heavy traffic, densely populated parts of the city, etc.

The fieldwork was carried out as follows: The most suitable micro-locations were selected. Precise geographic coordinates were determined using a GPS, and each location was photographed from different angles. Within a perimeter of 5 m, 11 measurements were performed using the SM-30 instrument, and the mean value was presented as the MS measurement for each location. At each measurement point, grass cover (or leaf cover in forested locations) was removed before performing the measurements.

3.2. Sampling and Sample Preparation

After a detailed statistical evaluation of the in situ measurements, the 25 most interesting ones (20% of in situ studied locations) were selected for soil sampling and the geochemical analysis of elements using the ICP-OES method. The results are presented in Appendix A. When selecting these locations, we applied to following criteria: locations with MS statistical anomalies (extremes or outliers), locations near possible sources of pollution (landfill Jakuševec, industry, etc.), locations representing each of the three clusters obtained via the Q-mode cluster statistical analysis, and locations with low MS values suggesting low heavy metal concentrations.

During sampling and sample preparation, the following protocol was followed:

1. At each sampling location, first, the micro-location of the previous in situ measurement was found, and the sample was taken from this exact point.
2. Grass or leaf cover was removed to reveal the bare surface of the soil. A square with sides of 25 cm was marked with a spade, and the soil was sampled to a depth of 2 cm.
3. Soils were sampled using a spade, packed in PVC bags, and transported to the laboratory.
4. Soil samples were dried at 40 °C in cardboard boxes under airflow. The dried soil was first sieved through a 12-mesh (approximately 2 mm) sieve and then ground in a mechanical mortar.
5. Then, 40 g of each sample thus prepared was separated and stored in a plastic container for ICP-OES analysis, and the rest of the sample was stored.
6. In each separated sample prepared for ICP-OES analysis, MS was measured under laboratory conditions before the ICP-OES analysis, also using the SM30 instrument.

One of the samples, from Mikuševa Street, Dubec, in the eastern part of the city, was taken from two layers: depths of 0–2 cm and 2–4 cm. Each of the sampled layers was treated as a separate sample. This location was chosen due to it having the lowest MS value relative to all other studied locations, and because it is probably completely free of anthropogenic pollution. In another location, Novi Jelkovec, where the MS value was also very low, two layers were also sampled—at 0–2 cm and 15–25 cm—to investigate the presence of any heavy metal migration towards deeper layers, and to determine whether there are significant differences in the MS values and element concentrations between surface and deeper layers. Any significant differences observed between the two layers could have been taken as the focus of a new study.

3.3. Magnetic Susceptibility Measurements

For the determination of MS (expressed as SI units), an SM30 instrument—a small magnetic susceptibility meter manufactured by ZH Instruments, Brno, Czech Republic—was used. This is a sensitive (sensitivity 10 times greater than those of competing instruments) and accurate tool used for both field and laboratory measurements of the MS of outcropping rocks, soils, drill cores, or rock samples. Due to its high sensitivity, besides the applications mentioned, it can also accurately assess diamagnetic materials such as limestone, quartz, and water.

The sensitivity of SM30 is 1×10^{-7} SI units, and its results are displayed in 1×10^{-3} SI units. The sensor is designed to derive 90% of its signal from the first 20 mm of the rock; this is a relatively deep penetration, which allows more accurate readings on uneven surfaces of all rock types. The SM30 has an 8 kHz LC oscillator with a large pick-up coil used as a sensor.

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

3.4. Determination of Geochemical Composition Using ICP-OES

The soil samples were analyzed via the optimized BCR three-step sequential extraction procedure. The original protocol was modified with the use of aqua-regia for the residual fraction (fourth step). The sequential extraction method used in this research has been described in detail in [29,30]. In this study, we have used results regarding the total quantities of the extracted elements, defined as the sum of the contents of the elements in the three fractions plus the content of the residue extractable using aqua regia.

The element concentrations in the water obtained at each BCR extraction step were determined using Inductively Coupled Plasma–Optical Emission Spectrometry (Thermo Scientific ICP-OES iCap 6500 Duo, Thermo Scientific ICP-OES iCap 6500 Duo, Loughborough, UK). The quality of the analytical data was controlled using laboratory quality assurance and quality control methods, including the use of standard operating procedures, calibration with said standards, and analyses of both reagent blanks and replicates [30].

The accuracy and precision of the obtained results were checked by analyzing the sediment reference material (BCR 701) via three-step sequential extraction. The values obtained regarding the accuracy for all three fractions are as follows: Cd (83.13–120%), Cr (77.90–99.45%), Cu (79.90–96.43%), Ni (82.92–105%), Pb (80.00–108%) and Zn (86.98–108%). The limit of detection for all investigated elements was 0.1 $\mu g\ L^{-1}$. Acceptable levels of accuracy (80–120%) and precision (≤20%) were achieved for the metals in all steps of sequential extraction. The soil data used in this study are reported on a dry weight $mg\ kg^{-1}$ basis.

3.5. Statistical Analyses

All statistical analyses were performed using the program Statistica 6.0 (StatSoft GmbH, Hamburg, Germany) [31], which is a software suite that has been verified globally for use in analyzing and visualizing data, and which can offer insights and predictions and deliver solutions tailored to users. This software has more than 1 million users worldwide from a broad range of industries. Among other things, it is very user-friendly, offering complete visualization of the analytical processes in its interface.

The following analyses were performed:

(a) The determination of basic statistical parameters—N (number of cases), mean, geometric mean, median, mode, frequency, minimum, maximum, standard deviation, skewness and kurtosis. These were determined to more clearly represent the experimentally determined values, without presenting the whole dataset.

(b) Correlation analysis was performed by calculating Pearson's correlation coefficient, which has been presented in the form of a correlation matrix and was used to determine the strength of the linear correlations between the mass fractions of analyzed elements and MS. The values obtained were statistically significant at $p < 0.05$. Pearson correlation assumes that the two variables are measured on interval scales, and determines the extent to which the values of the two variables are "proportional" to each other. The value of correlation (i.e., correlation coefficient) does not depend on the specific measurement units used. The presence of proportionality means the values are linearly related; that is, the correlation is strong if it can be "summarized" by a straight line (sloped upwards or downwards), which line is called the regression line or the least squares line because it is determined in such a way that the sum of the squared distances of all data points from the line is as low as possible.

(c) The boxplot method was used to identify anomalies in the sediment samples. Normal or lognormal boxplots were constructed based on empirical plots of cumulative distribution. The box length represents the interquartile range, with outlier values defined as those situated between 1.5 and 3 box lengths from the upper or lower edge of the box. Extremes are defined as values situated more than 3 box lengths from the edge of the box [32,33].

(d) The cluster analysis of Q-mode, in which clusters of samples are sought, was performed to identify groups of similar samples. Cluster analysis is used to derive multivariate statistics, and is a hierarchical method [34].

4. Results and Discussion

4.1. Distribution of MS within the City of Zagreb Based on In Situ Measurements

The results of in situ measurements taken at 125 locations throughout the study area are presented in Appendix A, and the basic statistical parameters are presented in Table 1.

Table 1. 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 the data more illustrative and to aid their interpretation (Appendix B).

The data presented show that the mean value for the whole study area is 0.374×10^{-3} SI units. The range (2.973) between the minimal (0.054×10^{-3} SI units) and maximal (3.027×10^{-3} SI units) values is rather wide. The minimum value was received on a meadow in Mikuševa Street in the Dubec residential area in the eastern part of the city, while the maximum value was taken on a meadow at the Sljeme peak of Medvednica Mountain, at an altitude of 1035 m—the highest point in the city of Zagreb (Figure 3—point *79).

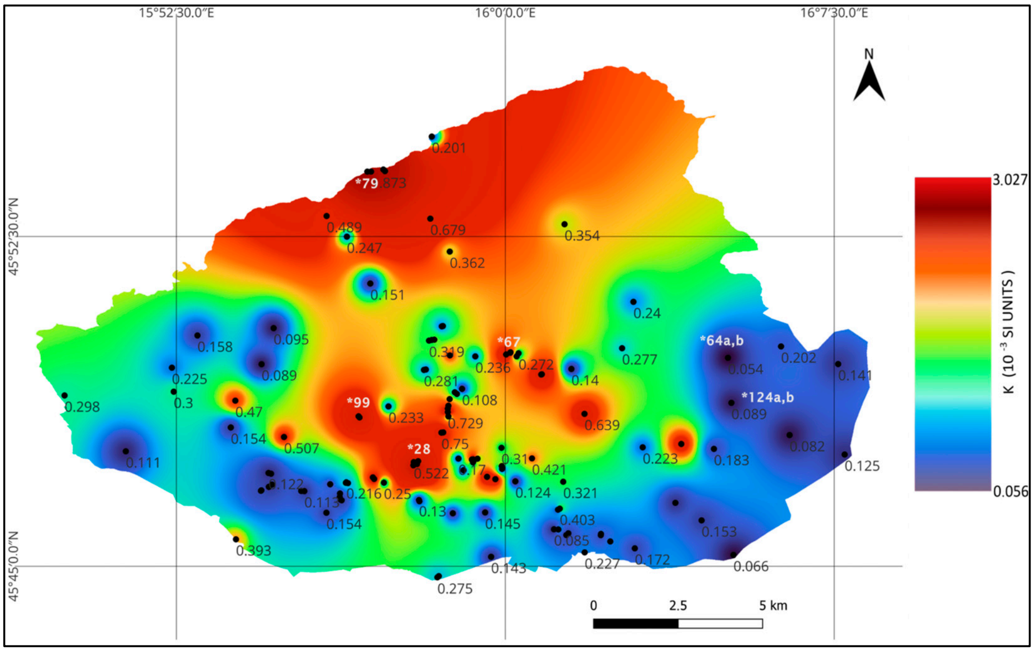

Figure 3. Zagreb city's area volume-specific MS contour map produced in the QGIS software shows the range and pattern of MS values in the research area. The highest MS values can be observed in the upper left part of the investigated area, while the lowest MS values are shown in the right and lower left part of the investigated area. Important locations are marked with the *symbol and a number (Appendix A), as follows: *28—Prisavlje—uz Savu (1), *64 a,b—Mikuševa ulica—Dubec), *67—Jaruga Rebar Kozjak (1), *79—Sljeme Vrh—livada, *99—Park Pravednika među narodima—jaruga and *124 a,b—Novi Jelkovec.

Notably, according to the large difference between the mean and median values (0.245×10^{-3} SI units), the distribution could be interpreted as irregular, and large anomalies could be expected within the dataset.

The next step of the statistical evaluation of in situ measured MS data was the boxplot statistical analysis of anomalies, as presented in Figure 4.

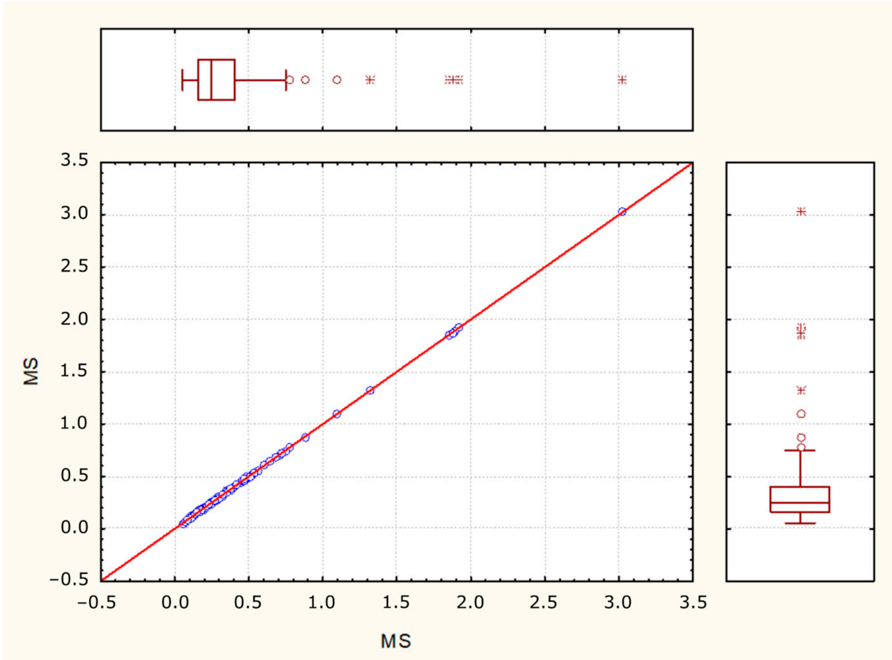

Figure 4. Statistical evaluation of in situ measured MS data—boxplot statistical analysis of anomalies. Stars present extreme values, while circles present outliers.

The boxplot evaluation revealed six extreme values and three outliers. The four most significant extremes are concentrated around Sljeme, the highest peak of Medvednica Mountain, and the surrounding ski slopes. These values are associated with the local geological background. The other two extreme values were measured at Prisavlje (samples 1 and 2 from this location—see Figure 3), which is located very close to the Sava River and is within its inundation area. These elevated MS values could be interpreted as related to the composition of the sediments of the Sava River's overbank, deposited in the area after having been carried by the Sava River from the old metallurgic region in Celje, Slovenia. According to the available literature [35], the mineralogical composition of soils from along the Sava River comprises quartz, calcite, muscovite/illite, smectite, chlorite, vermiculite, plagioclase, potassium feldspar, amphibole, and kaolinite. Regarding the outliers, one (Trnjanski nasip 2) was measured in the area near the Sava River, so the same influence could be inferred. Another possible explanation is that this location is very close to Kunišćak weir, where there is an inflow of the Kunišćak stream, bringing material from Medvednica Mt. to the Sava River. The remaining two very weak outliers were both measured in the park Pravednika među narodima (Figure 3), situated exactly 400 m west of the chimney of the city's thermal power and heating plant, which burns oil fuel; these anomalies could thus be interpreted as anthropogenic.

The next step in explaining and presenting the distribution of MS within the city of Zagreb was the Q-mode cluster statistical analysis, by which three clusters were extracted. The results of the Q-mode cluster analysis are presented in Table 2 (cluster means), Table 3 (Euclidean distances between clusters), and Appendix B, wherein the members of each cluster are listed and the distances from the centers of their respective clusters are given.

Table 2. 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 3. 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

The Q-mode cluster analysis yielded the following three clusters:

Cluster 1, with a mean MS value of 0.638 $\times$ 10^{-3} SI units, comprises 25 locations. In this cluster, different locations with elevated MS values are present from different city parts, which values are caused by different factors. Some of these locations are close to the Sava River influence and its old branches, some are affected by industrial pollution, some are affected by different anthropogenic influences from the central and more densely inhabited parts of the city, while some show naturally elevated MS values due to their locations on the slopes of Medvednica Mountain, and the geological composition in this area. Some locations are also affected by irresponsible waste disposal.

Cluster 2, with a mean MS value of 2.112 $\times$ 10^{-3} SI units, comprises five locations, four of which are located around the Sljeme peak on Medvednica Mountain and are thus under the natural influence of this area's geological composition, while one location is in Prisavlje, within the inundation area of Sava River, and thus affected by the influence of river sediment.

Cluster 3, with a mean MS value of 0.213 $\times$ 10^{-3} SI units, comprises the majority of the locations assessed (95 locations). In this cluster, the anthropogenic influence present is not significant, despite some of the locations being very close to the Jakuševec landfill, highways with heavy traffic, sewage purification plants, warehouses of cleaning companies, etc. Also, the locations within this cluster are further away from the strong influence of the local geology of Medvednica Mountain. Also, the mean MS value of this cluster—0.213 $\times$ 10^{-3} SI units—is very close to the median value for the entire dataset (0.245 $\times$ 10^{-3} SI units) and could thus be used as the average MS value for the whole city of Zagreb.

4.2. Distribution of MS within the City of Zagreb, Based on Laboratory Measurements of Selected Samples

The MS values of the samples collected from 25 selected locations were measured in a laboratory. The results of the laboratory MS measurements of all the samples collected (including two deeper layers) are presented in Appendix A.

The basic statistical parameters of the samples measured in the laboratory are presented in Table 4.

Table 4. Euclidean distances between clusters—laboratory 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

The data show that the mean value (mean) of all samples assessed in the laboratory (25 samples from the 0–2 cm layer) (0.442 $\times$ 10^{-3} SI units) is higher than the mean value of the 125 in situ measurements. Also, the median of the former measurements is much higher than that of the in situ measurements—0.319 $\times$ 10^{-3} SI units. The range between the minimum and maximum values is slightly narrower for samples measured in the laboratory, with the minimum values of both sets of measurement being almost the same and taken from the same place (Mikuševa Street in Dubec), while the maximum values were also taken in the same place (Sljeme, the top of Medvednica Mt.), but with that from the set of laboratory measurements being much lower, although still very high.

Regarding these rather large deviations between the mean/median values of the in situ and laboratory measurements, the main explanation is that the locations of the set measured in the laboratory were selected according to the most significant in situ measurements and the locations thereof, and one of the main criteria for selection, among other things, was an increased value of MS at the given location.

So, despite the presence of many deviations between the in situ and laboratory measurements for the same locations, the data from the field (in situ) and the laboratory are very highly statistically correlated (correlation factor 0.90).

Notably, all the samples except for two yielded mostly much higher values when measured in situ than in the laboratory. At the location, Park Pravednika među narodima, ravine, the values measured in the laboratory are slightly higher than those measured in situ and can be said to be essentially equal, while only at Jakuševec East (2) there is a noticeable difference, with the value measured in the laboratory being significantly higher than that taken in the field. It is necessary to investigate the causes of this phenomenon, which could be identified in soil moisture and the presence of vegetation, as well as the fact that, under laboratory conditions, only 40 g of material was assessed, while an "unlimited amount" was available in situ, etc. Further, the in situ measurements certainly incorporated some humidity, while the samples measured under laboratory conditions were completely dry.

The statistical analysis of anomalies was performed using the boxplot method, and the results are presented in Figure 5.

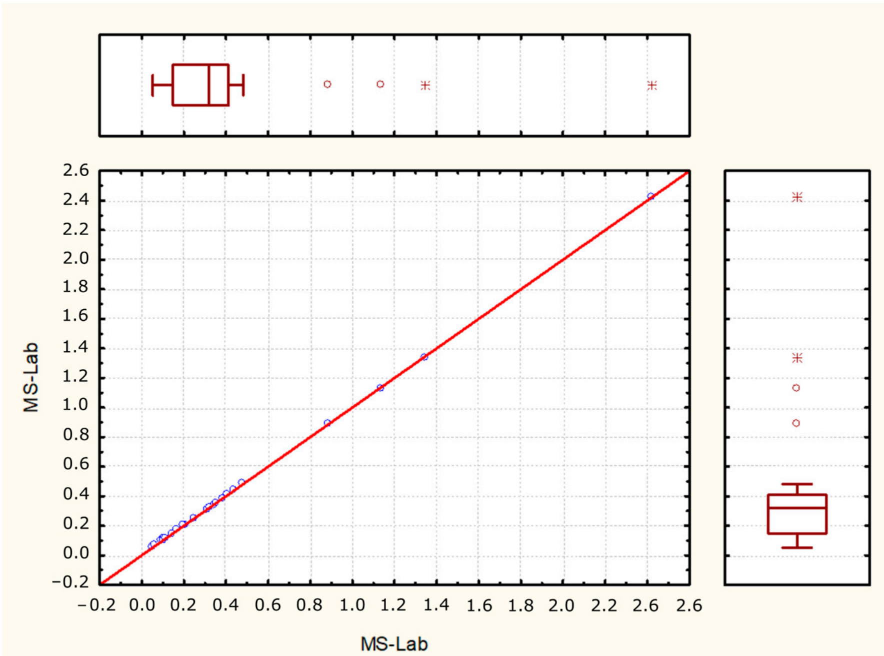

Figure 5. Statistical evaluation of laboratory-measured MS data—boxplot statistical analysis of anomalies. Stars present extreme values, while circles present outliers.

The boxplot analysis of the laboratory-measured data for 25 samples revealed two extreme values and two 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 derived for the 125 samples measured in the field. Specifically, again, the top of Medvednica Mt. was shown to be extremely anomalous, with extreme values yielded by the samples from Sljeme peak—meadow, and Činovnička meadow—lower part in the forest. The outliers are from Prisavlje near the Sava River (1) and the ravine in the Park pravednika među narodima. As already assumed based on in situ measurements, the extreme values yielded from the peak of Medvednica are obviously related to the geological structure of this terrain. The outlier derived from Prisavlje is probably related to the old alluvium of the Sava, while that from the mentioned ravine in the mentioned park can be attributed to the influence of the nearby heating plant.

The next step in explaining and presenting the distribution of MS values derived from the 25 samples collected in the city of Zagreb was Q-mode cluster statistical analysis, via which three clusters were extracted. The results of the Q-mode cluster analysis are presented in the following tables: Table 5 (cluster means), Table 6 (Euclidean distances between clusters), and Tables 7–9, in which the members of each cluster are listed and the distances from the centers of their respective clusters are given.

Table 5. 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 6. 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

Table 7. Laboratory measurements—Members of cluster 1 and distances from the respective cluster center. The cluster contains 3 cases.

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

Table 8. Laboratory measurements—members of cluster 2 and distances from the respective cluster center. The 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 1, with a mean MS value of 1633×10^{-3} SI units (very high), comprises three samples, two of which (Činovnička livada—lower part in the forest and Sljeme vrh —meadow) were taken at the top of Medvednica Mt., while one (Prisavlje near the Sava River (1)) is from the inundation area near the Sava (see Figure 3). The causes of the elevated MS values in this cluster are natural—those on Medvednica Mt. are due to the influence of local geology, and those from Prisavlje are related to the influence of old alluvium from the Sava River.

Table 9. Laboratory measurements—members of Cluster 3 and distances from the respective cluster center. The 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 2, with a mean value of MS 0.422×10^{-3} SI units (moderately elevated), comprises 11 locations from all over the city. A combination of natural and anthropogenic influences can be inferred here. Natural influences (local geology) likely pertained at the Church of St. Jakov and the bottom of the Činovnička meadow on Medvednica Mt., and these were possibly also at least partly to blame in the areas of Maksimir and the Rebar-Kozjak ravine, as well as near Borongaj. On the Trnjanski nasip (2), both anthropogenic and natural influences could have been felt, with the latter being the possible delivery of alluvium by the Kunišćak stream. The Park Pravednika među narodima (ravine) likely felt the anthropogenic impact of the nearby thermal power plant, while samples from the JANAF oil terminal in Žitnjak undoubtedly felt the anthropogenic impact of said terminal, and in Jakuševac-East, the impact of the waste dump is clear. The central part of the city (near the City Poglavarstvo, and in Strossmayer Square) almost certainly reflects anthropogenic impacts, since this is a very densely populated and built-up area with a lot of traffic.

Cluster 3, with a mean value of 0.137×10^{-3} SI units, comprises the 11 remaining locations, from all parts of the city. It is very interesting that in this cluster, which shows the lowest MS values of all, there are also two locations next to the busiest highway in Croatia (Bauhaus Buzin, and the Hrušćica interchange), and one location is right next to the Jakuševec landfill, suggesting that these locations are not strongly affected by an anthropogenic influence.

4.3. Element Distribution in Soils of Zagreb Area

The results of the ICP-OES analysis for the 20 elements at the 25 selected locations are presented in Table 10. In total, there are 27 results, as an additional layer was sampled for comparison of two locations (in addition to the 0–2 cm layer, on which sampling was initially performed).

The basic statistical parameters of these results are presented in Table 11.

To get a better insight into the element distribution, the boxplot statistical method was applied to the ICP-OES data, and the results are presented in Appendix C.

As shown in Appendix C, 9 of the 20 studied elements (45%) show no anomaly, and most of them have a regular normal distribution. The elements with no anomalies are Al, Ca, Cu, Fe, K, Li, Mg, Ni, and Pb. The rest of the elements mostly show only one anomaly, among which outliers prevail.

Table 10. Results of ICP-OES 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 concentrations 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	63,370	0.39	5.76	14.05	17.14	15,567	936	13.52	13,584	444	22.75	19.37	15.21	1.22	49.46	59.7
Bauhaus Buzin	8865	4.94	3.76	57.3	65,982	0.50	8.29	17.28	20.55	19,513	1079	18.63	15,449	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	58,844	0.38	4.73	10.75	14.22	13,453	946	10.95	13,776	442	7.27	14.89	15.45	0.88	32.17	52.1
Borongaj cesta-šuma	14,757	9.08	1.34	46.4	6024	0.57	18.97	34.02	44.94	32,471	1311	25.97	5125	766	5.65	38.11	20.79	4.20	13.71	73.1
Bundek-istok	11,806	3.18	3.14	93.8	24,978	0.57	18.27	36.81	34.82	26,024	1520	14.28	9175	665	7.06	30.52	21.93	3.86	26.83	73.3
Crkva Sv. Jakov	16,895	1.61	0.77	79.4	7073	0.86	23.51	71.53	54.73	25,735	626	15.28	6947	861	2.55	41.04	68.82	6.00	18.41	85.4
Činovnička livada—donji dio—šuma	19,627	2.42	1.46	53.1	4609	0.93	23.42	49.14	33.31	30,134	726	17.93	5051	1334	8.64	26.99	43.93	6.71	16.29	92.5
Činovnička livada—dno (2)	17,985	2.84	1.37	70.0	2660	1.16	11.86	24.86	31.13	25,659	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	49,963	0.54	9.09	21.00	28.11	17,905	960	15.37	13,560	577	28.42	23.81	42.98	1.98	31.97	87.7
Grubišnopoljski put—Rudeš	10,857	5.44	4.01	80.8	35,585	0.56	9.71	22.55	36.74	22,132	992	16.81	10,786	587	10.19	28.28	32.56	2.13	23.85	94.5
Jakuševec Istok (2)	6730	3.76	3.85	56.4	60,186	0.38	7.68	16.53	18.06	16,171	917	10.44	11,971	425	20.28	17.33	20.30	1.78	43.66	110.4
Jakuševec Sredina (2)	5147	3.12	1.24	92.8	82,694	0.37	4.58	15.37	17.11	12,038	787	12.26	14,452	331	20.10	14.24	42.99	1.63	42.63	69.0
Janaf Terminal Žitnjak	2929	1.53	0.91	54.5	60,634	0.44	9.63	14.25	12.52	9770	325	5.70	12,988	211	13.03	46.20	45.20	1.09	32.42	85.8
Jaruga Rebar—Kozjak (1)	15,450	4.75	7.35	135.4	9418	0.75	12.14	29.20	45.63	25,123	1904	14.31	2789	368	11.56	18.54	39.08	2.28	30.90	130.6
Potok u Maksimiru blizu Bukovačke	11,748	6.00	2.56	93.1	17,372	0.67	19.17	35.01	31.76	27,881	1166	12.46	6878	880	8.70	23.57	60.30	3.27	22.39	89.6
Mala Mlaka—uz vodocrpilište (1)	13,293	6.71	6.40	84.6	40,083	0.74	11.41	23.86	47.76	24,904	1542	23.35	10,909	825	26.12	35.93	31.09	1.63	29.95	86.1
Mikuševa ulica—Dubec. 0–2 cm	14,993	4.98	3.48	91.2	9016	0.64	8.30	30.10	25.85	22,960	1308	18.67	3974	285	7.59	32.16	18.25	2.09	47.76	66.2
Novi Jelkovec. 0–2 cm	18,496	4.40	2.98	92.2	9744	0.73	7.09	34.85	28.27	26,461	1338	20.32	4244	219	6.14	31.48	19.90	1.95	48.48	77.7
Park Pravednika među narodima—jaruga	14,292	12.07	8.31	79.1	23,999	0.71	14.16	36.19	37.47	25,872	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	82,630	0.72	5.88	25.30	26.37	17,616	684	13.24	13,279	392	104.63	18.53	34.22	1.96	81.11	127.7
Sljeme Vrh—livada	17,470	0.33	0.79	73.6	8048	0.95	26.30	49.14	46.35	35,025	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	46,635	0.62	12.48	27.12	43.03	21,675	1108	15.09	11,520	692	30.36	25.04	58.45	3.25	37.08	100.2
Šire područje oko Ustave Kunišćak	16,021	6.31	4.45	114.0	10,058	1.02	12.87	28.23	31.47	28,312	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	33,054	0.60	8.09	21.93	26.93	17,140	1383	11.80	8040	463	23.80	31.25	36.52	2.15	31.06	108.1
Tuškanac-livada	14,391	6.17	0.81	93.6	5075	0.40	10.33	27.00	20.53	22,357	652	16.34	3567	355	11.06	17.62	77.83	2.06	9.57	58.7
Mikuševa ulica—Dubec. 2–4 cm	13,841	4.81	2.18	92.1	7390	0.65	7.85	27.21	24.75	22,314	961	16.74	3727	272	4.73	30.52	19.06	1.50	45.19	64.0
Novi Jelkovec. 15–25 cm	21,964	6.01	3.41	104.9	8768	0.90	9.42	40.79	33.25	31,012	1474	23.94	4561	329	14.94	35.74	20.89	2.32	49.31	85.7

Table 11. 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	12,456.38	13,293.04	336,322.3	2929.395	21,963.72	19,034.33	23,708,144	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	30,884.88	23,999.33	833,891.7	2660.019	82,693.63	80,033.61	687,813,701	26,226.20
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	22,786.01	22,959.73	615,222.2	9770.359	35,024.52	25,254.16	40,204,133	6340.67
K	27	1124.87	1078.96	30,371.4	324.710	2033.26	1708.55	155,497	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	230,443.4	2788.817	15,448.99	12,660.17	16,525,554	4065.16
Mn	27	627.89	576.95	16,953.0	211.495	1640.70	1429.21	140,427	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

According to the boxplot analysis, the majority of the studied elements show a natural distribution, suggesting anthropogenic influence is not likely (at least, not a large one), especially when taking into account that the maximal concentrations of the elements are not high, but this will be discussed later. There are only two extreme values, of Ba and Na, which were measured at Prisavlje near the Sava River. However, at this stage, we do not know the origins of Ba and Na at this location, and this will be the subject of some future work. However, it is highly likely that they were carried in by the Sava River, which floods this location and deposits overbank sediments. All the other anomalies found are outliers, and most of them are very weak. Also, all elements showing anomalies show only one, except Sb, which shows three.

Within the whole of Zagreb city, only three zones with anomalous concentrations of some elements can be defined (see Figure 3):

1. Park pravednika među narodima jaruga (around location 99). This location is situated within a ravine located very close to the thermal power plant/heating plant, which is run on fuel oil. This ravine is surrounded by a fence and in the past was part of the plant, and there are signs that fuel oil has contaminated the soil here. This is therefore the most likely reason for the anomalies in As and B at this location [36,37].

2. The highest part of Medvednica Mountain (around location 79), represented by several locations—Sljeme vrh livada (at the top of the mountain), Činovnička livada donji dio šuma, Činovnička livada dno, and Crkva Sv. Jakov. At these locations, several outliers are present in the heavy metal measures, such as for Cd, Cr, Mn, Sb, Co, and Zn. This area is far away from any source of pollution, so it could be assumed that these anomalies are of natural origin, due to the geological composition of the metamorphic rocks. In this part of the research area, Pb–Zn ore bodies are present inside the ortometamorphic rocks [26]. These bodies are usually associated with the aforementioned heavy metals. Therefore, the outliers in this area are probably related to its geological background [38].

3. Prisavlje uz Savu (around location 28). This location is situated within the area of inundation of the Sava River, and the soils here are partially composed of overbank sediments of the Sava River. Only two extreme values were found here, Ba and Na, and the value of Na is extremely high. Besides these, outliers of Sr are present at this location, too.

4.4. Determination of Correlations between MS and Elements

The correlations between MS values measured in situ and in the laboratory and the total contents of the 20 elements determined using ICP-OES are presented in Table 12.

Table 12. Correlation matrix between in-situ and laboratory MS measurements (SI units) and elements determined using ICP-OES. Marked correlations (in red) are significant at $p < 0.05$, $n = 27$.

	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

The highest correlations can be observed between elements and volume-specific MS measured in situ, while slightly lower correlations can be found for those measured under laboratory conditions. The strongest correlations with MS have been found for Zn, Mn, Sb, Co, and Cd, and weaker (but also significant) ones have been found for Fe, Cr, Pb, and Na.

The next step was to compare anomalies between the boxplot results of magnetic parameters and elements. The boxplot determination of anomalies in the results of laboratory measurements taken using the SM-30 device shows two extreme values and two outliers. It was shown again that the top of Medvednica Mt. is generally extremely anomalous, with extreme values present in the samples from Sljeme peak—meadow and Činovnička meadow—the lower part of the forest. Outliers arose at Prisavlje near the Sava River (1) and in the ravine in Park Pravednika među narodima. When we compare these findings with the boxplot results of the 20 chemical elements, we can see anomalies in these exact locations, plus two more locations (Činovnička livada dno (2) and Crkva Sv. Jakov) within the same area on Medvednica Mt., with MS values measured here also being somewhat elevated.

It can be concluded that measuring MS directly in the field using a small field instrument like the SM-30 is a very effective way to screen large areas when searching for potential heavy metal pollution. In such a way, many unnecessary chemical analyses can be avoided, and the whole process can be sped up. Figures 6 and 7 show the concentrations of Co and Zn, respectively; these two elements show the highest correlations with MS, meaning that the similarities between their concentration distributions and the distribution of MS values can be assessed.

4.5. Estimation of State of Anthropogenic Pollution of Zagreb, Determination of Average MS Value of Urban Soils and Recommendations for Future

Based on the distributions of the element concentrations and the low number of (mostly weak) anomalies, as well as the fairly low maximal concentrations, it could be stated that, generally, the anthropogenic influence in Zagreb city (concerning heavy metals) is not very high. The anomalies identified indicate some degree of anthropogenic pollution in two cases: possible fuel oil contamination at Park Pravednika među narodima jaruga (ravine) and unknown contamination at Prisavlje near the Sava River (1), most probably induced by the Sava River, which floods this area. It is very interesting that at locations around the large communal landfill at Jakuševec, the MS values and element concentrations show no anomalies, with similar findings made at locations near the largest highways.

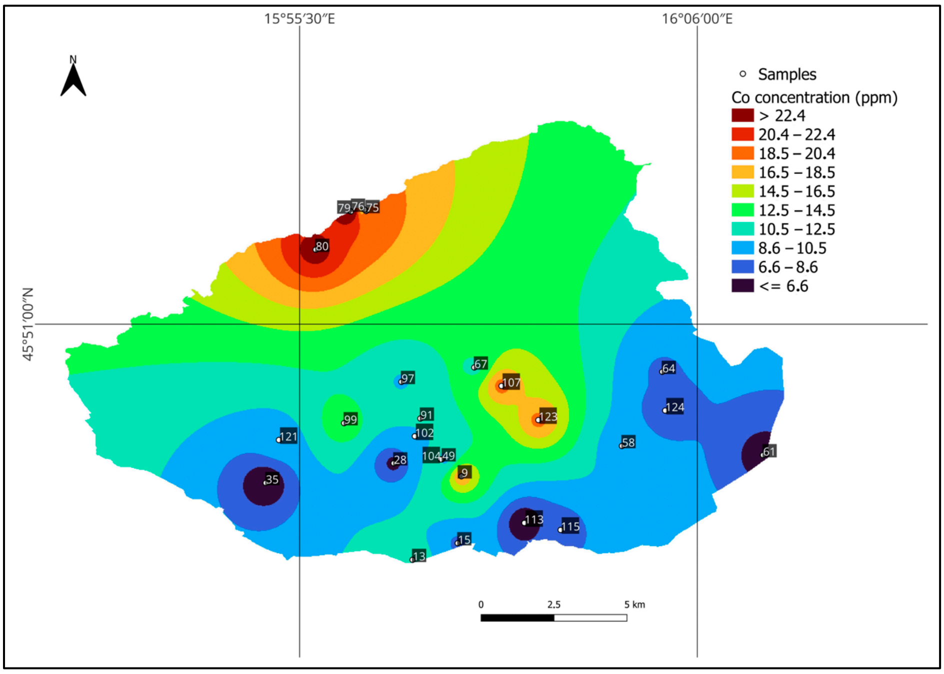

Figure 6. Spatial distribution map of the concentration of Co in the Zagreb area, produced using the QGIS software.

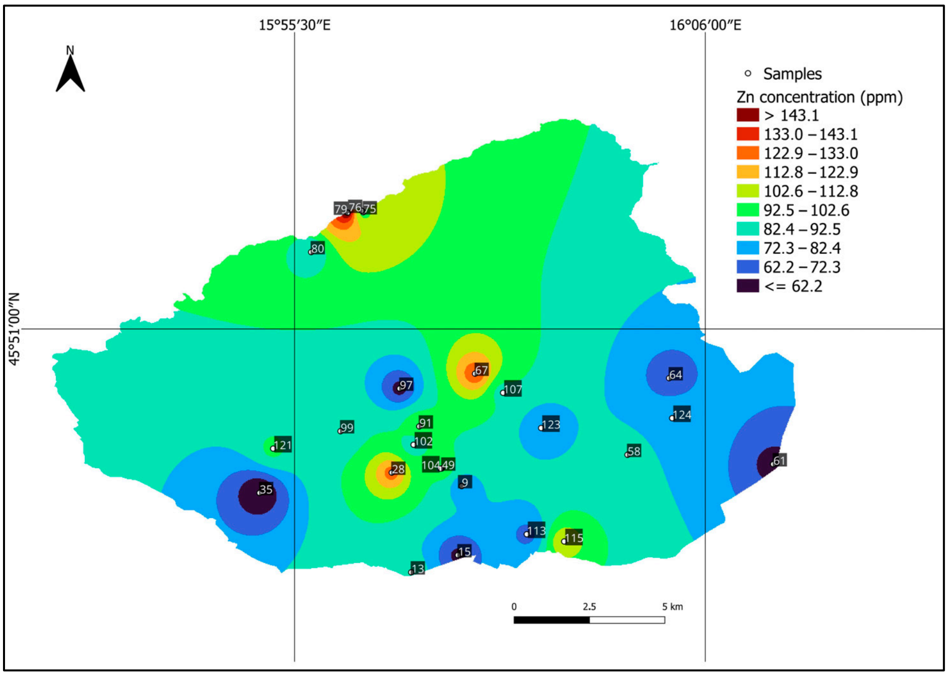

Figure 7. Spatial distribution map of the concentration of Zn in the Zagreb area, produced using the QGIS software.

We propose that the median value of 0.245×10^{-3} SI units, which was obtained by in situ measurements under the current work, be used in the future as the average value for soils in the Zagreb city area. This value is much more realistic than the mean value of 0.374×10^{-3} SI units, as this value is distorted by the presence of several extreme values, significantly elevating it.

When the geochemical data of the current research are compared with those from several other cities (Palermo, Lisbon, and Ljubljana), as well as with the world average, we can see that the heavy metal concentrations in Zagreb are not very high, thus more clearly illustrating the heavy metals contamination situation in Zagreb (Table 13, Figure 8).

Table 13. Comparison of selected heavy metals' concentrations (ppm) between Zagreb, several European cities, and the world average. Data derived from [39,40].

Element/City	Zagreb—Current Study	Palermo [39]	Lisbon [40]	Ljubljana [40]	World Average (16 Cities) [40]
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

A few cases of specific heavy metals are discussed in short below.

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

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

The Cd concentrations in Zagreb are lower than those in Palermo but higher than those in Lisbon. Data for Ljubljana does not exist. In comparison with the world average, the concentrations in Zagreb are a bit higher.

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

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

The Ni concentrations in Zagreb are a bit higher than those in Palermo, about two times lower than those in Lisbon, and significantly lower than those in Ljubljana and the world average.

Our research is also very important for this entire region, as there has been a lack of such data for Croatia and its capital Zagreb. It therefore enables comparisons of the quality of the environment in these cities with respect to heavy metal concentrations in soils.

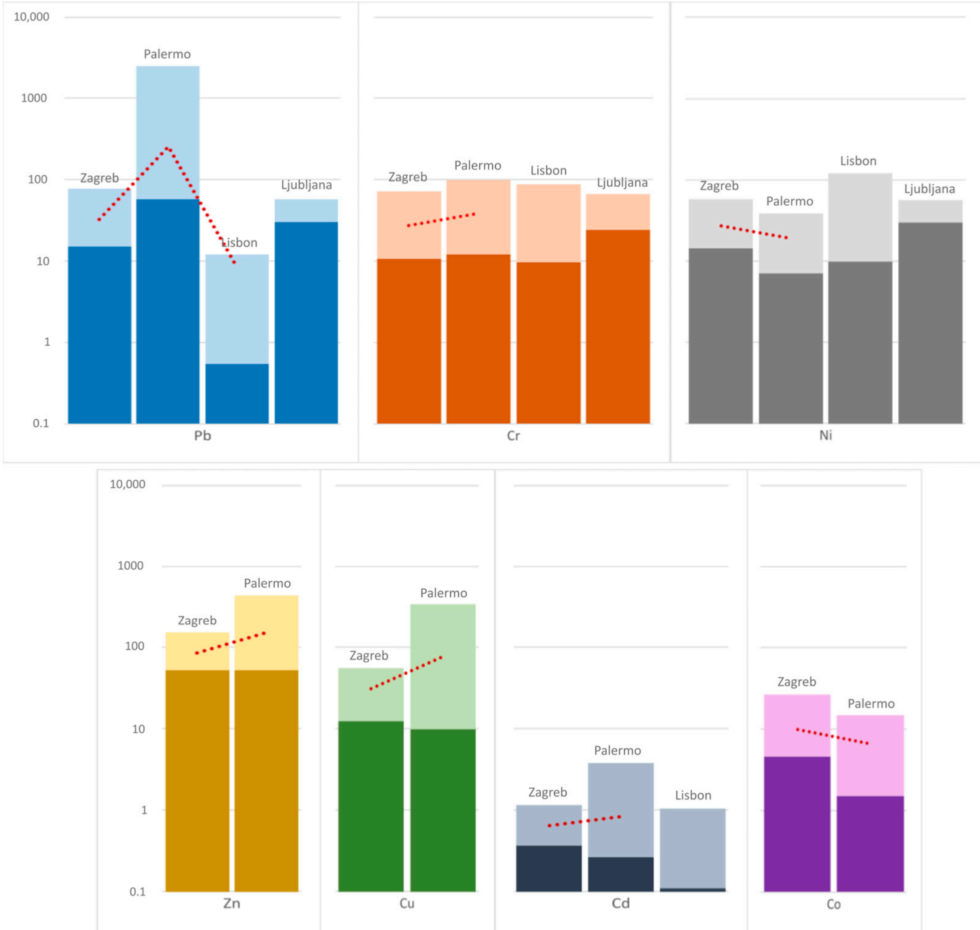

Figure 8. Selected heavy metal concentrations in Zagreb soils vs. those in several European cities. Dark colors indicate minimum, while light colors indicate maximum concentrations. The dashed red line indicates median values. The ordinate scale is logarithmic. Data were derived from Table 13.

In Croatia, no specific legislation exists concerning heavy metals in "urban soils". However, there is legislation regarding agricultural soils, with which we can make comparisons (Table 14).

Table 14. Selected heavy metal concentrations (mg kg^{-1}) are allowed in soils according to the Croatian Legislation for the protection of agricultural soil from contamination [41].

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 the following categories: sandy soil, powdery–loamy soil, and clay soil. Based on our long-term field studies and visual observations, the soils in Zagreb vary from sandy near the Sava River to clay in some locations. As such, generally speaking, Zagreb is most represented by powdery–loamy soils, despite the lack of soil type analyses in the current research.

When the concentrations of heavy metals found in our study are compared with those set out in Croatian legislation for agricultural soils, we can see that the mean concentrations of Pb, Cu, Cr, and Ni found here are within the limits of the strictest rules, which also applies for sandy soils. The concentrations of Zn and Cd are within the limits of the rule set out for powdery–loamy soils. When we compare the maximum values of those elements with those values in the legislation for agricultural soils, the majority have maximal values that are within the range of concentrations allowed for powdery–loamy soils and no element has a maximal value that exceeds the range allowed for clay soils. This indicates that the soil studied within the city of Zagreb is relatively unpolluted with heavy metals. Also, we should be aware that the soils from the studied locations are not used for agriculture, as they are situated in parks and other green areas within mostly urban zones, meaning their value is even more permissible.

Much of our research suggests that the area within Zagreb that we investigated is relatively unpolluted with heavy metals and that known pollution sources, e.g., road traffic, the Jakuševec landfill, and some industrial entities, do not significantly influence the heavy metal concentrations in their surroundings. However, there are some exceptions, e.g., the thermo-power and heating plant. That said, regular monitoring is advised for each case, and in addition to heavy metals, organic pollutants should also be included.

Importantly, here, in situ MS measurements were proven to be a very efficient tool for use in the initial screening of a large area when searching for possible heavy element contamination. However, other parameters also affect the correlation between MS and pollution, e.g., the mineralogical composition of sediments, which should be addressed in future research.

5. Conclusions

Our research has led to the following conclusions:

- This study was performed to derive the first insights into the distribution of MS in the city of Zagreb and to establish correlations between magnetic parameters and concentrations of heavy metals.
- The median value of 0.245×10^{-3} SI units, obtained via in situ measurements, should be used in the future as the average value of MS in Zagreb.
- The 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 the values set out in the Croatian legislation for agricultural soils, as well as when compared to the values reported for several other cities in Europe and to the world average.
- The boxplot analysis showed that 9 of the 20 elements studied (45% of them) show no anomalies, and most of them have a regular, normal distribution. The elements showing no anomalies include Al, Ca, Cu, Fe, K, Li, Mg, Ni, and Pb. The rest of the elements (As, B, Ba, Cd, Co, Cr, Mn, Na, Sb, Sr, and Zn) mostly showed only one anomaly, among which outliers were the most prevalent.
- The boxplot analysis confirmed that heavy metal anomalies are located at the same sampling points as MS anomalies.
- The correlation analysis between the measured magnetic parameters and the chemical elements analyzed showed a very good correlation, especially for in situ measurements, with values of 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).
- The in situ MS measurements suggest that there is no contamination in some areas where one would expect it (close to industrial areas, landfills, etc.). In the Zagreb city area, we mostly see a geogenic influence driving the changes in MS.
- In situ MS measurements were proven to be a very efficient tool for use in the initial screening of a large area when searching for possible heavy element contamination, thus enabling the cheap and fast assessment of the environmental conditions across the whole of Croatia.
- The proposed methodology, consisting of in situ MS measurements accompanied by sampling on about 20% of locations, on which samples chemical analyses are then performed, could be standardized to enable uniform soil and sediment quality investigations worldwide for heavy metals. In particular, it could be of great benefit to less

developed countries, wherein the number of such investigations could be increased due to the much lower costs compared to classical geochemical investigations, with the main goal of increasing environmental quality.

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Appendix A

In this Appendix, we provide the sample list for the Zagreb study area, followed by geographical coordinates and the results of MS in situ/laboratory measurements for each sampling location.

Table A1. Samples from Zagreb area (* ICP-OES analysis conducted on marked samples).

Sample Code	Sample Name	Geographical Coordinates	MS In Situ/Laboratory Measurements (10^{-3} SI Units)
1	Domovinski Most Žitnjak	45.7740439918759,16.0646237216045	0.134
2	Domovinski Most—Desna Obala	45.7674046988826,16.0745809092195	0.153
3	Sajmišna cesta—istočno od željezničkog mosta	45.756796267067,16.0492017620444	0.172
4	Jakuševec—uz ogradu	45.7617897301369,16.0362761114126	0.132
5	Jakuševec—uz ogradu preko nasipa	45.7622696325107,16.0363446304065	0.262
6	Jakuševec—zapadna strana	45.7714542709519,16.0200244441544	0.135
7	Jakuševec—zapadna strana preko nasipa	45.7718331798484,16.0206753280813	0.403
8	Most Mladosti južna strana	45.7821987831065,16.0037965441551	0.124
9	Bundek—istok *	45.7830193018431,15.9962064322574	0.610/0.171
10	Bundek—sredina	45.7838999603551,15.9930464354659	0.649
11	Bundek—zapad	45.7864101071037,15.9841058651128	0.170
12	Dugave—kod Mamutice	45.7704076311764,15.9923265221306	0.145
13	Mala Mlaka—uz vodocrpilište (1) *	45.7462743121562,15.9747169833504	0.265/0.208
14	Mala Mlaka—uz vodocrpilište (2)	45.7458158117247,15.9741739778074	0.275
15	Bauhaus Buzin *	45.7535884190359,15.9945891742625	0.143/0.094

Table A1. *Cont.*

Sample Code	Sample Name	Geographical Coordinates	MS In Situ/Laboratory Measurements (10^{-3} SI Units)
16	Radmanovačka ulica	45.7700832241245,15.9800396998299	0.159
17	Park Mladenaca	45.7746465500553,15.9673445410879	0.245
18	Park Mladenaca—igralište	45.7751032381159,15.9671763910422	0.130
19	Jadranski most—jug	45.7816941593734,15.95385283141	0.250
20	Park kod bolnice Blato	45.7702962415937,15.9319913022756	0.154
21	Lučko—ispod mosta	45.7602249116831,15.8976352840539	0.393
22	Jankomirski most	45.7935806269139,15.8557617081342	0.111
23	Podsused most—lijeva obala	45.8147444165568,15.832490854702	0.298
24	Dom zdravlja Špansko	45.8026157149214,15.8956596797069	0.154
25	Studentski dom SR	45.7836971448718,15.949668145084	0.487
26	Studentski dom SR—preko nasipa	45.7831088570426,15.9501293702797	0.557
27	Prisavlje—između Kockice i nebodera	45.7898336898784,15.9668565159461	0.363
28	Prisavlje—uz Savu (1) *	45.7887563568321,15.9664180126452	1.920/1.133
29	Prisavlje—uz Savu (2)	45.788273653519,15.9650386659405	1.320
30	Prisavlje (3)	45.78947905595,15.965193478511	0.522
31	Klub Jedrenja (1)	45.7850940879971,15.9109551956364	0.128
32	Klub Jedrenja (2)	45.7853682681368,15.9099933080156	0.122
33	Bejzbol Klub Jarun Uz Savu (1)	45.7786274233417,15.9071087533958	0.184
34	Bejzbol Klub Jarun Uz Savu (2)	45.7787906539309,15.9072969096575	0.165
35	Bejzbol Klub Jarun Uz Savu (3) *	45.7801066807969,15.9101155889901	0.135/0.099
36	Beach Bar Jarun	45.7809718414207,15.9113074612978	0.154
37	Kanu Klub Končar	45.7784918701123,15.9236021302682	0.113
38	Kanu Klub Končar (2) livada	45.7785522055982,15.9224291015104	0.191
39	Sava uz Malo jezero (1)	45.7750205542008,15.9377868606528	0.166
40	Sava uz Malo jezero (2)	45.7752701022045,15.9373544410025	0.124
41	Sava uz Malo jezero (3)	45.7762136901334,15.9370593778734	0.173
42	Aquarius klub	45.7775885288217,15.9371615960587	0.188
43	Potok Črnomerec (1)	45.7818410885191,15.9395530439582	0.216
44	Potok Črnomerec (2)	45.781652000251,15.9393982757416	0.345
45	Šuma uz potok Črnomerec	45.7815276611746,15.9401798570782	0.248
46	Beach Champ Jarun	45.7810855242149,15.9334304834393	0.185
47	IRB	45.8295539829427,15.9885922853691	0.236
48	Trnjanski nasip (1)	45.7907795593901,15.989418541487	0.269
49	Trnjanski nasip (2) *	45.7905337201412,15.9877194091573	1.099/0.410
50	Trnjanski nasip—uz Savu	45.7894111411263,15.9876947623034	0.177
51	Trnjanski nasip (3)	45.7897506796707,15.9878386872978	0.175
52	Petlja na Slavonskoj aveniji	45.7949043519747,15.9985295899873	0.310

Table A1. *Cont.*

Sample Code	Sample Name	Geographical Coordinates	MS In Situ/Laboratory Measurements (10^{-3} SI Units)
53	NK Croatia Savica -uz Savu (1)	45.7869301745477,15.9987511612843	0.137
54	NK Croatia Savica -uz Savu (2)	45.7873074549235,15.9988529488188	0.215
55	NK Croatia Savica -uz Savu (3)	45.7879704748768,15.9986244868195	0.448
56	Džamija Borovje	45.7909066922319,16.010126155733	0.421
57	Bauhaus Žitnjak—spremište Čistoće	45.795090534933,16.0522047747407	0.223
58	Janaf Terminal Žitnjak *	45.7963635020115,16.0668635105983	0.542/0.437
59	Pročišćivač otpadnih voda	45.7944971923019,16.0792669788523	0.183
60	Ivanjorečka cesta	45.7997428089496,16.1080182735642	0.082
61	Autocesta petlja Hrušćica *	45.7923624810942,16.1289417187834	0.125/0.107
62	Sesvete—ulica Blage Zadre	45.8266542930915,16.1264660690146	0.141
63	Sesvete—livada pored škole	45.8333274377861,16.1047794554278	0.202
64A	Mikuševa ulica—Dubec, 0-2 cm *	45.8290197790321,16.0846014842222	0.054/0.052
64B	Mikuševa ulica—Dubec, 2-4 cm *	45.8290197790321,16.0846014842222	0.054/0.054
65	Grad Mladih	45.8502332704355,16.0486783087879	0.240
66	Markuševec	45.8796577000474,16.0224982866012	0.357
67	Jaruga Rebar Kozjak (1) *	45.8309304456805,16.0019013715374	0.505/0.349
68	Jaruga Rebar Kozjak (2)	45.8311316923503,16.0019578417402	0.381
69	Barutana Ambulanta	45.830298022013,16.0003100063588	0.704
70	Radićevo šetalište	45.8299267617057,15.9789251453309	0.452
71	Mihaljevac (Šuma)	45.8410611257105,15.9762674617809	0.314
72	Mihaljevac (Livada)	45.8409545836944,15.9758714311076	0.171
73	Bliznec	45.8692829898902,15.9788763017586	0.362
74	Adolfovac	45.8817654556618,15.971492964021	0.679
75	Činovnička livada—donji dio—šuma *	45.899776961168,15.9542611013382	1.848/1.343
76	Činovnička livada—dno (2) *	45.9003829526604,15.9536296894939	1.890/0.387
77	Hunjka—Sjeverna padina	45.91287765, 15.97204607	0.201
78	Sljeme—vrh (šuma)	45.8996025441563,15.9489672898962	1.873
79	Sljeme Vrh—livada *	45.8995911580052,15.9475478174519	3.027/2.423
80	Crkva Sv. Jakov *	45.8827660820915,15.9320763181073	0.489/0.341
81	Medvedgrad	45.8749433988795,15.9397800238047	0.247
82	Šestine	45.8571843417814,15.9486809780265	0.151
83	Groblje Gornje Vrapče	45.8266002015263,15.9073627455591	0.089
84	Livada Gorenci	45.84026938, 15.91193877	0.095
85	Šalata Livada	45.8172538901291,15.9835428187165	0.108
86	Ribnjak	45.8159532277393,15.9807901895536	0.260
87	Ribnjak (2)	45.815320650954,15.9815977932001	0.286
88	Javni Wc—livada	45.8133675983546,15.9788184221939	0.372

Table A1. *Cont.*

Sample Code	Sample Name	Geographical Coordinates	MS In Situ/Laboratory Measurements (10^{-3} SI Units)
89	Zrinjevac	45.8108508502514,15.9783604621421	0.472
90	Zrinjevac (2)	45.8097653623494,15.9781230138765	0.469
91	Strossmayerov Trg *	45.8084638970296,15.9781433068071	0.729/0,409
92	Tomislavac	45.8068231503416,15.9783594968143	0.239
93	Cmrok Livada (1)	45.8357858085536,15.9720231989523	0.304
94	Cmrok Šuma	45.8355394958674,15.9709901723723	0.319
95	Cmrok Livada (2)	45.8358960003264,15.9730086646345	0.352
96	Tuškanac—šuma	45.8244339310412,15.9690668982057	0.281
97	Tuškanac—livada *	45.8245872401338,15.969796949185	0.220/0.202
98	Trg Dr. Franje Tuđmana	45.8105932741351,15.9555789537231	0.233
99	Park Pravednika među narodima—jaruga *	45.806420820498,15.9445828324816	0.878/0.883
100	Park Pravednika—višlje od jaruge	45.8068482552254,15.9442174534753	0.782
101	Poglavarstvo grada Zagreba	45.8007451874247,15.9764039623233	0.378
102	Poglavarstvo grada Zagreba (2) *	45.8006493678313,15.9757123995982	0.750/0.307
103	Trnjanski nasip—most Slobode Sjeverna strana	45.7908131003426,15.9821906196011	0.170
104	Šire područje oko Ustave Kunišćak *	45.7904523086803,15.9872517164222	0.232/0.149
105	Maksimir (1) oko crkve Sv. Jurja	45.8247877135216,16.02510956668	0.140
106	Maksimir (2) Bukovačka—zapad	45.8226922910388,16.0136379971368	0.476
107	Potok u Maksimiru blizu Bukovačke *	45.8227843572939,16.0138624328225	0.727/0.319
108	Barutana—jaruga spoj	45.8307385076353,16.0050223679232	0.272
109	Barutana—Križanje Tučanove i Salopekove ulice	45.8295679372952,16.0042876216259	0.281
110	Jakuševec Zapad 1	45.7639685124364,16.0201527031963	0.275
111	Jakuševec Zapad 2	45.7640265632125,16.0185065326186	0.085
112	Jakuševec Sredina 1	45.7618346258767,16.0231848000554	0.152
113	Jakuševec Sredina 2 *	45.7624959067962,16.023948068522	0.180/0.112
114	Jakuševec Istok 1	45.7552667080561,16.0301438022254	0.227
115	Jakuševec Istok 2 *	45.7594193882746,16.039880584166	0.223/0.321
116	Petina—kraj aerodroma	45.7543014786061,16.086694405318	0.066
117	Zelena Magistrala	45.8374880265475,15.8829942804282	0.158
118	Zelena Magistrala 2	45.8252727590539,15.8732968793435	0.225
119	Gajnice Park	45.8161784451918,15.8739764208085	0.300
120	Vrapče—blizu bolnice	45.8127733323109,15.8973861147384	0.470
121	Grubišnopoljski put—Rudeš *	45.7989998655385,15.9158978041369	0.507/0.248
122	Savica	45.7820387895255,16.0219886767542	0.321
123	Borongaj cesta-šuma *	45.8077755773537,16.0300792820734	0.639/0.483
124a	Novi Jelkovec, 0-2 cm *	45.8119603937189,16.0858977873957	0.089/0.066
124b	Novi Jelkovec, 15-25 cm *	45.8119603937189,16.0858977873957	0.089/0.074
125	Gornja Dubrava	45.8326561893296,16.044362686839	0.277

Appendix B

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

Table A2. In-situ measurements – Members of Cluster Number 1 and distances from respective cluster center. Cluster contains 25 cases.

Locality	Distance
Bundek—istok	0.028480
Bundek—sredina	0.010520
Studentski dom SR	0.151480
Studentski dom SR—preko nasipa	0.081480
Prisavlje—uz Savu (2)	0.681520
Prisavlje (3)	0.116480
Trnjanski nasip (2)	0.460520
NK Croatia Savica -uz Savu (3)	0.190480
Janaf Terminal Žitnjak	0.096480
Jaruga Rebar Kozjak (1)	0.133480
Barutana Ambulanta	0.065520
Radićevo šetalište	0.186480
Adolfovac	0.040520
Crkva Sv. Jakov	0.149480
Zrinjevac	0.166480
Zrinjevac (2)	0.169480
Strossmayerov Trg	0.090520
Park Pravednika među narodima—jaruga	0.239520
Park Pravednika—višlje od jaruge	0.143520
Poglavarstvo grada Zagreba (2)	0.111520
Maksimir (2) Bukovačka—zapad	0.162480
Potok u Maksimiru blizu Bukovačke	0.088520
Vrapče—blizu bolnice	0.168480
Grubišnopoljski put—Rudeš	0.131480
Borongaj	0.000520

Table A3. In-situ measurements – Members of Cluster Number 2 and distances from respective cluster center. Cluster contains 5 cases.

Locality	Distance
Prisavlje—uz Savu (1)	0.191600
Činovnička livada—donji dio	0.263600
Činovnička livada—dno (2)	0.221600
Sljeme—vrh (šuma)	0.238600
Sljeme vrh—livada	0.915400

Table A4. In-situ MS measurements—Members of Cluster Number 3 and distances from respective cluster center. Cluster contains 95 cases.

Locality	Distance
Domovinski most Žitnjak	0.078526
Domovinski most—Desna obala	0.059526
Sajmišna cesta—istočno od željezničkog mosta	0.040526
Jakuševec—uz ogradu	0.080526
Jakuševec—uz ogradu preko nasipa	0.049474
Jakuševec—zapadna strana	0.077526
Jakuševec—zapadna strana preko nasipa	0.190474
Most Mladosti južna strana	0.088526
Bundek—zapad	0.042526
Dugave—kod Mamutice	0.067526
Mala Mlaka—uz vodocrpilište (1)	0.052474
Mala Mlaka—uz vodocrpilište (2)	0.062474
Bauhaus Buzin	0.069526
Park Mladenaca	0.032474
Park Mladenaca—igralište	0.082526
Radmanovačka ulica	0.053526
Jadranski most—jug	0.037474
Park kod bolnice Blato	0.058526
Lučko—ispod mosta	0.180474
Jankomirski most	0.101526
Podsused most—lijeva obala	0.085474
Dom zdravlja Špansko	0.058526
Prisavlje—između Kockice i nebodera	0.150474
Klub Jedrenja (1)	0.084526
Klub Jedrenja (2)	0.090526
Bejzbol Klub Jarun Uz Savu (1)	0.028526
Bejzbol Klub Jarun Uz Savu (2)	0.047526
Bejzbol Klub Jarun Uz Savu (3)	0.077526
Beach Bar Jarun	0.058526
Kanu Klub Končar (1)	0.099526
Kanu Klub Končar (2) livada	0.021526
Sava uz Malo jezero (1)	0.046526
Sava uz Malo jezero (2)	0.088526
Sava uz Malo jezero (3)	0.039526
Aquarius klub	0.024526
Potok Črnomerec (1)	0.003474
Potok Črnomerec (2)	0.132474
Šuma uz potok Črnomerec	0.035474
Beach Champ bar Jarun	0.027526
IRB	0.023474
Trnjanski nasip (1)	0.056474
Trnjanski nasip—uz Savu	0.035526

Table A4. *Cont.*

Locality	Distance
Trnjanski nasip (3)	0.037526
Petlja na Slavonskoj aveniji	0.097474
NK Croatia Savica -uz Savu (1)	0.075526
NK Croatia Savica -uz Savu (2)	0.002474
Džamija Borovje	0.208474
Bauhaus Žitnjak—spremište Čistoće	0.010474
Pročišćivač otpadnih voda	0.029526
Ivanjorečka cesta	0.130526
Autocesta petlja Hrušćica	0.087526
Sesvete—ulica Blage Zadre	0.071526
Sesvete—livada pored škole	0.010526
Mikuševa ulica—Dubec	0.158526
Grad Mladih	0.027474
Markuševec	0.144474
Jaruga Rebar Kozjak (2)	0.168474
Mihaljevac (Šuma)	0.101474
Mihaljevac (Livada)	0.041526
Bliznec	0.149474
Hunjka—Sjeverna padina	0.011526
Medvedgrad	0.034474
Šestine	0.061526
Groblje Gornje Vrapče	0.123526
Livada Gorenci	0.117526
Šalata Livada	0.104526
Ribnjak	0.047474
Ribnjak (2)	0.073474
Javni Wc—livada	0.159474
Tomislavac	0.026474
Cmrok Livada (1)	0.091474
Cmrok Šuma	0.106474
Cmrok Livada (2)	0.139474
Tuškanac—šuma	0.068474
Tuškanac—livada	0.007474
Trg Dr. Franje Tuđmana	0.020474
Poglavarstvo grada Zagreba	0.165474
Trnjanski nasip—most Slobode Sjev.	0.042526
Šire područje oko Ustave Kunišćak	0.019474
Maksimir (1) oko crkve Sv. Jurja	0.072526
Barutana—jaruga spoj	0.059474
Barutana—Križanje Tučanove i Salopekove	0.068474
Jakuševec Zapad 1	0.062474
Jakuševec Zapad 2	0.127526

Table A4. *Cont.*

Locality	Distance
Jakuševec Sredina 1	0.060526
Jakuševec Sredina 2	0.032526
Jakuševec Istok 1	0.014474
Jakuševec Istok 2	0.010474
Petina—kraj aerodroma	0.146526
Zelena Magistrala	0.054526
Zelena Magistrala 2	0.012474
Gajnice Park	0.087474
Savica	0.108474
Gornja Dubrava	0.064474
Novi Jelkovec	0.123526

Appendix C

In this Appendix, the results of the boxplot statistical analysis applied to the ICP-OES results, as regards element distribution, are shown.

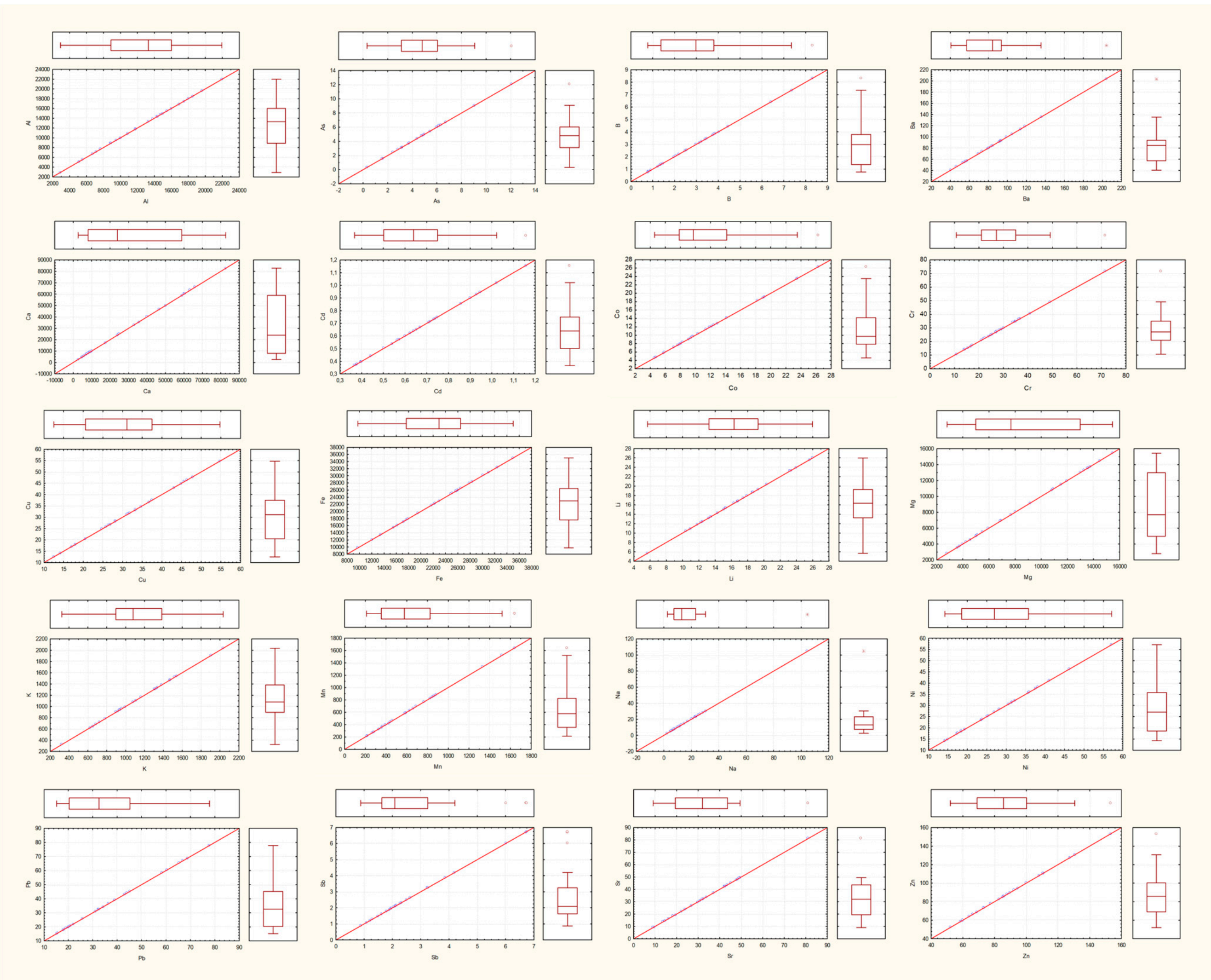

Figure A1. The results of the boxplot statistical analysis applied to the ICP-OES results.

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