Urban Environmental Assessment: The Role of Soil Magnetic Susceptibility in Geochemical Investigations - A Case Study from Maksimir Park, Zagreb, Croatia

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https://doi.org/10.29227/IM-2025-02-03-25
Submission date: *2025-04-30* | Review date: *2025-06-03*

Abstract

Research aimed to determine the spatial variability of soil geochemical properties and soil magnetic susceptibility (MS) in the Maksimir Park, along with to validate the efficacy of MS as a rapid screening tool for urban environmental assessment. The park, encompassing 316 hectares, is situated in Zagreb, Croatia and attracts over two million visitors annually. MS in-situ measurements at 79 locations, coupled with soil sampling at 12 locations within the park were carried out in summer 2023. Prior to the detection and quantification of selected parameters, the soil samples were air-dried, ground, sieved, and homogenized. The pH (w/v 1:5, 1 mol/L KCl) and organic matter (OM, wet combustion) content were determined by standard laboratory methods, while total Pb, Cu, Cr, Ni, As, Zn, Nb, Rb, Sr, Y, Zr, Ti, Mn, Fe and Si content by portable X-ray fluorescence Vanta C Olympus analyzer. MS in-situ and MS Lab (in collected and prepared soil samples) measurements were performed using a SM30 susceptibility meter. The deterministic spatial interpolation technique Inverse Distance Weighting (IDW) was used to display the spatial variability of the soil properties. The results reveal that low MS in-situ values predominate across the majority of park, with smaller localized areas exhibiting increased values. The most pronounced anomalous MS in-situ values were detected in the southwestern corner of the park and are associated with the vicinity of an old streambed. Spatial analysis also indicates that acid soil predominates in the northern forested section of Maksimir park, whereas alkaline soils are predominantly found in the southern areas, particularly near roads. Soils in the park are quite (4.0%) to very highly supplied (13.9%) by organic matter. The average concentrations of accumulated elements were as follows: 48.2 mg Pb/kg, 32.1 mg Cu/kg, 97.9 mg Cr/kg, 33.1 mg Ni/kg, 15.2 mg As/kg, 97.8 mg Zn/kg, 21.1 mg Nb/kg, 84.3 mg Rb/kg, 115.1 mg Sr/kg, 33.9 mg Y/kg, 355.7 mg Zr/kg, 7274 mg Ti/kg, 713 mg Mn/kg, 33.9 g Fe/kg, and 232.2 g Si/kg. Across all examined sites within the park, the levels of lead, copper, arsenic, and nickel were below the thresholds values. However, in the northern park areas with acidic soil conditions, chromium levels exceeded the prescribed thresholds (40 mg Cr/kg), with recorded values ranging between 88.0–99.5 mg/kg. MS Lab results from soil near roads and the entrance to Zagreb Zoo indicate partial anthropogenic impact, supported by higher levels of copper, nickel, and arsenic in these areas. In addition, results point to that most geochemical parameters showing statistically significant and stronger relationships with MS Lab data compared to those achieved with MS In-situ measurment, highlighting the critical role of soil sample preparation as an essential step in ensuring precise and reliable results. Using the example of Maksimir Park in Zagreb, the magnetic susceptibility method has demonstrated its effectiveness as a rapid screening tool for Fe (r=0.9054), Nb (r=-0.9679), Zr (r=-0.9353), Sr (r=0.8910), Ni (r=0.8296), Si (r=-0.8202), Cu (r=0.8610), Rb (r=-0.8135) and Zn (r=0.7456).

Keywords: *urban park, soil quality, heavy metals, magnetic susceptibility, correlation statistical analysis*

1. Introduction

Urbanization, characterized by the transformation of rural areas into urban ones, population growth, and the spread of urban lifestyles, has increased the need for natural retreats. In Zagreb, Croatia's capital, with around 760,000 inhabitants [1], green infrastructure like parks, urban forests, and public gardens play a crucial role. They provide ecosystem services, mitigate the heat island effect, reduce air pollution, provide habitat for plant and animal species and offer recreational spaces [2]. Croatia's Nature Protection Act [3] outlines nine categories of spatial protection, including strict reserves, national parks, special reserves, nature parks, regional parks, natural monuments, significant landscapes, forest parks and monuments of park architecture. The Act aims to preserve biodiversity, landscape diversity, and geodiversity, ensure sustainable resource use, and mitigate harmful human impacts. Maksimir Park in Zagreb, protected as a monument of park architecture, was established in the late 18th century on the property of the bishop of Zagreb that was covered with an old and dense oak forest, meadows and arable land, now is valued for its aesthetic, cultural, and educational significance. As the first public park in Southeast Europe and among first in the world, it is now surrounded by urban development [4]. In 2024, it attracted 2,347,202 visitors, underscoring its recreational importance.

Urban park soils, crucial for ecological regulation, face challenges from human activities and environmental fragmentation. Different soil cover (trees, shrubs, bark, grasslands) and exposure to roads can divide the urban park area into smaller fragments with different microenvironmental conditions that can contribute to the variability of soil chemical properties [5]. Therefore, monitoring soil quality is essential to maintain the park's ecological health. Urban soils exhibit pronounced spatial heterogeneity due to diverse exogenous material inputs and the mixing of parent materials. While their evolution is influenced by the same factors as natural soils, human activities induce significantly accelerated transformation cycles compared to those prevalent under natural conditions [6]. In urban areas geochemical investigations are focused on synthetically, geogenically and biogenically sourced compounds in soil. All cities share common properties forming an urban baseline and research mostly target on identifying both the shared characteristics of urban geochemistry and the unique features of specific cities or specific part of the city [7].

Geochemical analysis of urban and peri-urban soils increasingly focuses on the accumulation, transformation, and spatial distribution of potentially toxic elements (PTEs) (e.g., As, Cd, Co, Cr, Cu, Ni, Pb, Se, Sb, Zn) [8, 9]. These elements can be detected and quantified using classical analytical methods such as Atomic Absorption Spectroscopy (AAS), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), or more recently, by non-destructive methods like portable X-ray Fluorescence (pXRF) [10, 11]. pXRF is precise, a cost-effective technique capable of simultaneously analysing 20-23 elements in real-time. As the popularity of this method grows, the range of methodologies complementing pXRF analyses continues to expand. For instance, recent research strongly supports the introduction of magnetic susceptibility (κ) measurements in soil studies, as they also enable rapid and low-cost screening of large areas. Early research in Košice, Slovakia, near a large metallurgical plant, demonstrated that increased magnetic susceptibility (MS) values in soil samples correlate with higher concentrations of PTEs, suggesting its utility as a prompt and affordable preliminary detection method [12]. Similar findings confirmed significant correlations between MS, numerous PTEs (Fe, Mn, Zn, Ni, Co, Cr, Pb) and soil organic matter [13, 14], while some authors advanced the research by proposing pXRF as an effective tool for geochemical verification of MS hotspots in areas impacted by industrial and urban activities [15]. Recently, a pioneering investigation in Croatia was conducted in the broader area of Zagreb city [16]. The authors identified a median MS value of 0.245 x 10^{-3} SI units and observed strong correlations with PTEs (Cd, Co, Fe, Mn, Na, Pb, Sb, and Zn). This study highlighted the relevant role of soil magnetic susceptibility in detecting heavy metal content during geochemical surveys of large urban areas.

The current study was prompted by findings from investigations conducted in 2022 which included two locations in Maksimir Park [16]. Authors discovered that MS and PETs were very low in the southeastern part of the park, among the lowest in Zagreb, while the southwestern part exhibited very high values. This inspired a detailed investigation of Maksimir Park, hypothesizing significant variability and heterogeneous distribution of MS and heavy metal content. The primary objective of this research was to evaluate the spatial variability of soil geochemical and geophysical properties within Maksimir Park. Additionally, the study aimed to validate, through correlation analysis, the efficacy of soil magnetic susceptibility as a rapid screening tool for urban environmental assessment, serving as a preliminary predictor of heavy metal content in urban park soils.

2. Materials and methods

2.1 Location, magnetic susceptibility in-situ measurements and soil sampling

The research was conducted in the central part of Croatia, in Zagreb, within the Maksimir Park area (45°83'N; 16°02'E, 120 - 167 m a.s.l.) (Figure 1a). The Park covers an area of 356 hectares and is located 2.8 km from the centre of Zagreb (Figure 1b). The average annual air temperature in the park area is 11°C, the annual precipitation is 870 mm, and the most frequent wind direction is north-northeast [4]. The field research was carried out in two phases in August 2023. Initially, *in-situ* measurements of magnetic susceptibility, (MS *In-situ*), were performed at 79 locations within the park (Figure 1c) using an SM30 susceptibility meter (ZH Instruments, Brno, Czech Republic). This highly sensitive instrument (1×10^{-7} SI Units) offers ten times greater sensitivity than competing devices, capable of detecting low-magnetic and diamagnetic materials such as limestone and quartz. At each location MS measurements were conducted in triplicate and mean values from each location were used for spatial analyses of *in-situ* readings.

Following the assessment of the verified MS values and analysis of their spatial distribution, soil sampling was conducted at 12 strategically selected points/locations (Figure 1d). These locations were chosen based on MS *in-situ* measurements, predominant human activities within the park, and land use patterns. Four locations were directly influenced by the proximity of roadways (M1-M4), six forest locations experienced varying levels of visitation and accessibility (M5-M10), and two meadows were characterized by prominent human recreational activities (M11-M12). Twelve composite surface soil samples, each comprising four sub-samples, were collected from the specified locations at a depth of 0-30 cm. The soil sampling was performed using a non-toxic steel hand auger (Eijkelkamp, 2009).

2.2 Laboratory measurements of geochemical and geophysical soil properties

Preparation of soil samples (drying, milling, sieving, homogenizing) for chemical and physical analysis was conducted in compliance with HRN ISO 11464 (2004) method. Geochemical properties in twelve soil samples were quantified in duplicates using standard analytical procedures. Organic matter content was determined using the Tjurin method (bichromate volumetric method, modified HRN ISO 14235:2004 protocol). Soil pH was measured in 1 mol/L KCl solution (w/v 1:5) following potentiometric method with the Beckman F72 pH-meter (HRN ISO 10390, 2005). The total concentrations of metals (Pb, Zn, Cu, Cr, Si, Ti, Mn, Fe, Ni, As, Rb, Sr, Y, Zr, Nb) were determined by the portable X-ray fluorescence method using the Olympus Vanta C portable XRF analyser according to the loose powder method [17]. The accuracy and precision of the analyses were controlled using certified (SRM 2711A) and reference soil samples (ISE 989), with results deemed acceptable (accuracy: recovery < 5%; precision: RSD < 5%). Geophysical soil property, magnetic susceptibility (MS Lab) was also determined in duplicates in prepared soil samples, again using an SM30 susceptibility meter.

2.3 Statistical analyses

Basic statistics such as minimum (Min), maximum (Max), mean, standard deviation (Std.Dev.), coefficient of variation (CV), skewness and kurtosis were analysed for all geochemical and geophysical soil properties. To evaluate the spatial variability of soil properties relative to sampling points within the park, the deterministic spatial interpolation technique, Inverse Distance Weighting (IDW), was employed. Soil sampling locations were georeferenced using the ArcMap 9.3 software package with defined boundary of Maksimir Park. Analytical results of geochemical properties (pH, organic matter and five selected pollutants, Pb, Cu, Cr, Ni, As) and geophysical properties (MS Lab and MS *In-situ*) were assigned to each of twelve sampling points in the attribute table, and IDW interpolation was performed for each individual soil property. To validate the efficacy of soil magnetic susceptibility as a rapid screening tool for urban environmental assessment correlation analysis was performed by calculating Pearson's correlation coefficients between wide range of metals (Pb, Zn, Cu, Cr, Si, Ti, Mn, Fe, Ni, As, Rb, Sr, Y, Zr, Nb) and measured MS values (MS *In-situ* and MS Lab). The descriptive statistical parameters and correlation coefficients were calculated using SAS 9.1.3. statistical program.

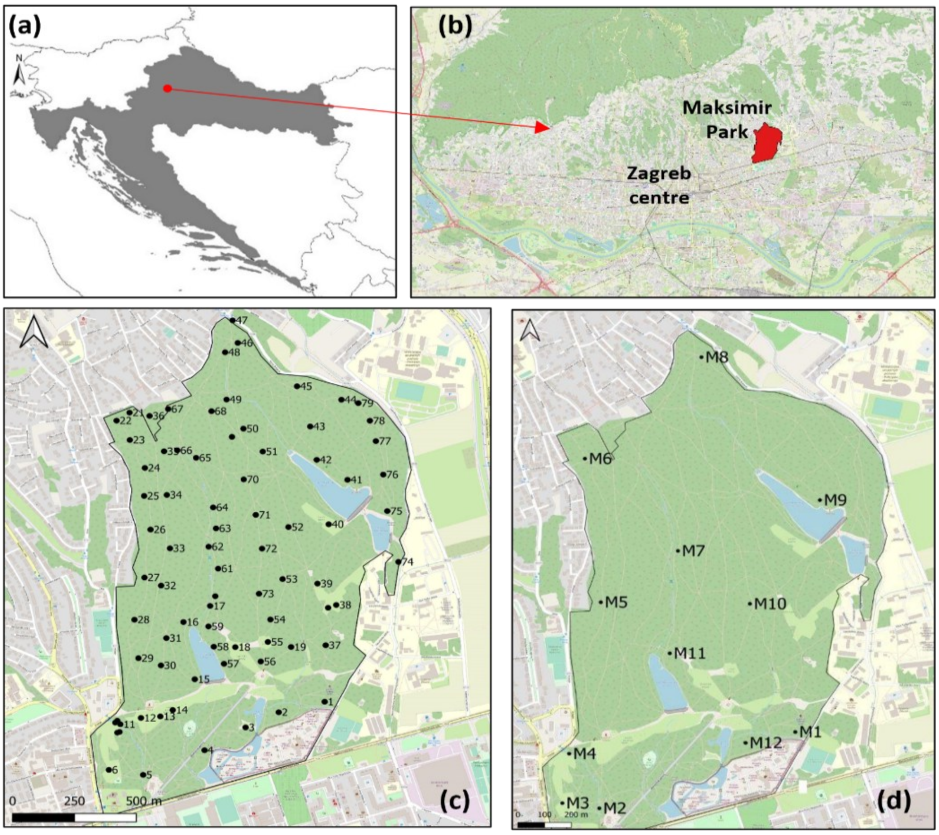

Fig 1. Study area: location of Croatia in European comparison (a); location of the study area (red area, b); locations of MS *in-situ* measurements (c) and locations of soil sampling (d)

3. Results and discussion

3.1 Spatial variability of geochemical and geophysical soil properties

Table 1 presents the descriptive statistics for the geochemical and geophysical properties of the soil within Maksimir Park. Results reveal that the soil pH values ranged from 3.22 to 7.25, indicating a variation from highly acidic to alkaline reactions, which reflects a certain variability of this parameter (CV = 35.8%). The organic matter content ranged from 4.0% to 13.9%, with a mean value (6.84%) suggesting that the soil in the park can be classified as highly humic. The mean content of accumulated metals was: 48.2 mg Pb/kg, 32.1 mg Cu/kg, 97.9 mg Cr/kg, 33.1 mg Ni/kg, 15.2 mg As/kg, 97.8 mg Zn/kg, 21.1 mg Nb/kg, 84.3 mg Rb/kg, 115.1 mg Sr/kg, 33.9 mg Y/kg, 355.7 mg Zr/kg, 7274 mg Ti/kg, 713 mg Mn/kg, 33.9 g Fe/kg, and 232.2 g Si/kg, with lead showing the highest variability (CV = 67.2%). Scientists from Italy associated higher coefficient of variation for Hg (250%), Cd (94%), Pb (82%), Zn (59%) and Cu (58%) in urban soils of Benevento city (Campania region, Italy) with anthropogenic causes [9] which could partly explain the high variability of lead in Maksimir Park. Southern parts of the Maksimir park are bordered by roads and traffic may be the main source of accumulated lead. For example, assessed soil quality from 36 parks and gardens in Vigo City (Spain) exposed to different degrees of traffic intensity and activity indicate moderate contamination by lead [18]. In contrast to the lead, determined manganese (713 mg/kg) and iron (33949 mg/kg) content in Maksimir park is most likely of natural origin and as indicated in the Geochemical Atlas of the Republic of Croatia, their concentrations closely approximate the median values of these elements prevalent in Croatian soils (722 mg Mn/kg, 34000 mg Fe/kg) [19]. Compared to some urban parks in Europe, soil of Maksimir park, despite the pronounced urbanization and many different environmental threats, in average present lower amounts of Cu, Pb and Zn than those detected in Seville (68 mg Cu/kg, 137 mg Pb/kg, 145 mg Zn/kg) [20], Krakow (55 mg Cu/kg, 120.5 mg Pb/kg, 176.7 mg Zn/kg) [21], Prague (50 mg Cu/kg, 67 mg Pb/kg, 152 mg Zn/kg) [22] and Sosnowiec (70.2 mg Cu/kg, 1113.5 mg Pb/kg, 1737 mg Zn/kg) [23] as a reflection to historical legacies and rapid urbanization in the aforementioned cities. Regarding the deviation of the obtained results from the normal distribution, the skewness values indicate excellent symmetry for the pH values and the contents of Cu, Cr, Ni, As, Zn, Nb, Rb, Y, Zr, Ti, Mn, Fe, and Si (between -1 and +1), acceptable symmetry for the organic matter content and strontium (between -2 and +2), and significant deviation from the normal distribution for the lead content (beyond -2 and +2). The kurtosis measure relates to the convexity of the normal distribution curve of the obtained results, indicating that the negative values for most of the presented soil chemical properties denote a flatter data distribution than normal, while the positive kurtosis values for organic matter, Pb, Cr, Sr, and Ti indicate a peaked data distribution compared to the normal distribution.

The results of soil geophysical properties from table 1 point to much higher variability of *in-situ* measurements (CV = 83.4% and 100.4%) in comparison with laboratory measurements (Ms Lab, CV = 56.3). One of the most probable reasons is rather large inhomogeneity of soils within Maksimir Park. Because of such large inhomogeneity, it was almost impossible to sample the same material which was measured *in-situ*. Even less than one-meter distance from the measured spot could mean that sampled material is different from material measured *in-situ*. Also, there are some other factors, e.g. in laboratory conditions are same for all samples -

room temperature, samples are dried, etc., while in the field those conditions cannot be controlled – percentage of moisture in samples, temperature during measurements and some other factors vary from measurement to measurement. Therefore, laboratory measurements showed to be much more reliable, but despite that *in-situ* measurements showed to be very efficient for initial screening of large area, which enables fast detection of anomalous spots, on which more precise measurements as well as soil sampling will be performed.

Tab. 1. Descriptive statistics of geochemical and geophysical soil properties

Soil properties	N	Min	Max	Mean	Std.Dev.	CV, %	Skewness	Kurtosis
MS *In-situ* (10^{-3} SI units)	79	0.045	0.896	0.200	0.167	83.4	2.347	5.590
MS *In-situ* (10^{-3} SI units)	12	0.084	0.896	0.266	0.267	100.4	1.969	2.680
MS Lab (10^{-3} SI units)	12	0.057	0.344	0.174	0.098	56.3	0.674	-1.047
Organic matter (%)	12	4.0	13.9	6.84	3.05	44.6	1.287	1.184
pH	12	3.22	7.25	5.21	1.86	35.8	0.004	-2.407
Pb (mg/kg)	12	22.5	146.5	48.2	32.4	67.2	2.923	9.328
Cu (mg/kg)	12	16.0	53.5	32.1	13.9	43.4	0.312	-1.565
Cr (mg/kg)	12	75.5	126.5	97.9	12.9	13.3	0.689	1.432
Ni (mg/kg)	12	24.5	45.5	33.1	6.33	19.1	0.195	-1.533
As (mg/kg)	12	11.0	18.5	15.2	2.43	16.0	-0.095	-1.344
Zn (mg/kg)	12	63.0	150.5	97.8	29.1	29.8	0.706	-0.437
Nb (mg/kg)	12	13.0	27.5	21.1	5.29	25.1	-0.484	-1.122
Rb (mg/kg)	12	60.5	98.0	84.3	11.9	14.0	-0.935	-0.146
Sr (mg/kg)	12	91.5	161.0	115.1	21.9	19.1	1.034	0.119
Y (mg/kg)	12	28.5	40.0	33.9	3.47	10.2	0.099	-0.757
Zr (mg/kg)	12	247.0	431.0	355.7	69.8	19.6	-0.525	-1.584
Ti (mg/kg)	12	5873	8310	7274	712	9.78	-0.371	0.009
Mn (mg/kg)	12	285.5	1015	713	243	34.1	-0.576	-0.097
Fe (mg/kg)	12	26112	44818	33948	5945	17.5	0.264	-1.129
Si (mg/kg)	12	197008	257434	232204	22226	9.57	-0.492	-1.397

Spatial distribution of MS, based on 79 in-situ measurements is presented in Figure 2. The results reveal that low MS values predominate across the majority of Maksimir Park, with smaller localized areas exhibiting increased values. The most pronounced anomalous MS values are in the southwestern corner of the park. This MS anomaly was previously documented [16] and is associated with the vicinity of an old streambed. This stream is no longer active, as it was artificially redirected and has ceased flowing through the area. However, it served as a source of material transport over an extended period. This evidence also explains the elevated MS values detected in soil samples collected from this part of the park (sampling locations M2-M4, as illustrated in Figure 3). Additional MS anomalies are primarily situated in the central region of Maksimir Park, near the Third Maksimir Lake and along the stream that supplies this artificial lake. Streams traversing Maksimir Park originate from the southern slopes of Medvednica Mountain. Previous investigation in Zagreb [16] recorded the highest MS values, statistically classified as extreme outliers, on Medvednica Mountain. These elevated MS values have a natural origin, attributed to the geological composition of rocks in the region. The same authors also observed elevated MS values along streams descending from Medvednica Mountain and on its slopes, findings consistent with observations in Maksimir Park. These streams transport particles enriched with MS and heavy metal content from the mountain. The prominent MS anomaly in the southwestern part of Maksimir Park is also in proximity to a busy road and residential areas. Nonetheless, this anomaly is primarily attributed to the natural factors. Although previous investigation did not identify elevated MS and heavy metal concentrations near major highways in the broader Zagreb area [16], Figure 3 indicates that MS Lab values in soil samples collected near roads (sampling locations M2-M4) and at the entrance to Zagreb Zoo (location M1) suggest a partial anthropogenic influence. This is further supported by the spatial distribution and elevated concentrations of copper, nickel, and arsenic at these locations (Figures 7, 9, and 10). The small MS anomaly at north-eastern edge of park (Figure 2) close to houses is most probably of anthropogenic influence, probably irresponsible garbage disposal.

Considering that soil pH significantly affects the mobility of metals [24], and that the immobilization of heavy metals is influenced by humic substances from soil organic matter [25], coupled with the growing recognition of metals such as Pb, Cu, Cr, Ni, and As as common urban soil contaminants [26] which pose an ecological threat and health risks to human populations [27], this section provides a detailed spatial variability of pH, organic matter content, and concentrations of Pb, Cu, Cr, Ni, and As within the Maksimir park, as presented in Figures 4-10. Organic matter represents a crucial component within the contemporary framework of sustainable land management, owing to its essential role in preserving soil quality [28]. Soil organic matter exerts a significant influence on various soil properties and processes, including water retention capacity, aggregate stability, pH regulation, buffering capacity, cation exchange mechanisms, mineralization, and the sorption of pesticides and agrochemicals. Additionally, it plays a pivotal role in enhancing soil infiltration and aeration [29]. Figure 4 indicate elevated variability of organic matter in park soils sculpting two forest locations (M5 and M6) with substantial content (13.9% and 10.2% respectively). Scientists from southern Poland determined significant content of organic matter (11.12%) in the topsoil samples of forest Dietla park in Sosnowiec area which was related to the development of the park and partly fertilized materials during the organization of the park [23]. Organic matter content at M5 location partly contributed to higher accumulation of copper (41.5 mg/kg, Figure 7) and arsenic content (17.5 mg/kg, Figure 10). Based on the measured pH values, spatial variability disclose that the park area can be classified into two distinct zones: the northern region, characterized by strongly acidic soils (sampling locations M5-M10), and the southern region, where soils exhibit a neutral to alkaline reaction (sampling locations M1-M4 and M11-M12) due to different parent material, oxidation-reduction processes in the soil and soil water content [30].

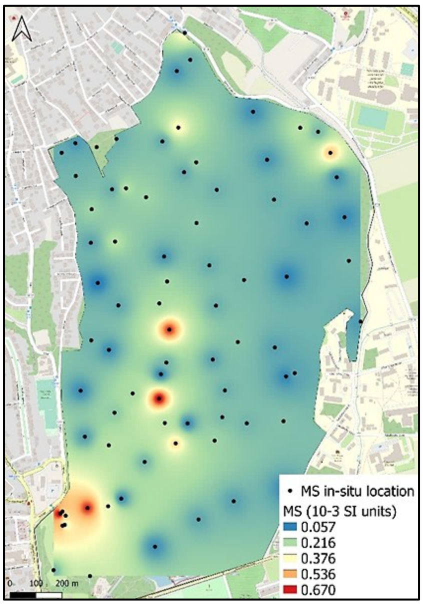

Fig 2. Spatial variability of MS *In-situ* values

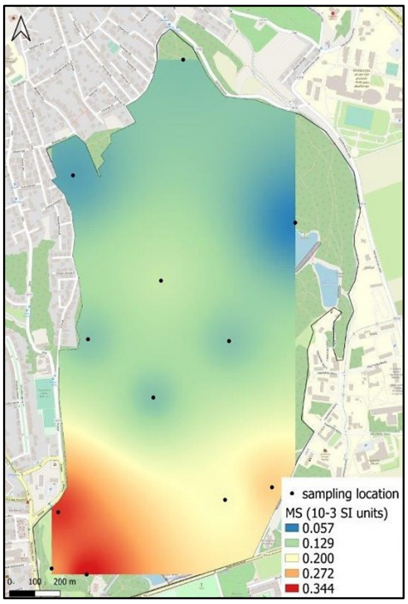

Fig 3. Spatial variability of MS Lab values

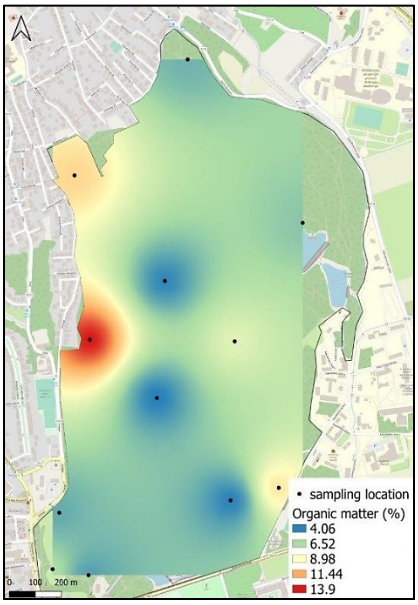

Fig 4. Spatial variability of organic matter

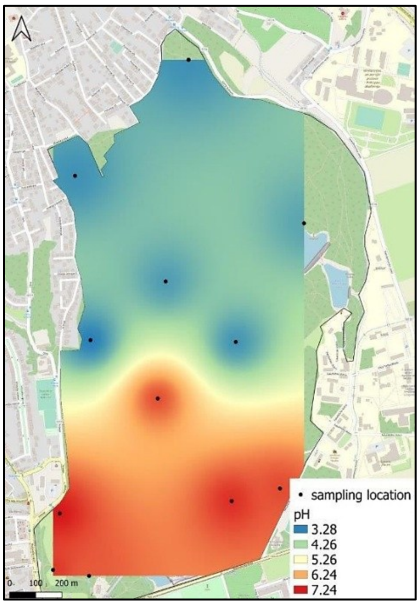

Fig 5. Spatial variability of soil pH

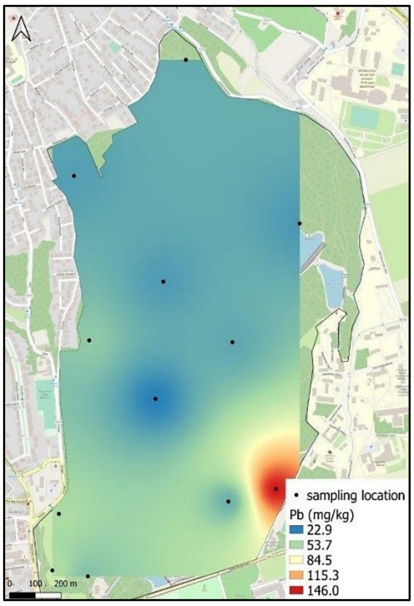

Fig 6. Spatial variability of Pb content in soil

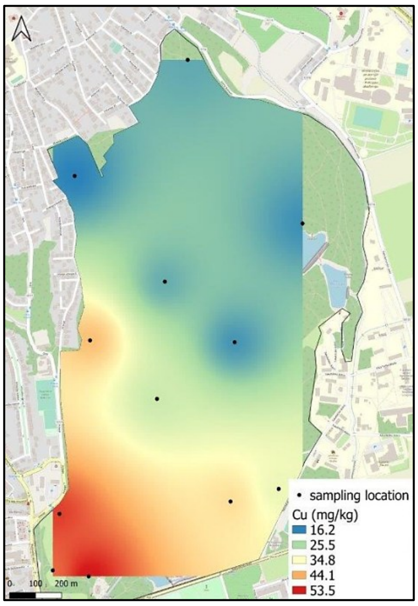

Fig 7. Spatial variability of Cu content in soil

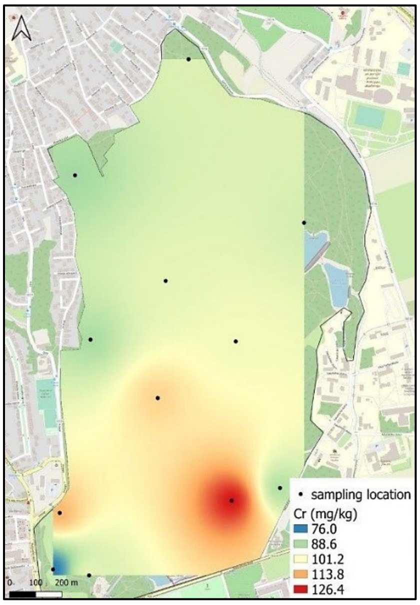

Fig 8. Spatial variability of Cr content in soil

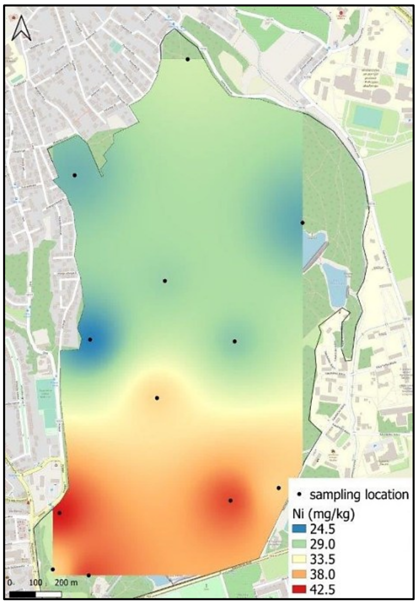

Fig 9. Spatial variability of Ni content in soil

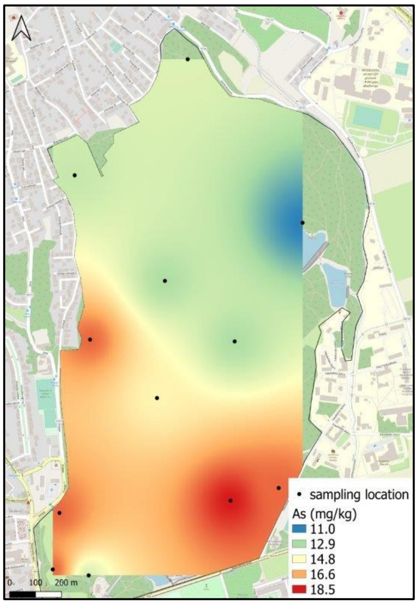

Fig 10. Spatial variability of As content in soil

To enhance comprehension, it is important to note that the neutral to alkaline reaction observed in the southern part of the park can be attributed to geological materials, including limestone, gypsum, rock salt, and various rock types. These materials are commonly utilized in the construction of infrastructure such as roads, buildings, retaining walls, and other structures located in the vicinity of this section of the park. Furthermore, the concrete present at these locations is primarily composed of silicon-rich crushed rock and calcium-rich cement binder, combined with various additives [7]. This composition likely contributed to the elevated silicon levels in the soil, while over the long term, inducing alterations in the soil's reaction, transitioning from acidic to alkaline. Although, forest communities typically thrive on acidic soils, and this soil reaction does not significantly hinder their development, it is important to emphasize that acidic soils (pH < 5.5) which predominate in the northern part of the park, are associated with several limiting factors. These include deficiencies in calcium and magnesium, toxicity resulting from elevated levels of aluminium and manganese, and reduced availability of essential plant nutrients such as phosphorus and molybdenum, along with the metal accumulation in ionic forms, which are readily accessible to plants. In contrast, at higher pH levels, these metals tend to bind to soil constituents such as carbonates and phosphates, resulting in their immobilization within the soil matrix [31]. In Croatia, the maximum allowable concentrations (MAC) of metals in soil are regulated based on soil pH [32]. Consequently, the values of metal content illustrated in Figures 6-10 can be interpreted relative to the prescribed limits for acidic soils (pH <5: 50 mg Pb/kg, 60 mg Cu/kg, 40 mg Cr/kg, 30 mg Ni/kg and 15 mg As/kg) in the northern parts of the park, and with respect to the permissible concentrations (150 mg Pb/kg, 120 mg Cu/kg, 120 mg Cr/kg, 75 mg Ni/kg and 30 mg As/kg) applicable to soils with a pH >6 prevailing in the southern parts of the park. Based on the spatial distribution of lead (Figure 6), it is evident that location M1 (ZOO Entrance) exhibits the highest lead concentration (146 mg/kg), whereas the lowest content (22.5 mg/kg) was observed at location M11 (meadow adjacent to cafes frequented by visitors). If the quantified lead content in the soil is evaluated in relation to soil pH and MAC values, it can be concluded that the lead levels in the park's soil remain within acceptable limits and do not pose an environmental threat. However, it is advisable to conduct permanent monitoring of lead content in the soil, particularly at location M5 (pH 3.22; 47.5 mg Pb/kg; 13.9% organic matter), where the recorded lead concentration approaches the prescribed MAC (50 mg/kg). Additionally, specific soil properties, such as the organic matter content, can influence lead accumulation, while the soil's pH value may affect the bioavailability of lead to plants. The cycling of copper within soil systems is governed by the geochemical processes associated with soil organic carbon, iron-manganese (Fe-Mn) oxides, and various clay minerals present in the soil [33]. Figure 7 reveals that copper content remain below MAC values across the entire park area with decreasing trend within the soil as one moves deeper into the northern and northeastern regions of the Park's forested area. A comparable pattern was observed in the distribution of chromium (Figure 8), nickel (Figure 9), and arsenic (Figure 10), with elevated concentrations detected in the meadows (locations M11-M12) situated in the southern section of the park, as opposed to the forest soils in the northern areas (M5-M10). This observation aligns with findings of scientists from Finland [34]. They determined that soils under lawn (meadow) in Helsinki's parks had generally higher pools of metals (e.g, Cr, Mn, Ni, Fe, Zn, Cu), often in young and particularly in intermediate parks, while all metals were low in soils under deciduous forests in young parks, and under evergreen trees in the older parks, similar to the forest type characteristic of the northern regions of Maksimir Park. Considering that chromium is classified as one of the most carcinogenic elements by the International Agency for Research on Cancer [35], it is crucial to emphasize that its content surpasses the MAC values in a frequently visited meadow located in the southern section of the park (M12), as well as in all forest soils within the northern regions of the park (Figure 8). In contrast to the chromium content, the nickel and arsenic levels in the soil across all sampled locations within the park remain below the MAC thresholds.

3.2 Efficacy of Soil Magnetic Susceptibility in Geochemical Investigations

Pearson correlation coefficients were calculated to examine the relationships between geochemical and geophysical soil properties, with results presented in Table 2. The coefficients were determined separately for 12 selected *in-situ* MS measurements at locations approximately corresponding to soil sampling sites and for laboratory analyses of the prepared soils samples (MS Lab). As shown in Table 2, all correlations between *in-situ* MS measurements and geochemical soil properties were not statistically significant. Nevertheless, weak yet discernible positive correlations were observed between *in-situ* MS values and pH, Cu, Cr, Ni, Zn, Sr, and Fe, suggesting elevated concentrations of these parameters at locations with higher *in-situ* MS values. In contrast, correlations derived from laboratory MS measurements demonstrated significantly stronger associations, with most geochemical parameters showing statistically significant correlations with MS Lab data. The strongest positive correlation was observed with Fe (r = 0.9054), accompanied by other very strong relationships with pH (r = 0.7734), Zn (r = 0.7456), Cu (r = 0.8610), Ni (r = 0.8296), and Sr (r = 0.8910). Although not statistically significant, content of Pb, As, Y, and Mn displayed weak but noticeable positive correlations with MS Lab data. When comparing MS correlations with heavy metals across the broader Zagreb area, the findings align with the observations from Maksimir Park. Notably, the correlation between MS and Fe in the wider region is markedly stronger than that observed across the entire city [16]. Also, correlations of MS with other elements are stronger within Maksimir Park, than those observed across the entire city. This can be explained with the fact that there is no "universal correlation" between MS and particular metals and in every studied region MS is linked to different elements with different correlation coefficients. It proved that usually correlations are much higher in smaller areas, especially if there is one dominant source of pollution. As whole Zagreb city area is much larger than Maksimir Park, which is only one small part of it, in that larger area there are much more pollution sources, also soil and rock composition are of much greater diversity, etc., therefore the highest observed correlation in the Zagreb area (it was correlation of MS with Zn) was 0.75, what is significantly lower than correlations determined within the current research of Maksimir Park. Yet there are no other published data on MS correlation with heavy metals in soils in Croatia and nearby countries, but there are several studies performed on river sediments. The largest study was performed by scientist from Zagreb in 2014 on river sediments from three karstic and flysch regions of Slovenia and Croatia [36]. They successfully applied for the first time this fast, cheap and simple method for estimation of pollution with toxic metals in those areas of Slovenia and Croatia. Highest correlations between MS and heavy metals were found in their studied region "b", which is a karstic region in Slovenia, belonging to the Sava River drainage basin, to which Zagreb area also belongs. Their research was performed on sediments of Rak, Cerknišnica, Unec and Ljubljanica rivers. Highest correlations of MS which they found were those with Cr (0.89), Mn (0.84), Fe (0.86), Co (0.81), Ni (0.79), Cu (0.81), Zn (0.89), Cd (0.89) and Ba (0.83). So, those concentrations from their research are comparable and very similar to correlations found within the current research. Results of the current study, as well as results of numerous other studies worldwide show that despite of some limitations magnetic measurements can serve as a very useful tool for initial fast and economical screening of soils and sediments, to detect potential locations with elevated heavy metal concentrations. For instance, researchers from Iran conducted studies to investigate the application of magnetic susceptibility measurements in assessing metal concentrations within soils derived from various parent materials in the northwestern region of Iran [13]. Their findings revealed robust positive statistical correlations between MS and several elements, including Fe (0.87), Mn (0.78), Zn (0.74), Ni (0.90), Co (0.78), and Cr (0.90). Based on these results, they concluded that the association between metals and ferrimagnetic minerals facilitates the prediction of metal concentrations in soils. Another study conducted in Iran [14] examined the correlations between MS and selected heavy metals such as As, Cr, Cd, and Pb, alongside the physico-chemical properties of soils collected in District 5 of Tehran Municipality. The researchers identified significant correlations between MS and Pb, as well as Cr. Additionally, they observed a notable correlation between MS and soil organic matter. From these findings, they concluded that MS measurements can be utilized for rapid assessment of heavy metal levels and monitoring changes in organic matter within soils.

Tab. 2. Pearson correlation coefficients between geochemical and geophysical soil properties

Soil properties	MS *In-situ*	MS Lab
Organic matter	-0.3778^{NS}	-0.2604^{NS}
pH	0.4589^{NS}	0.7734^{**}
Pb	-0.1903^{NS}	0.4058^{NS}
Cu	0.3438^{NS}	0.8610^{***}
Cr	0.4162^{NS}	0.0678^{NS}
Ni	0.4782^{NS}	0.8296^{***}
As	0.1713^{NS}	0.5232^{NS}
Zn	0.4015^{NS}	0.7456^{**}
Nb	-0.3461^{NS}	-0.9679^{***}
Rb	-0.1916^{NS}	-0.8135^{**}
Sr	0.3500^{NS}	0.8910^{***}
Y	0.1335^{NS}	0.3838^{NS}
Zr	-0.2561^{NS}	-0.9353^{***}
Ti	-0.1729^{NS}	-0.5822^{*}
Mn	0.1279^{NS}	0.5721^{NS}
Fe	0.3558^{NS}	0.9054^{***}
Si	-0.1631^{NS}	-0.8202^{**}

Correlations between observed values are significant at $^*p < 0.05$, $^{**}p < 0.01$, $^{***}p < 0.001$ and ns: not significant.

4. Conclusions

Nowadays, when the critical importance of soil is increasingly acknowledged and safeguarded through numerous regulations, including the most recent directive from the Council of the European Union, the "Soil Monitoring Law", this research highlights the indispensable need for permanent monitoring of urban soils, particularly of soils in large urban parks, which serve as recreational spaces for the population. Findings reveal that among the five examined potentially toxic elements (PTEs), Pb, Cu, Cr, Ni, and As, the chromium content at certain locations within Maksimir Park exceeds the thresholds values. Consequently, further research should incorporate ecological and health risk assessments, considering the cumulative presence of PTEs in these soils.

Additionally, the study emphasizes the necessity of employing soil magnetic susceptibility measurements as a preliminary predictive tool and screening method for elements such as Fe, Cu, Zn, Ni, Si, Nb, Rb, Sr and Zr in air-dried and homogenized soil samples. Future investigations should extend to a broader spectrum of soils with diverse uses and varying chemical and physical characteristics. These studies should aim to establish regression models that elucidate the relationships between specific geochemical soil properties and magnetic susceptibility values in order to derive regression equations capable of accurately estimation the metals content in soil based on magnetic susceptibility measurements, and thus, in some cases, partially for screening, replaced conventional analytical methods. This approach would further validate the critical role of magnetic susceptibility measurements in advance geochemical investigations.

Acknowledgments

We thank doctoral student Josip Peco from Faculty of Science, University of Zagreb, for help during in-situ measurements.

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