

Article

Mobility of Potentially Toxic Elements in Urban Soils of Zagreb: A Single-Step Extraction Approach for Evaluating the Efficiency of Three Extraction Agents

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Abstract

This study extends previous investigations of soils in Zagreb, the capital of Croatia, by focusing on 25 urban samples selected on the basis of their magnetic susceptibility values. A single-step extraction was performed using 1 M HCl, 2 M HNO₃, and 1 M CH₃COONH₄ as extraction reagents. The contents of As, Ba, Cd, Co, Cr, Cu, Fe, K, Mn, Ni, Pb, Sb, and Zn in the extracts were determined using inductively coupled plasma–optical emission spectrometry (ICP-OES). Extraction efficiency was evaluated by comparing element contents obtained with each reagent and their ratios to the corresponding total element contents. Efficiency varied significantly; 1 M HCl showed the highest average efficiency for most elements (range 0.64–59.9%), while 2 M HNO₃ achieved the highest maximum efficiency values (0.31–75.6%). The 1 M CH₃COONH₄ was more efficient for K and Ba than for other elements (0.010–57.7%). The extraction efficiency of the two acids followed a clear pattern—similar recoveries for some samples, HCl-favoured for others, and HNO₃-favoured for the rest. The elemental contents were found to reflect contributions from Mount Medvednica, the Sava River floodplain, and anthropogenic sources. These results indicate that single-step extraction is a valuable method for estimating element mobility.

Keywords: single-step extraction; Zagreb; contaminated urban soil; toxic elements; environmental risk; element mobility



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1. Introduction

Soil is a complex heterogeneous system consisting of mineral and organic solids, gaseous and liquid components, and living organisms [1,2]. Like other segments of the environment, it is subject to various negative natural and anthropogenic impacts [2]. Contamination with potentially toxic elements is considered one of the most significant and ubiquitous environmental problems due to their persistence and inability to biodegrade [3–5]. They include metals and non-metals that can potentially have harmful effects on organisms when present at high contents. Although some of these elements are essential for the

normal functioning of living organisms, others can be toxic even at very low contents [6,7]. Emission and deposition over a long period of time can lead to enrichment in surface layers [5]. However, total element contents in the soil do not provide complete insight into their actual impact, as they do not reflect their extractability or potential mobility. The mobility and availability of elements primarily depend on their reactivity and on how they bind to components of the soil matrix [6,8].

Urban soils are formed under long-term or intensive anthropogenic influence, inheriting characteristics from parent rock that shape their physicochemical properties and nutrient cycles, unlike natural and agricultural soils [9–11]. They generally show irregular layering, fragile structures, and high trace element content [12,13]. Further urbanization and industrialization continue to disrupt the functions of soil ecosystems, such as paving, which is a significant example of disruption to the hydrological cycle and energy balance [14]. Although seldom used for agricultural purposes, the potential for metal extraction from urban soils is still important to assess their environmental and health effects [15]. The accumulation of potentially toxic elements also arises from increased traffic and population density in areas of intensive urbanization. Consequently, exposure risk is particularly high in locations often perceived as clean, such as parks, historic complexes, and religious buildings [14,16]. However, the influence of various urban factors on contamination levels and the corresponding risks to human health has not yet been fully elucidated [16,17].

Single-step extraction methods are widely used to evaluate the extractable and potentially mobile fractions of metals due to their simplicity, relative safety, and short time of execution. For this purpose, many extraction reagents have been proposed [18]. 1 M HCl is an adequate extraction reagent for the evaluation of potentially mobile and extractable metal fractions in soil and sediments. Its ability to reduce certain matrix phases contributes to the release of metals bound to Fe and Mn oxides, which, in oxidized sediments, often represent significant reservoirs of trace elements. In addition, it exhibits high efficiency in decomposing amorphous sulfides and labile organic phases—both of which are key factors controlling the distribution and mobility of metals in anoxic and partially oxidized sediments [19,20]—as well as some clay minerals, potentially leading to an overestimation of the extractable metal fraction [21,22]. Similar to that, 2 M HNO₃ is used to assess potentially mobile and mobilizable metal forms; this extraction agent efficiently dissolves iron and manganese oxides, as well as metal fractions bound to sulfides and phosphates [23]. The metal content obtained through this extraction reflects the maximum amount that could potentially be mobilized. This method provides a more relevant basis for ecological risk assessment than measuring the total metal content [24,25].

Ammonium acetate (1 M CH₃COONH₄, pH 7) is widely used and considered an effective cationic exchange reagent that releases metals weakly bound by electrostatic forces. It is efficient due to the relatively high concentration and the chelating ability of the acetate ion, which reduces the possibility of reabsorption and reprecipitation [26]. Additionally, ammonium salt solutions are characterized not only by high extraction efficiency but also by an analytical advantage over alkali and alkaline earth metal salts. They cause less spectral interference, such as background noise and light scattering (ICP-OES) [27].

In this paper, urban soil samples from the city of Zagreb, the capital of the Republic of Croatia, Europe, were examined by a one-step extraction method with three different extraction agents: 1 M HCl, 2 M HNO₃, and 1 M CH₃COONH₄. The city is characterized by two major geomorphological features: Mount Medvednica, with its highest peak, Sljeme (1033 m), located in the north, and the lowland plain along the Sava River in the south. The goal was to evaluate the potentially mobile and extractable fractions of potentially toxic elements and macroelements and to compare the effectiveness of each reagent in extracting 13 elements from 25 soil samples. Inductively coupled plasma–optical emission

spectroscopy was used for quantitative determination of As, Ba, Cd, Co, Cr, Cu, Fe, K, Mn, Ni, Pb, Sb, and Zn content.

This research continues the work of Frančišković-Bilinski et al. [28] and Sakan et al. [16] on soils of Zagreb. Frančišković-Bilinski et al. [28] investigated magnetic and geochemical parameters to evaluate anthropogenic impacts and the association of magnetic susceptibility (MS) with element contents. Sakan et al. [16] evaluated contamination levels (enrichment factor, risk assessment code) and human health risks, and applied the optimized BCR sequential extraction scheme to characterize elemental fractionation. The present study focuses on the mobility of potentially toxic elements through single-step extraction procedures, with a comparative assessment of extractant efficiencies. The essential differences between this study and earlier publications should be highlighted together with the principal terms and methods used in each. Francisković-Bilinski et al. [28] focused on magnetic and geochemical characterization and total element contents, whereas Sakan et al. [16] addressed contamination assessment, human health risk, and BCR sequential extraction. The principal methods and topics of the present study are single-step extraction, comparative extractant efficiency, extractable-to-total ratios, and mobility-oriented interpretation.

The novelty of this study is systematic comparison of three single-step extractants and the quantification of extractable-to-total ratios for 13 elements in urban soils of Zagreb. The 25 locations were intentionally selected from 125 sites based on magnetic susceptibility anomalies and potential contamination sources. Therefore, the dataset is not representative of average Zagreb urban soil; it overrepresents potentially contaminated locations. This is the first study, to our knowledge, that systematically compares these three extractants on potentially contaminated urban soils in Zagreb and evaluates the extracted-to-total ratios for As, Ba, Cd, Co, Cr, Cu, Fe, K, Mn, Ni, Pb, Sb, and Zn. The present dataset (single-step extraction results) has not been published previously. Although the sampling was targeted rather than random and the dataset overrepresents potentially contaminated locations, so the results cannot be generalized to Zagreb's average urban soil, the findings remain valuable for identifying contamination hotspots and anomalous sites. Given that the mobility and availability of potentially toxic elements largely determine their behavior in contaminated urban soils, the insights gained here also have direct implications for the design and optimization of remediation strategies.

2. Materials and Methods

2.1. Study Area and Sample Collection

Research in the current paper was conducted on samples collected in the study by Frančišković-Bilinski et al. [28] (the selection of 25 samples and locations is shown in Figure 1; a visual representation of the location is shown in the photographs in the Supplementary Material: Figures S1–S3). The selection of sample locations was based on several factors: field measurements of MS were carried out at 125 locations, and detailed statistical analyses were performed to find anomalous locations. It is known that locations with elevated MS values usually also have elevated heavy metal contents; therefore, this criterion was among the most important when selecting the 25 locations of interest. Besides that criterion, the locations of potential contamination sources, e.g., industry, landfills, ore-bearing rocks, etc., were also considered when selecting soil sampling locations in the Zagreb city area. For more details about the sample collection procedure, we refer to Frančišković-Bilinski et al. [28].

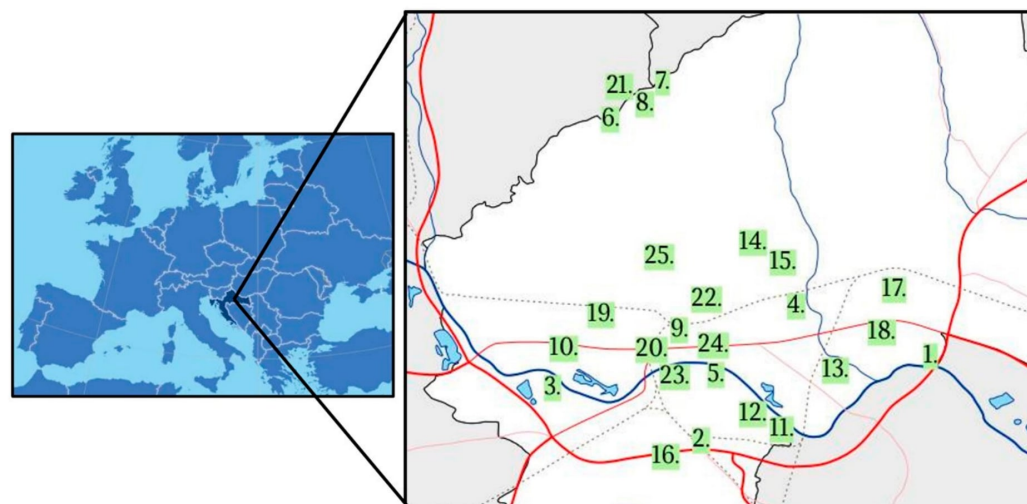


Figure 1. Sampling locations: 1. Hrušćica highway interchange; 2. Bauhaus mall Buzin; 3. Baseball Club Jarun, near the Sava River; 4. Borongaj; 5. Bundek, east; 6. St. Jakov church; 7. Činovnička meadow, lower part of the forest; 8. Činovnička meadow, bottom; 9. headship of the city of Zagreb; 10. Grubišnoplje Road, Rudeš; 11. Jakuševac landfill, east; 12. Jakuševac landfill, middle; 13. JANAF oil terminal Žitnjak; 14. Ravine Rebar Kozjak; 15. stream in Maksimir Park, near Bukovačka street; 16. Mala Mlaka, near water supply station; 17. Mikuševa street, Dubec; 18. Novi Jelkovec; 19. Park pravednika među narodima; 20. Prisavlja, along the Sava River; 21. Sljeme peak, meadow; 22. Strossmayer Square; 23. the wider area around the Kuniščak weir; 24. Trnjan embankment; 25. Tuškanac, meadow (modified from: https://www.d-maps.com/pays.php?num_pay=4967&lang=en; <https://mapswire.com>; accessed on 16 July 2026).

The sampling campaign was carried out on 8th and 9th November 2022 on 25 previously selected locations according to the criteria described in the previous paragraph. This database was used for research that was published in [28]. The samples in the current research numbered from 1 to 25 were not numbered in the research published in [28], but were named according to names of their locations. The database of ICP-OES results of total contents of 20 chemical elements is published in Table 10 in [28].

The sampling procedure was as follows: 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 after grass or leaf cover was removed to reveal the bare surface of the soil, within a square with sides of 25 cm, from which the soil was sampled to a depth of 2 cm. This depth of the layer was selected due to the fact that the signal of the used MS-measurement instrument enters up to 2 cm deep, so sampled material could be compared with previously done in-situ measurements. A spade was used to sample the soils, which were then packed into PVC bags and transported to the laboratory, where the 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. A total of 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 for later analysis. 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.

2.2. Analysis of the Soil Samples

Single-step extraction of the soil samples was performed using three different agents: 1 M HCl, 2 M HNO₃, and 1 M CH₃COONH₄.

For extraction with HCl, 1 g of the soil sample was measured into a 50 mL centrifuge tube, and 20 mL of 1 M HCl was added to each tube. The 1 M HCl solution was prepared

by mixing 83.3 mL of concentrated acid with distilled water to a final volume of 1 L in a volumetric flask. The extraction was carried out for 1 h at room temperature on a rotary shaker (Heidolph) [20].

For the 2 M HNO₃ extraction, 2 g of the soil sample was measured into a 50 mL centrifuge tube, and 20 mL aliquots of 2 M HNO₃ were added to each tube. The 2 M HNO₃ solution was prepared by mixing 139.4 mL of concentrated 65% nitric acid with distilled water to a final volume of 1 L in a volumetric flask. The extraction also lasted 1 h at room temperature on a rotary shaker (Heidolph) [25].

A 1 M CH₃COONH₄ solution was prepared by dissolving 77 g of the solid salt in distilled water and diluting to 1 L in a volumetric flask. The pH of the freshly prepared 1 M CH₃COONH₄ solution was measured with a calibrated pH meter at 25 °C. The measured pH was 7.0 ± 0.1 , confirming the neutral character of the solution. For analysis, 1 g of the sample was weighed into a 50 mL centrifuge tube, and 40 mL of 1 M CH₃COONH₄ was added to each tube. The suspension was shaken on a rotary shaker (Heidolph) for 2 h at room temperature [29].

The three extraction protocols differ in soil-to-solution ratio and extraction time, which are inherent to the standard procedures for each reagent. These differences may influence the absolute amounts extracted and therefore limit direct quantitative comparison of the reagents. For this reason, the comparison presented in this study is based primarily on the relative patterns of extractable-to-total ratios and on the spatial and element-specific trends.

Upon completion of the extraction, all samples were centrifuged at 3000 rpm for 10 min (Hettich Zentrifugen–Universal 320). The supernatants were filtered, then diluted to a total volume of 50 mL with 1 M HNO₃ and stored in polyethylene bottles until further analysis. For each procedure, a cuvette containing only the extraction solution was also prepared as a blank sample and treated in the same way as the other samples.

The quantitative determination was performed by ICP-OES (iCAP 6500 Duo ICP, Thermo Fisher Scientific, Cambridge, UK). Analysis was performed on a spectrometer equipped with a RACID86 CID (Charge Injection Device, Thermo Fisher Scientific, Cambridge, UK) detector, a concentric nebulizer, a quartz torch, and an alumina injector. External calibration solutions were prepared using two certified plasma standard solutions: Multi-Element Plasma Standard Solution 4, Specpure® (1000 µg/mL), and Arsenic Plasma Standard Solution, Specpure® (As 1000 µg/mL), both sourced from Thermo Scientific Chemicals.

2.3. ICP-OES Measurement Conditions and Quality Assurance

The emission lines employed in the ICP-OES analysis were selected based on an internal interference assessment conducted during method development. For each analyte, two to three emission lines were monitored simultaneously across all samples. The final selection of wavelengths for quantification was made by comparing sample and standard spectra, taking into account the absence of spectral overlaps, signal intensity, signal-to-background ratio, and the quality of the calibration curve fit. Furthermore, the full width at half maximum (FWHM) of each emission line was considered to ensure adequate spectral resolution and to minimize potential inter-element interferences. The exact wavelengths used are listed in Table S1.

The limits of detection (LODs) and quantification (LOQs) were automatically calculated by the iTEVA software (Thermo Scientific) based on calibration curve statistics (3σ and 10σ criteria, respectively), and ranged from 0.05 to 1.5 µg L^{−1} for LOD and from 0.1 to 5 µg L^{−1} for LOQ. Individual LOD and LOQ values for each element are listed in Table S2, expressed both in µg L^{−1} and in mg kg^{−1} of the soil, calculated based on the sample preparation protocol (1.00 g in 50 mL).

Quality control procedures included the use of blank samples, matrix-matched calibration solutions, and duplicate analyses of each sample. The reliability of measurements was confirmed by a relative standard deviation (RSD) of less than 1%. The correlation coefficients exceeded 0.99 for all calibration curves within the measured concentration ranges. Analytical quality control (QC) was performed using the water-based certified reference material (CRM) EPA Method 200.7 LPC Solution (ULTRA Scientific, North Kingstown, RI, USA), which was used to verify the accuracy of instrument calibration, with recoveries ranging from 98% to 103%.

Method accuracy was assessed using addition (spike-and-recovery) experiments. Known concentrations of metal standards were added to previously analyzed soil samples with low background levels. The samples were stored for one month at room temperature in sealed containers and mixed daily to ensure homogenization and metal complexation. Spiked samples were subjected to the same extraction and analysis procedure as unspiked samples. Recovery was calculated as: $\text{Recovery (\%)} = [(C_{\text{spiked}} - C_{\text{unspiked}}) / C_{\text{added}}] \times 100$. Acceptable recoveries ranged from 90% to 110%, confirming the method's reliability for this soil matrix. Uncertainty of the measurement for all elements was max. 3% while expanded uncertainty with a coverage factor of 2 was max. 6%.

2.4. Non-Parametric Analysis of Element Contents Obtained by Three Reagents

To evaluate the differences in element contents extracted by three different extraction agents, the Related-Samples Friedman's Two-Way Analysis of Variance by Ranks was employed. This test allows for a direct comparison of three or more related groups simultaneously, providing a reliable omnibus test to determine whether the extraction method significantly affects the measured concentrations.

3. Results and Discussion

3.1. Element Contents

Element contents were determined using three extraction agents, 1 M HCl, 2 M HNO₃, and 1 M CH₃COONH₄, as presented in Figures 2 and 3, and Table 1. The efficiency of the applied extractants was evaluated and discussed. This assessment included calculating elemental content ratios using different extractants, as well as the ratios of extracted to total elemental content. Extractable-to-total ratios were calculated as $(\text{extractable content} / \text{total content}) \times 100$. Total contents, which were determined after total digestion and expressed on a dry-weight basis (mg kg⁻¹), were taken from Frančičković-Bilinski et al. [28]. These comparisons provided insight into the relative extraction performance of the reagents and the proportion of each element that could be mobilized under the applied extraction conditions.

3.1.1. As

The lowest arsenic content extracted with HCl was recorded in sample 25, a meadow in a park located in the northern residential part of the city, on the slopes of Medvednica Mt (0.20 mg kg⁻¹), and the highest in sample 20, a meadow in the inundation area within embankments near the Sava River, which is flooded almost every year, so the influence of overbank sediments brought there from the Slovenian Alps could be expected (2.48 mg kg⁻¹). Sample 21 was not included in further processing due to certain deviations. Arsenic contents were below the detection limit in several samples (13, 15–17, 23, and 25) using HNO₃ for extraction. Content ranged from 0.029 mg kg⁻¹ in sample 14 (forest within the Rebar–Kozjak ravine on Medvednica Mt slopes, surrounded by residential areas) to 1.35 mg kg⁻¹ in sample 8 (ski slope at the top of Medvednica Mt). The element content obtained using CH₃COONH₄ was below the instrument's detection limit. Greater As con-

tents were obtained at locations 7 and 8 by applying HCl and HNO₃ as extraction agents, and at locations 19–22 by applying HCl. HCl proved to be the most effective extraction agent, especially for samples 11–25, while for samples 1–10, HNO₃ exhibited comparable extraction efficiency (a similarity criterion of $\leq 15\%$ difference was applied).

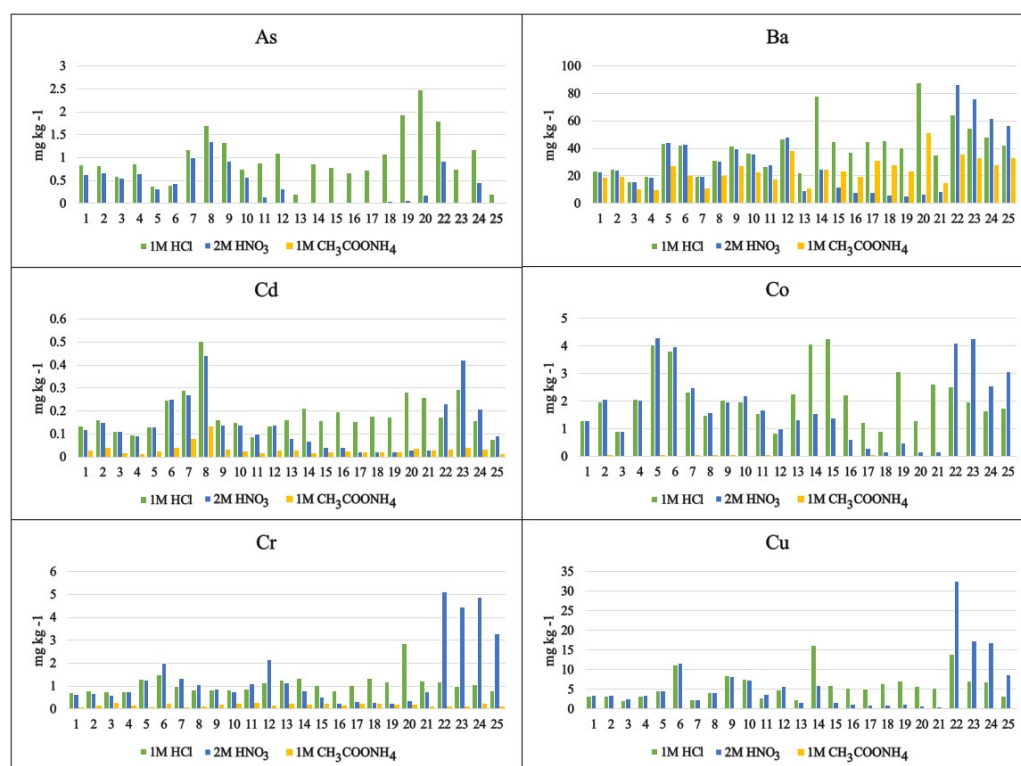


Figure 2. Extracted contents of As, Ba, Cd, Co, Cr, and Cu from soil using different reagents.

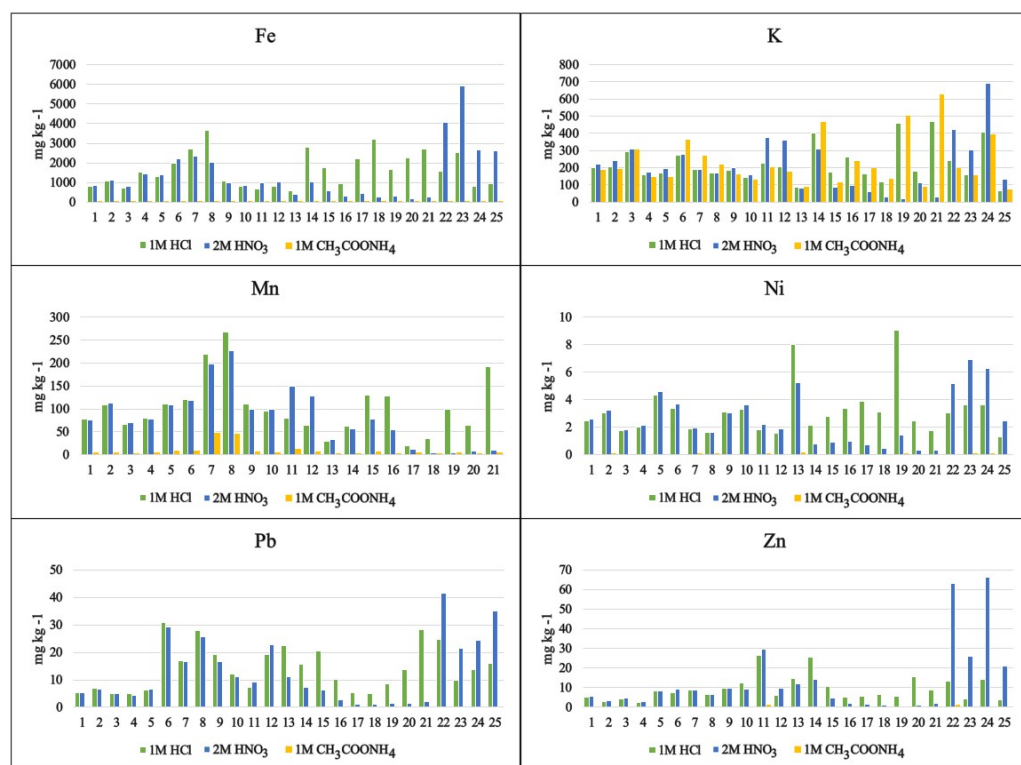


Figure 3. Extracted contents of Fe, K, Mn, Ni, Pb, and Zn from soil using different reagents.

Table 1. Minimum, maximum, and average element contents (mg kg^{−1}) extracted from soil.

	1 M HCl			2 M HNO ₃			1 M CH ₃ COONH ₄			Overall Values		
	min	max	av	min	max	av	min	max	av	min	max	av
As	0.20	2.48	0.98	0.029	1.35	0.51	<dl	<dl	<dl	0.029	2.48	0.78
Ba	15.9	87.5	40.7	5.54	86.3	29.6	9.41	51.3	23.9	5.54	87.5	31.4
Cd	0.075	0.50	0.19	0.021	0.44	0.14	0.014	0.13	0.032	0.014	0.50	0.12
Co	0.85	4.27	2.17	0.15	4.30	1.83	0.008	0.033	0.019	0.008	4.30	1.76
Cr	0.70	2.86	1.09	0.25	5.13	1.43	0.074	0.28	0.17	0.074	5.13	0.90
Cu	2.22	16.3	5.96	0.62	32.5	6.08	<dl	<dl	<dl	0.62	32.5	6.02
Fe	596	3656	1646	167	5928	1400	2.18	7.83	4.72	2.18	5928	1017
K	68.2	468	224	21.2	694	211	73.5	625	232	21.2	694	222
Mn	20.3	267	103	3.21	226	82.2	2.32	47.4	9.54	2.32	267	64.9
Ni	1.29	9.07	3.14	0.34	6.90	2.58	0.015	0.16	0.069	0.015	9.07	1.93
Pb	4.90	30.8	14.3	1.12	41.6	12.7	<dl	<dl	<dl	1.12	41.6	13.5
Sb	0.013	0.046	0.032	0.006	0.12	0.043	0.005	0.033	0.025	0.005	0.12	0.033
Zn	2.52	26.3	9.39	0.74	66.3	12.9	0.46	1.44	1.01	0.46	66.3	10.6

dl—detection limit (0.01–0.057 mg kg^{−1}); av—average.

3.1.2. Ba

Barium content extracted with HCl showed significant variability (15.9–87.5 mg kg^{−1}), with the lowest value obtained in sample 3 and the highest in sample 20. It is worth noting that both locations are near the Sava River and are strongly influenced by it. The application of HNO₃ also showed a wide content range (5.54–86.3 mg kg^{−1}), with the minimum in sample 19, a ravine in a park near the large thermo-power and heating plant, and the maximum in sample 22, a location within an urban park, located in the inner city center, surrounded by very busy streets, buildings, and many pedestrians walking nearby. In the case of CH₃COONH₄ extraction, the lowest content was 9.41 mg kg^{−1} (sample 4), whereas the highest value was 51.3 mg kg^{−1} (sample 20), as was the case with HCl extraction. Higher Ba contents were obtained by applying HCl at locations 14, 20, and 22, and by applying HNO₃ at locations 22–24, which may be the result of the Sava River floodplain and anthropogenic influence. Overall, HCl exhibited the highest extraction efficiency, with no significant difference compared to HNO₃ for samples 1–12. For samples 13–21, HCl performed significantly better than the other extractants; however, acetate also proved highly effective for this group, surpassing HNO₃. In contrast, HNO₃ was more efficient for samples 22–25. Barium, in particular, showed high mobility across all extractions.

3.1.3. Cd

Cadmium was extracted in low contents. The lowest values were obtained in samples 25 (0.075 mg kg^{−1}) and 18, uninhabited areas of forests, meadows, and shrubby vegetation in the eastern outskirts of Zagreb (0.02 mg kg^{−1}), with the application of HCl and HNO₃, respectively; with CH₃COONH₄, the lowest contents were extracted from samples 4 and 25 (0.014 mg kg^{−1}). The maximum extracted content of Cd was from sample 8 using all three extraction agents: 0.50 mg kg^{−1} with HCl, 0.44 mg kg^{−1} with HNO₃, and 0.133 mg kg^{−1} with CH₃COONH₄. Hydrochloric acid proved to be the most effective agent, especially for samples 13–21; nitric acid was better for samples 22–25, whereas they showed comparable efficiency for samples 1–12.

3.1.4. Co

The lowest cobalt contents were obtained in samples 12 (0.85 mg kg^{-1}) using HCl, and 18 and 20 (0.15 mg kg^{-1}) using HNO_3 , while the highest were in samples 15 and 5 (4.27 and 4.30 mg kg^{-1}), using HCl and HNO_3 as extraction agents, respectively. The use of $\text{CH}_3\text{COONH}_4$ resulted in very low cobalt levels, with many values below the detection limit. Several locations stand out for their Co content: 5 and 6 (use of HCl and HNO_3), 14 and 15 (use of HCl), and 22 and 23 (use of HNO_3). Nitric acid showed slightly higher extraction efficiency, particularly for samples 22–25. For the first 12 samples, HCl showed comparable efficiency, but for samples 13–21, HCl achieved a significantly greater performance.

3.1.5. Cr

The minimum chromium content extracted with HCl was 0.70 mg kg^{-1} in sample 1, whereas the maximum reached 2.86 mg kg^{-1} in sample 20. Sample 20, with maximum Cr content extracted with HCl, is located within Sava River embankments, which are regularly flooded by the waters of the Sava River, so it can be assumed that Cr is being brought from the Slovenian Alps by the river. The lowest values obtained with HNO_3 were found in sample 16, a rural area with farmlands and meadows south of the Zagreb urban area near the water supply station, within the water protection zone, and sample 19 (0.25 mg kg^{-1}), and the highest in sample 22 (5.13 mg kg^{-1}). Locations 6, 12, and especially 22–25 stand out for their higher extracted content using HNO_3 . Using $\text{CH}_3\text{COONH}_4$ resulted in lower extraction levels, with the minimum in sample 7 (0.074 mg kg^{-1}) and the maximum in sample 11 (0.28 mg kg^{-1}). Generally, HCl shows higher extraction efficiency, especially in samples 14–21, while nitric acid performs better in samples 22–25.

3.1.6. Cu

Copper contents were extracted over a wider range of values: 2.22 – 16.3 mg kg^{-1} with HCl and 0.62 – 32.5 mg kg^{-1} with HNO_3 . The lowest content obtained with HCl was recorded for sample 3, a meadow within the Jarun sport-recreational area, between Big Jarun Lake and the Sava River embankment, while the highest was recorded for sample 14. Using HNO_3 , the lowest content was obtained in sample 21, a small meadow at the top of Medvednica Mt, surrounded by a large TV tower and some tourist facilities, and near the ski slope, on which, during winter, artificial snow is used. The contents extracted using $\text{CH}_3\text{COONH}_4$ were below the instrument's detection limit. The higher copper contents were extracted at locations 6 (with HCl and HNO_3), 14 (with HCl), and 23 and 24 (with HNO_3). As well as for some other elements, HNO_3 is more effective for samples 22–25, while HCl is noticeably better for samples 14–21; meanwhile, they are almost equal for samples 1–10.

3.1.7. Fe

The extracted iron content exhibits significant variability. The ranges are 596 – 3656 mg kg^{-1} for HCl, 167 – 5928 mg kg^{-1} for HNO_3 , and 2.18 – 7.83 mg kg^{-1} for $\text{CH}_3\text{COONH}_4$. The lowest values were obtained in samples 13, 20, and 12, whereas the highest values were recorded in samples 8, 23, and 7, using HCl, HNO_3 , and $\text{CH}_3\text{COONH}_4$, respectively. Locations with the highest contents are located at the top part of Medvednica Mt and near the Sava River, near the Kuniščak stream inflow, which brings material from the Medvednica Mt. The more effective extraction agent for samples 14–21 was HCl, while for samples 22–25 it was nitric acid.

3.1.8. K

The lowest potassium contents were obtained from sample 25 (68.2 and 73.5 mg kg⁻¹) using HCl and CH₃COONH₄, and from sample 19 (21.2 mg kg⁻¹) using HNO₃, while the highest K contents were extracted from sample 21 using HCl and CH₃COONH₄ (468 and 625 mg kg⁻¹), and from sample 24, a meadow near the embankment of Sava River close to ex-flow of Kuniščak stream and weir, using HNO₃ (694 mg kg⁻¹). All extraction agents exhibited good efficiency, indicating that potassium is a highly mobile element. In samples 11–12 and 22–25, nitric acid showed greater extraction efficiency, while in samples 14–21, HCl was more effective. On the other hand, CH₃COONH₄ stood out as the most effective agent in samples 6–8, 13–14, 17–19, and 21, where K is likely to occur in a readily exchangeable cationic form.

3.1.9. Mn

Manganese was extracted over a wider range of values, with the lowest contents obtained from samples 17 (20.3 mg kg⁻¹), 19 (3.21 mg kg⁻¹), and 13 (2.32 mg kg⁻¹), using HCl, HNO₃, and CH₃COONH₄, respectively. The values obtained for samples 22–25 were excluded from further data analysis due to certain deviations. The highest values were recorded in sample 8 (267 and 226 mg kg⁻¹) using HCl and HNO₃, and in sample 7 (47.4 mg kg⁻¹) when CH₃COONH₄ was applied. Those two samples are located at a ski slope at the top part of Medvednica Mt, and most probably the elevated Mn content originates from magmatic and metamorphic rocks present in the rock formations of this mountain. The locations that stand out for their Mn content are 7 and 8 (with the application of all three reagents), and 21 (use of HCl); this may be a consequence of the rock composition, since all three samples originate from Medvednica. Overall, HCl demonstrated superior efficiency as an extraction agent for Mn. Its effectiveness was notably higher in samples 14 through 21, whereas in samples 11 and 12, HNO₃ was more effective.

3.1.10. Ni

The nickel contents extracted with HCl varied significantly, from 1.26 to 9.07 mg kg⁻¹, with the lowest in sample 25 and the highest in sample 19. Using HNO₃, the minimum was found in sample 20 (0.34 mg kg⁻¹) and the maximum in sample 23 (6.90 mg kg⁻¹), a meadow near the embankment of the Sava River close to the ex-flow of the Kuniščak stream and weir. The area is rich in stream sediments brought by the Kuniščak stream, which flows from the Medvednica Mt, and is rich in magmatic and metamorphic rocks and ore occurrences; Sava River overbank sediments are also present. Extraction with CH₃COONH₄ resulted in low Ni levels, with the minimum in sample 18 (0.015 mg kg⁻¹) and the maximum in sample 13 (0.16 mg kg⁻¹), an area with shrubby vegetation near a large oil terminal in the Žitnjak industrial zone in the eastern part of the Zagreb city area. Elevated HCl-extractable Ni contents were recorded at locations 13 and 19 within the Zagreb city area. Because the difference relative to the remaining locations is substantially greater than expected natural variability, this supports the assumption of an anthropogenic source. HNO₃ proved to be a more effective extraction agent for samples 22–25. For samples 13–21, HCl was notably more efficient, whereas both acids were similarly effective in the first 12 samples.

3.1.11. Pb

Lead contents extracted with HCl and HNO₃ showed notable variability, with minimum values in sample 4, meadow and forest surrounded by residential areas, different industrial plants and abandoned military objects (4.90 mg kg⁻¹) (HCl), and sample 18 (1.12 mg kg⁻¹) (HNO₃), and maximum values in sample 6, meadow surrounded by forest

near a small church of St. Jakov on the top part of Medvednica Mt, an area with magmatic and metamorphic rocks and ore occurrences (30.8 mg kg^{-1}) (HCl), and sample 22 (41.6 mg kg^{-1}) (HNO_3). Obviously, at location 6, elevated Pb content is the result of natural influences from magmatic and metamorphic rocks and ore occurrences in this part of Medvednica Mt, whereas at location 22, anthropogenic influence is most likely. Lead contents determined after extraction with $\text{CH}_3\text{COONH}_4$ were below the instrumental detection limit in all analyzed samples. Considerably higher lead contents were extracted at locations 6, 8, and 21 using HCl, and at locations 6, 8, 22, and 25 using HNO_3 , which may be a consequence of the soil composition, since most of those samples are from Medvednica Mt. For the first 12 samples, both acids showed similar efficiency, with HNO_3 slightly more effective. HCl showed significantly greater efficiency for samples 13–21, whereas HNO_3 was more efficient for samples 22–25.

3.1.12. Sb

By applying all three extraction agents, extremely low antimony contents were obtained, with many samples below the instrument's detection limit. For this reason, its contents are not shown in Figures 2 and 3. Due to the low Sb content in the extracts, it is not possible to identify the most effective extraction agent.

3.1.13. Zn

Zinc content extracted with HCl was measured over a wider range, $2.52\text{--}26.3 \text{ mg kg}^{-1}$, with the lowest value in sample 4 and the highest in sample 11, located near the fence of the large Jakuševac communal waste landfill in its eastern part; at this location, elevated Zn content is obviously originating from the landfill. A wide range of values, $0.74\text{--}66.3 \text{ mg kg}^{-1}$, was also observed using HNO_3 , with a minimum in sample 19 and a maximum in sample 24. The maximum at this location could originate from overbank sediments of the Sava River, or possibly from the ex-flow of the Kuniščak stream, which flows and brings material from the Medvednica Mt. Extraction with $\text{CH}_3\text{COONH}_4$ detected only three samples above the instrument's detection limit, with the highest value obtained in sample 22 (1.44 mg kg^{-1}). The two acids showed a similar spatial pattern of extraction efficiency for Zn, as well as for Ba, Cd, Co, Cr, Cu, Fe, K, Ni, and Pb. For samples 1–10, both acids exhibited similar spatial extraction trends; HCl was more efficient for samples 14–21, while HNO_3 was more efficient for samples 22–25. This difference in extraction efficiency is expected and simply reflects natural variability in soil chemistry across the sampled locations.

3.2. Analysis of the Ratios of Extracted Contents Obtained Using Different Extraction Agents

A comparison of extraction ratios across different agents enables the identification of the most efficient reagent for a given element. Descriptive statistics for ratios are shown in Table 2. A similarity criterion of $\leq 15\%$ difference was applied to determine whether the extracted contents between the two acids were comparable or significantly different.

3.2.1. HCl/ HNO_3

When comparing the extraction efficiencies of 1 M HCl and 2 M HNO_3 , only for As can it be said that HCl is more efficient across all samples; the only exception is sample 6. For other elements, there is a pattern: in samples 13–21, HCl outperforms in extraction efficiency (excluding Mn in sample 13), whereas nitric acid shows better results in samples 22–25 (Table 3). Ratios exceeding 100% should be interpreted with caution. They occur in samples where the total content is very low (close to the detection limit). These values are reported for completeness but are not used as a basis for interpretation. In the discussion, we focus on the relative patterns among extractants rather than on the absolute magnitude of the ratios.

Table 2. Descriptive statistics for element ratios and comparative extraction efficiencies of different reagents (expressed as percentages).

		As	Ba	Cd	Co	Cr	Cu	Fe	K	Mn	Ni	Pb	Sb	Zn
HCl/HNO ₃	minimum	93.0	71.7	69.5	46.7	21.7	37.9	31.2	51.9	50.1	52.0	45.4	217	16.2
	maximum	3079	1287	933	1450	817	868	1358	2154	3069	721	1406	217	1686
	average	719	267	291	257	170	233	285	266	396	217	255	217	235
CH ₃ COONH ₄ /HCl	minimum		31.6	7.00	0.39	6.33		0.12	48.6	2.66	0.48		65.2	4.25
	maximum		81.6	27.4	1.95	33.6		0.78	141	25.3	6.47		65.2	10.9
	average		59.7	16.7	0.98	16.7		0.35	101	8.81	2.47		65.2	7.90
CH ₃ COONH ₄ /HNO ₃	minimum		40.9	9.50	0.37	2.16		0.11	47.0	4.31	1.11			2.29
	maximum		754	113	3.23	77.9		4.32	2384	162	20.0			8.14
	average		153	39.1	1.27	26.5		0.74	298	23.8	4.25			4.74
Overall values	minimum	93.0	31.6	7.00	0.39	2.16	37.9	0.11	47.0	2.66	0.48	45.4	65.5	2.29
	maximum	3079	1287	933	1450	817	868	1358	2384	3069	721	1406	217	1686
	average	719	160	116	164	71.2	233	95.5	221.4	143	74.7	255	141	191

Table 3. Ratio of obtained element content after extraction with HCl and HNO₃ (expressed as a percentage (%)).

HCl/HNO ₃	As	Ba	Cd	Co	Cr	Cu	Fe	K	Mn	Ni	Pb	Sb	Zn
1	135	104	112	100	109	90.1	92.1	90.8	101	96.1	100		94.7
2	123	102	109	94.7	118	92.2	94.2	84.7	96.7	93.2	108		85.4
3	108	102	100	97.8	127	87.4	92.1	95.9	95.0	93.5	98.8		96.5
4	134	102	106	100	98.7	92.1	107	92.2	102	93.8	110		82.6
5	113	98.4	101	94	103	98.9	92.9	86.8	102	94.1	96.5		95.1
6	93	98.3	99.2	96.2	74.3	96.1	88.8	97.2	102	91.8	105		82.1
7	119	99.9	107	92.8	73.7	100	115	99.8	112	96.9	103		101
8	126	103	114	94.9	77.8	97.2	181	99.5	118	98.8	110		102
9	143	106	114	103	94.2	103	110	91.2	110	102	116		102
10	132	103	108	89.1	112	105	97.8	88.1	96.3	92.2	107		131
11	610	94.9	88	90.6	78.9	74.8	68.1	59.7	53.2	80.3	80.7		88.8
12	342	97.5	97.1	85	53.3	82.1	78.7	56.6	50.1	81.5	83.6		60.0
13		235	200	171	111	141	156	107	84.2	153	201		124
14	3000	310	304	266	168	272	265	129	112	266	222		180
15		377	395	309	202	339	309	199	167	302	330		231
16		470	490	354	312	410	313	262	233	340	390		277
17		589	775	407	325	501	523	263	172	516	424		371
18	2842	754	890	613	482	625	1219	397	739	676	458	217	582
19	3079	735	865	616	468	585	548	2154	3068	625	610		786
20	1401	1287	933	860	817	801	1358	160	778	721	917		1686
21	/	399	860	1450	161	868	1078	1703	1822	497	1406		449
22	192	74.4	74.8	61.5	23.2	42.9	39.0	57.4	/	59.0	59.3		21.1
23		71.7	69.5	46.7	21.8	41.0	42.8	52.7	/	53.0	46.0		16.2
24	255	77.3	74.8	63.8	21.7	40.4	31.2	58.5	/	58.6	56.8		21.7
25		74.6	83.3	56.9	24.3	37.9	36.6	51.9	/	52.0	45.4		17.5

Note: Values for which HCl exhibited higher extraction efficiency are highlighted in bold.

3.2.2. CH₃COONH₄/HCl

Analyzing the ratios of element contents obtained after extraction with CH₃COONH₄ and HCl (Table 4), it is evident that HCl is generally more effective. Higher efficiency with CH₃COONH₄ was noted only for K, across 11 samples (3, 6, 7, 8, 13, 14, 17, 18, 19, 21, and 25). This finding points to the high mobility of potassium and supports the use of ammonium acetate for extracting its mobile fractions. This observation likely reflects the absence of a significant non-exchangeable K pool for these samples; hence, all extractants

recovered the same readily exchangeable fraction, confirming that ammonium acetate was the methodologically correct choice for K extraction.

Table 4. Ratio of obtained element content after extraction with $\text{CH}_3\text{COONH}_4$ and HCl (expressed as a percentage (%)).

$\text{CH}_3\text{COONH}_4/\text{HCl}$	Ba	Cd	Co	Cr	Fe	K	Mn	Ni	Sb	Zn
1	79.7	21.6		10.7	0.47	93.3	5.91	2.53		8.60
2	77.7	23.3	0.39	18.4	0.5	95.8	4.96	2.88		
3	63.2	14.5		33.6	0.4	103	6.1	1.21		
4	48.2	14.7		18.8	0.35	91.9	7.46	2.83		
5	61.8	17.6	0.71	6.33	0.44	87.0	7.49	1.18		
6	47.7	16.5		15.3	0.29	133	7.37	1.39		
7	54.2	27.4	1.43	7.55	0.29	141	21.5	6.47		
8	63.7	26.5	1.03	12.2	0.13	131	17.3	6.02		
9	64.2	20.6	0.55	23.1	0.35	88.6	6.52	2.13		
10	62.6	15.2		25.7	0.47	91.8	4.47	2.17		
11	64.3	19.3	1.95	32.0	0.78	89.4	15.1	5.14		4.25
12	81.6	21.3		12.1	0.27	85.2	12.0	3.05		
13	48.9	16.9		18.0	0.54	103	8.08	1.93		
14	31.6	7.00		14.7	0.16	116	4.71	1.08		
15	52.4	13.3		21.7	0.37	65.0	5.40	1.42		
16	52.2	11.7		20.6	0.46	92.0	3.15	2.06		
17	68.9	12.2	0.79	21.0	0.12	123	25.3	1.16		
18	61.4	11.8		16.1	0.18	113	9.47	0.48		
19	57.3	12.1		14.9	0.20	111	5.27	1.38		
20	58.6	12.1		6.50	0.32	48.6	4.85	2.78		
21	41.4	10.5		10.6	0.13	133	2.66	2.24	65.2	
22	55.0	19.2		9.41	0.32	81.8	/	2.17		10.8
23	60.0	13.7		9.9	0.25	98.4	/	2.59		
24	58.5	19.7		22.9	0.71	97.1	/	3.39		
25	77.6	18.7		16.4	0.33	108	/	2.17		

Note: Values for which $\text{CH}_3\text{COONH}_4$ exhibited higher extraction efficiency are highlighted in bold.

3.2.3. $\text{CH}_3\text{COONH}_4/\text{HNO}_3$

When comparing the effectiveness of $\text{CH}_3\text{COONH}_4$ and HNO_3 (Table 5), HNO_3 consistently performs better for elements Co, Cr, Fe, Ni, and Zn across all samples. $\text{CH}_3\text{COONH}_4$ shows greater efficiency for Mn only in sample 19; for Cd in three samples—18, 19, and 20; for Ba in samples 13 and 15–21; and for K in samples 6–8, 13–19, and 21. A significant deviation, i.e., a much higher efficiency of $\text{CH}_3\text{COONH}_4$, is observed for Ba at locations 16–20 (especially 20) and for K in sample 18, and is significantly higher for samples 19 and 21. This indicates that Ba and K exhibit relatively greater mobility than the other elements investigated. Overall, no universal pattern emerges in the efficiency of the extraction agents; their effectiveness varies with the specific sample.

Table 5. Ratio of obtained element content after extraction with $\text{CH}_3\text{COONH}_4$ and HNO_3 (expressed as a percentage (%)).

$\text{CH}_3\text{COONH}_4/\text{HNO}_3$	Ba	Cd	Co	Cr	Fe	K	Mn	Ni	Zn
1	83.0	24.2		11.7	0.44	84.7	6.00	2.43	8.14
2	79.5	25.3	0.37	21.8	0.47	81.1	4.79	2.68	
3	64.5	14.5		42.7	0.37	99.1	5.79	1.13	
4	49.4	15.6		18.6	0.37	84.7	7.64	2.65	
5	60.8	17.7	0.67	6.53	0.41	75.5	7.64	1.11	
6	46.9	16.4		11.3	0.26	129	7.49	1.28	

Table 5. Cont.

CH ₃ COONH ₄ /HNO ₃	Ba	Cd	Co	Cr	Fe	K	Mn	Ni	Zn
7	54.2	29.3	1.32	5.56	0.33	141	24.0	6.28	
8	65.6	30.2	0.98	9.35	0.23	130	20.4	5.95	
9	68.2	23.6	0.57	21.7	0.38	80.8	7.20	2.18	
10	64.3	16.4		28.8	0.46	80.9	4.31	2.00	
11	61.1	17.0	1.77	25.2	0.53	53.3	8.03	4.13	3.78
12	79.6	20.7		6.45	0.21	48.2	6.02	2.49	
13	115	33.7		20.1	0.84	111	6.81	2.96	
14	98.2	21.4		24.7	0.42	150	5.27	2.87	
15	197	52.5		43.9	1.13	129	9.01	4.30	
16	245	57.5		64.4	1.45	241	7.34	7.00	
17	406	95.0	3.23	68.1	0.64	325	43.6	6.00	
18	463	105		77.9	2.19	450	70.0	3.26	
19	421	105		69.6	1.07	2384	162	8.62	
20	754	113		53.1	4.32	77.8	37.8	20.0	
21	165	90.0		17.1	1.44	2274	48.4	11.1	
22	40.9	14.3		2.18	0.12	47.0	/	1.28	2.29
23	43.6	9.5		2.16	0.11	51.8	/	1.38	
24	45.2	14.8		4.97	0.22	56.8	/	1.98	
25	57.8	15.6		3.98	0.12	56.0	/	1.13	

Note: Values for which CH₃COONH₄ exhibited higher extraction efficiency are highlighted in bold.

3.3. Evaluation of the Effectiveness of Extraction Agents

By calculating the ratio of the content of an element obtained using a specific extraction agent to the total content of that element in the sample, the percentage extracted from the total value is determined, providing insight into the efficiency of that reagent.

Based on the maximum fractions obtained (Table 6), HNO₃ proves to be more effective. Only in the case of As is the highest percentage extracted by HCl; in Cd, Co, Ni, and Sb, the proportions of acids and total content are similar. The highest yields of Ba, Cr, Cu, Fe, Mn, Pb, and Zn are achieved with HNO₃. Potassium is the only element for which the highest percentage is extracted using CH₃COONH₄.

Table 6. Minimum and maximum ratios of extracted to total element contents (expressed as %).

		As	Ba	Cd	Co	Cr	Cu	Fe	K	Mn	Ni	Pb	Sb	Zn
HCl/total	min	3.24	36.9	16.6	9.91	1.99	7.15	3.69	8.93	7.12	5.20	20.5	0.64	3.45
	max	59.9	57.7	43.3	33.7	11.3	35.6	14.2	43.4	19.3	17.4	49.4	2.47	23.8
HNO ₃ /total	min	0.52	3.34	2.73	0.68	0.69	1.34	0.72	1.04	0.54	1.38	3.09	0.31	0.73
	max	47.7	72.8	41.1	33.1	22.3	75.6	20.9	50.2	38.5	20.6	71.1	3.65	62.9
CH ₃ COONH ₄ /total	min		18.2	2.00	0.09	0.15		0.010	9.67	0.31	0.048		0.44	0.77
	max		41.2	11.5	0.39	2.34		0.041	57.7	3.55	0.53		1.45	1.44

If the average efficiency values are considered (Figure 4), HCl stands out as the most effective extraction agent for most elements, namely for As, Ba, Cd, Co, Mn, and Pb. For Cr, Cu, Ni, and Fe, the applied acids, HCl and HNO₃, are equally effective; only for Zn does nitric acid show a better effect. Comparing the mean efficiency values for K, no single extraction agent stands out, as all three are equally effective. On the contrary, for Sb, no conclusion can be drawn because the extracted contents are extremely low.

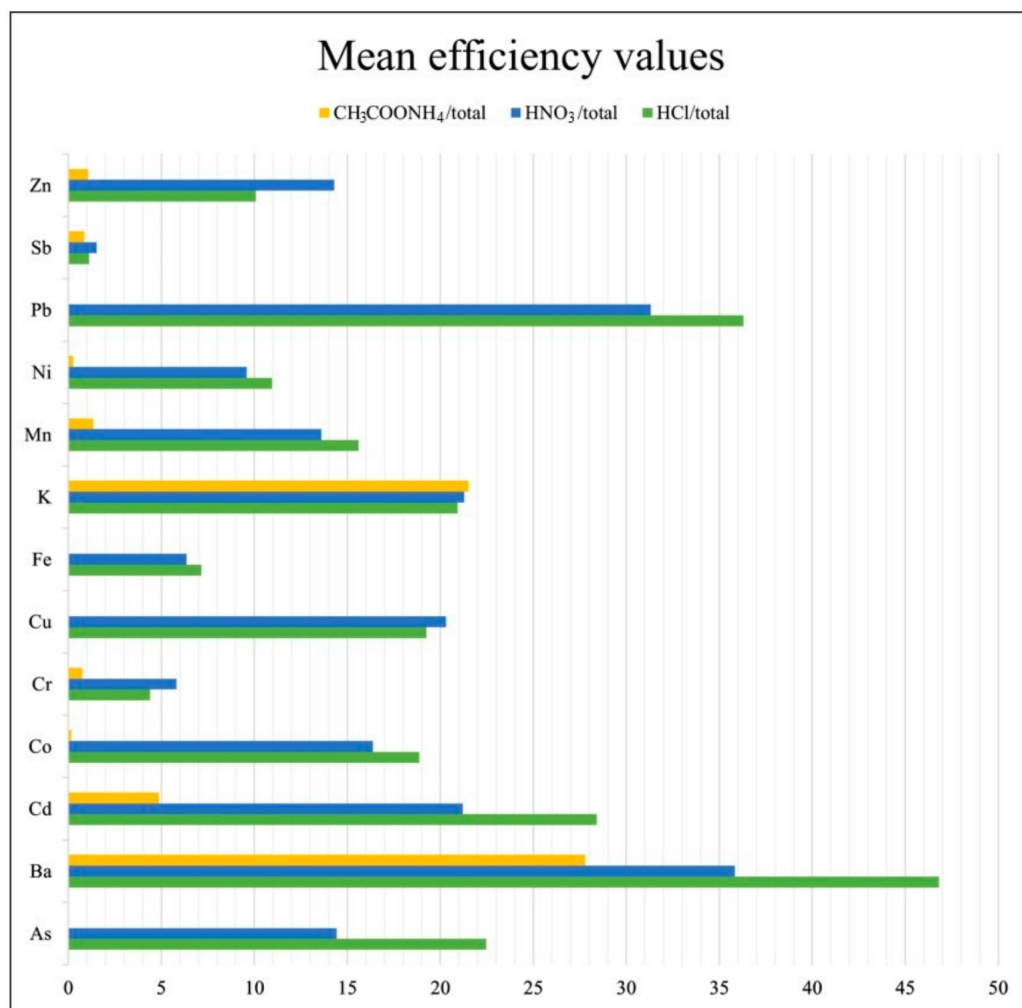


Figure 4. Mean extracted/total element ratios for each reagent (expressed as %).

3.4. Results of Non-Parametric Analysis

The results of the Friedman test are presented in Table 7. The Friedman test revealed a clear and consistent pattern across the majority of the analyzed elements. For As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn, the null hypothesis was rejected ($p < 0.001$), indicating a statistically significant difference in the concentrations extracted by the three different agents.

This finding demonstrates that the extraction efficiency is highly element-specific and dependent on the chemical nature of the extractant. The significant variability observed for these elements suggests that they are associated with different soil fractions (e.g., exchangeable, reducible, oxidizable, or residual) that respond differently to the chemical properties of each extraction agent (such as pH, chelating ability, or ionic strength). Consequently, the choice of extractant is critical when assessing the mobility, bioavailability, or total recoverable content of these elements. These findings indicate that the three extraction methods are not comparable for these elements.

In contrast, potassium (K) exhibited a distinct behavior. The Friedman test yielded a non-significant result ($p = 0.529$), leading to the retention of the null hypothesis. This indicates that the three extraction agents recovered statistically comparable concentrations of K. This lack of a significant difference suggests that K is present in a highly labile or readily extractable form in the tested soils, allowing all three agents to achieve similar extraction efficiencies. Therefore, for K, the choice of extraction method may be flexible, allowing for the selection of a faster, more cost-effective, or environmentally friendly

protocol without compromising data quality. Antimony (Sb) was excluded from the Friedman analysis due to its very low content in the studied soils and its absence in a significant number of samples.

Table 7. The results of Friedman’s test (Related-Samples Friedman’s Two-Way Analysis of Variance by Ranks).

Hypothesis Test Summary		
Null Hypothesis *	Significance	Decision
The distributions of As1, As2 and As3 are the same.	0.000	Reject the null hypothesis.
The distributions of Ba1, Ba2 and Ba3 are the same.	0.000	Reject the null hypothesis.
The distributions of Cd1, Cd2 and Cd3 are the same.	0.000	Reject the null hypothesis.
The distributions of Co1, Co2 and Co3 are the same.	0.000	Reject the null hypothesis.
The distributions of Cr1, Cr2 and Cr3 are the same.	0.000	Reject the null hypothesis.
The distributions of Cu1, Cu2 and Cu3 are the same.	0.000	Reject the null hypothesis.
The distributions of Fe1, Fe2 and Fe3 are the same.	0.000	Reject the null hypothesis.
The distributions of K1, K2 and K3 are the same.	0.529	Retain the null hypothesis.
The distributions of Mn1, Mn2 and Mn3 are the same.	0.000	Reject the null hypothesis.
The distributions of Ni1, Ni2 and Ni3 are the same.	0.000	Reject the null hypothesis.
The distributions of Pb1, Pb2 and Pb3 are the same.	0.000	Reject the null hypothesis.
The distributions of Zn1, Zn2 and Zn3 are the same.	0.000	Reject the null hypothesis.

Asymptotic significances are displayed. The significance level is 0.05. * The numbers next to the elements refer to the extraction reagents (1–HCl; 2–HNO₃; 3–CH₃COONH₄).

3.5. Comparison with the Literature

In the process of comparing the results obtained in this manuscript with the literature, attention should also be paid to the following limitations: differences in extractant concentration and soil-to-solution ratio strongly affect extraction efficiency; comparisons are therefore qualitative rather than quantitative; and the reported ranges should be interpreted with caution.

Zbiral [30] compared extraction efficiencies of aqua regia, 2 M HNO₃, and Mehlich 3 on 147 agricultural soils from the Czech Republic, covering all major soil types and climatic regions. For As, Cd, Co, Cr, Cu, Ni, Pb, and Zn, the reported minimum, maximum, and mean values, obtained with HNO₃, were generally higher than those determined in this study, with the exception of maximum Zn (57.4 mg kg^{−1}).

Takáč et al. [31] applied 2 M HNO₃ extraction to soils from the Central Spiš region (Slovakia), an area with a long history of mining and ore processing. Their reported Cu, Pb, and Zn contents were considerably higher than those measured in Zagreb, with maximum values reaching 398.6, 101.7, and 179.7 mg kg^{−1}, respectively.

Senila et al. [32] investigated the extractable fractions of Cu, Zn, and Cd in contaminated agricultural soils using 1 M HCl extraction. Their Cu and Zn contents were generally lower than the maximum values recorded in this study, whereas Cd levels were predominantly higher than the maximum measured in Zagreb (0.50 mg kg^{−1}).

Smoleń et al. [33] employed 1 M HCl extraction on soils sampled at three depths (0–30, 30–60, and 60–90 cm). Mean values for Ba, Cd, Cr, Fe, Mn, Pb, Zn, Cu (at 30–60 and 60–90 cm), and Ni (at 30–60 cm) exceeded the corresponding mean values obtained in this study.

3.6. Comparison of Elemental Contents with Regulatory Limits

In order to gain insight into the level of contamination, and with only elemental content available as data, the results were compared with the Serbian regulatory limits. According to the Serbian Regulation on limit values of polluting, harmful and dangerous substances in

soil (Official Gazette of the Republic of Serbia, Nos. 30/2018 and 64/2019) [34], permissible limits and remediation values are defined for As, Ba, Cd, Co, Cr, Cu, Ni, Pb, Sb, and Zn (Table 8).

Table 8. Regulatory limit values for element contents in soil [34].

Elements	Soil (mg kg ^{−1} Dry Matter)	
	Maximum Permissible Value	Remediation Threshold
Arsenic (As)	29	55
Barium (Ba)	160	625
Cadmium (Cd)	0.8	12
Cobalt (Co)	9.0	240
Chromium (Cr)	100	380
Copper (Cu)	36	190
Nickel (Ni)	35	210
Lead (Pb)	85	530
Antimony (Sb)	3.0	15
Zinc (Zn)	140	720

Elemental contents obtained with the tested extraction agents remained within permissible limits, whereas total contents frequently exceeded them. Arsenic, Cr, and Pb were within limits across all samples. Exceedances were observed for Ba and Zn in one sample each (204 and 153 mg kg^{−1}, respectively); Cd in samples 6, 7, 8, 21, and 23 (max 1.16 mg kg^{−1}); Co in multiple samples (max 26.3 mg kg^{−1}); Cu in samples 4, 6, 10, 14, 16, 19, 21, and 22 (max 54.7 mg kg^{−1}); Ni in samples 4, 6, 13, 16, 19, and 23 (max 57.1 mg kg^{−1}); and Sb in samples 4–7, 15, 21, and 22 (max 6.75 mg kg^{−1}). Importantly, none of the measured total contents exceeded the prescribed remediation values.

4. Conclusions

Single-step extraction with 1 M HCl, 2 M HNO₃, and 1 M CH₃COONH₄ was applied to 25 contaminated urban soil samples from Zagreb to assess potentially toxic element levels of As, Ba, Cd, Co, Cr, Cu, Fe, K, Mn, Ni, Pb, Sb, and Zn, and to evaluate the extraction efficiency of the three extractants. The results of the Friedman test for As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn show that there is a statistically significant difference among the three extractants ($p < 0.001$), so the choice of extractant significantly affects the assessment of mobility or total recoverable content of these elements. This means the three extraction methods are not comparable for these elements. For K, however, all three extractants yielded statistically comparable concentrations.

The observed spatial variability in extraction efficiency may reflect differences in soil mineralogy, particularly the distribution of carbonates, oxides, silicates, and organic matter. Based on the comparative performance of the three extractants, the following practical recommendations are proposed. For As, 1 M HCl is the reagent of choice. For exchangeable cations such as Ba and K, CH₃COONH₄ is recommended because its efficiency reflects their mobility. For most other elements investigated, 1 M HCl yields the best overall recovery and is preferable for routine monitoring, though 2 M HNO₃ may be a valuable complement in geologically heterogeneous samples where carbonate or silicate dominance influences extraction yields. Thus, a dual-acid approach (HCl and HNO₃) is suggested for comprehensive screening, whereas ammonium acetate may provide additional information on the operationally defined mobile fraction. Antimony contents were predominantly below the detection limit, thus precluding any reliable assessment of its extraction behavior. While total contents of the investigated elements (Cd, Co, Cu, Ni, Sb, Ba, Zn) sporadically exceeded the prescribed regulatory thresholds, they remained below the corresponding

remediation intervention values in all cases. All recommendations and conclusions are explicitly restricted to the studied conditions and to the targeted sample set.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/pr14213396/s1>, Table S1: Instrumental operating conditions for ICP-OES; Table S2: Limits of detection (LOD) and quantification (LOQ) for ICP-OES analysis. Values are expressed in $\mu\text{g L}^{-1}$ (solution) and recalculated to mg kg^{-1} (soil, based on 1.00 g in 50 mL preparation); Figure S1: Photographs of sampling locations: (a) Hrušćica highway interchange; (b) Bauhaus mall Buzin; (c) Baseball Club Jarun, near the Sava River; (d) Borongaj; (e) Bundek, east; (f) St. Jakov church; (g) Činovnička meadow, lower part of the forest; (h) Činovnička meadow, bottom; (i) Headship of the city of Zagreb; Figure S2: Photographs of sampling locations: (a) Grubišnopolje road, Rudeš; (b) Jakuševac landfill, east; (c) Jakuševac landfill, middle; (d) JANAF oil terminal Žitnjak; (e) Ravine Rebar Kozjak; (f) Stream in Maksimir Park, near Bukovačka street; (g) Mala Mlaka, near water supply station; (h) Mikuševa street, Dubec; (i) Novi Jelkovec; Figure S3: Photographs of sampling locations: (a) Park pravednika među narodima; (b) Prisavlje, along the Sava River; (c) Sljeme peak, meadow; (d) Strossmayer Square; (e) The wider area around the Kunišćak weir; (f) Trnjan embankment; (g) Tuškanac, meadow.

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References

1. Alloway, B.J. Heavy Metals in Soils. In *Blackie Academic and Professional*; Chapman and Hall: London, UK, 1995; p. 368. [\[CrossRef\]](#)
2. Stanojević, D.; Nikolić, Đ. The Content of Trace Elements in the Urban Soil of Šabac and Ecological Risk Assessment. *Zast. Mater.* **2021**, *62*, 83–94. [\[CrossRef\]](#)
3. Demková, L.; Árvay, J.; Bobuľská, L.; Tomáš, J.; Stanovič, R.; Lošák, T.; Harangozo, L.; Vollmannová, A.; Bystrická, J.; Musilová, J.; et al. Accumulation and Environmental Risk Assessment of Heavy Metals in Soil and Plants of Four Different Ecosystems in a Former Polymetallic Ores Mining and Smelting Area (Slovakia). *J. Environ. Sci. Health Part A* **2017**, *52*, 479–490. [\[CrossRef\]](#) [\[PubMed\]](#)
4. Kumar, S.J.C.; Rakshit, D.; Satpathy, K. Geochemical Speciation and Risk Assessment of Heavy Metals in Soils and Sediments. In *Environmental Risk Assessment of Soil Contamination*; InTech.: London, UK, 2014. [\[CrossRef\]](#) [\[PubMed\]](#)
5. Famuyiwa, A.O.; Davidson, C.M.; Ande, S.; Oyeyiola, A.O. Potentially Toxic Elements in Urban Soils from Public-Access Areas in the Rapidly Growing Megacity of Lagos, Nigeria. *Toxics* **2022**, *10*, 154. [\[CrossRef\]](#) [\[PubMed\]](#)
6. Sakan, S.; Frančišković-Bilinski, S.; Đorđević, D.; Popović, A.; Sakan, N.; Škrivanj, S.; Bilinski, H. Evaluation of Element Mobility in River Sediment Using Different Single Extraction Procedures and Assessment of Probabilistic Ecological Risk. *Water* **2021**, *13*, 1411. [\[CrossRef\]](#)
7. Antoniadis, V.; Shaheen, S.M.; Levizou, E.; Shahid, M.; Niazi, N.K.; Vithanage, M.; Ok, Y.S.; Bolan, N.; Rinklebe, J. A Critical Prospective Analysis of the Potential Toxicity of Trace Element Regulation Limits in Soils Worldwide: Are They Protective Concerning Health Risk Assessment?—A review. *Environ. Int.* **2019**, *127*, 819–847. [\[CrossRef\]](#) [\[PubMed\]](#)

8. Marković, J.; Jović, M.; Smičiklas, I.; Pezo, L.; Šljivić-Ivanović, M.; Onjia, A.; Popović, A. Chemical speciation of metals in unpolluted soils of different types: Correlation with soil characteristics and an ANN modeling approach. *J. Geochem. Explor.* **2016**, *165*, 71–80. [\[CrossRef\]](#)
9. Aslanidis, P.S.C.; Golia, E.E. Urban sustainability at risk due to soil pollution by heavy metals—case study: Volos, Greece. *Land* **2022**, *11*, 1016. [\[CrossRef\]](#)
10. Golia, E.E.; Papadimou, S.G.; Cavalaris, C.; Tsiropoulos, N.G. Level of contamination assessment of potentially toxic elements in the urban soils of Volos City (Central Greece). *Sustainability* **2021**, *13*, 2029. [\[CrossRef\]](#)
11. Papadimou, S.G.; Kantzou, O.D.; Chartodiplomenou, M.A.; Golia, E.E. Urban soil pollution by heavy metals: Effect of the lockdown during the period of COVID-19 on pollutant levels over a five-year study. *Soil Syst.* **2023**, *7*, 28. [\[CrossRef\]](#)
12. Ajmone-Marsan, F.; Biasioli, M. Trace Elements in Soils of Urban Areas. *Water Air Soil Pollut.* **2010**, *213*, 121–143. [\[CrossRef\]](#)
13. Golia, E.E.; Bethanis, J.; Xagoraris, C.; Tziourrou, P. Potentially Toxic Elements in Urban and Peri-Urban Soils—A Critical Meta-Analysis of their Sources, Availability, Interactions, and Spatial Distribution. *J. Ecol. Eng.* **2024**, *25*, 335–350. [\[CrossRef\]](#) [\[PubMed\]](#)
14. Roo, M.; Herbón, C.; Martín Sanz, J.; Barral, M.T.; Paradelo Núñez, R. Trace metal extractability and bioaccessibility in urban soils. *J. Soils Sediments* **2026**, *26*, 47. [\[CrossRef\]](#)
15. Madrid, F.; Reinoso, R.; Florido, M.; Barrientos, E.D.; Ajmone-Marsan, F.; Davidson, C.; Madrid, L. Estimating the extractability of potentially toxic metals in urban soils: A comparison of several extracting solutions. *Environ. Pollut.* **2006**, *147*, 713–722. [\[CrossRef\]](#) [\[PubMed\]](#)
16. Sakan, S.; Frančišković-Bilinski, S.; Peco, J.; Sakan, N.; Dojčinović, B.; Dević, G.; Đorđević, D. Potentially Toxic Elements in the Soil of an Urban Area in Croatia: A Multimethodological Approach for the Assessment of Mobility, Environmental and Human Health Risks. *Arch. Environ. Contam. Toxicol.* **2026**, *90*, 9. [\[CrossRef\]](#) [\[PubMed\]](#)
17. Dević, G.J.; Ilić, M.V.; Zildzović, S.N.; Avdalović, J.S.; Miletić, S.B.; Bulatović, S.S.; Vrvic, M.M. Investigation of potentially toxic elements in urban sediments in Belgrade, Serbia. *J. Environ. Sci. Health Part A* **2020**, *55*, 765–775. [\[CrossRef\]](#) [\[PubMed\]](#)
18. Choi, K.Y.; Kim, S.H.; Hong, G.H.; Kim, C.J. Metal Contamination and Potential Toxicity of Sediment from Lock Gate Port in South Korea. *J. Coast. Res.* **2013**, *65*, 31–35. [\[CrossRef\]](#)
19. Hall, G.E.M. *Determination of Trace Elements in Sediments. Manual of Physico-Chemical Analysis of Aquatic Sediments*; Mudroch, A., Azcue, J.M., Mudroch, P., Eds.; Lewis Publishers: Boca Raton, FL, USA, 1997; pp. 85–110.
20. Snape, I.; Scouller, R.; Stark, S.; Stark, J.; Riddle, M.; Gore, D. Characterization of the dilute HCl extraction method for the identification of metal contamination in Antarctic marine sediments. *Chemosphere* **2004**, *57*, 491–504. [\[CrossRef\]](#) [\[PubMed\]](#)
21. Chester, R.; Hughes, M. A chemical technique for the separation of ferro-manganese minerals, carbonate minerals and adsorbed trace elements from pelagic sediments. *Chem. Geol.* **1967**, *2*, 249–262. [\[CrossRef\]](#)
22. Rosandić, M. Procena Efikasnosti Ekstrakcije Mikro- i Makroelemenata Urbanog Zemljišta Grada Zagreba Primenom HCl, HNO₃ i CH₃COONH₄. Bachelor's Thesis, Faculty of Chemistry, University of Belgrade, Belgrade, Serbia, 2024.
23. Spajić, K.; Sakan, S.; Dordevic, D.; Sostaric, T.; Lopičić, Z.; Janicijevic, A.; Stojanovic, K. Comparison of extraction agents for metal determination in sediments from artificial lakes and rivers in Serbia. *Acta Period. Technol.* **2019**, *50*, 189–196. [\[CrossRef\]](#)
24. Valla, M.; Kozák, J.; Němeček, J.; Matula, S.; Borůvka, L.; Drábek, O. *Soil Science Practical Manual*; Czech University of Life Sciences Prague: Prague, Czech Republic, 2000.
25. Šmejkalová, M.; Mikanová, O.; Borůvka, L. Effects of Heavy Metal Concentrations on Biological Activity of Soil Micro-organisms. *Plant Soil Environ.* **2003**, *49*, 321–326. [\[CrossRef\]](#)
26. Ure, A. Single Extraction Schemes for Soil Analysis and Related Applications. *Sci. Total Environ.* **1996**, *178*, 3–10. [\[CrossRef\]](#)
27. Ure, M.; Thomas, R.; Littlejohn, D. Ammonium Acetate Extracts and Their Analysis for the Speciation of Metal Ions in Soils and Sediments. *Int. J. Environ. Anal. Chem.* **1993**, *51*, 65–84. [\[CrossRef\]](#)
28. Frančišković-Bilinski, S.; Peco, J.; Sakan, S.; Đorđević, D.; Indić, D. Magnetic and Geochemical Properties of Zagreb City Area Soils. *Minerals* **2023**, *13*, 1481. [\[CrossRef\]](#)
29. Sakan, S.; Popović, A.; Škrivanj, S.; Sakan, N.; Đorđević, D. Comparison of single extraction procedures and the application of an index for the assessment of heavy metal bioavailability in river sediments. *Environ. Sci. Pollut.* **2016**, *23*, 21485–21500. [\[CrossRef\]](#) [\[PubMed\]](#)
30. Zbiral, J. Effect of grinding on soil extraction by Aqua Regia, 2 M nitric Acid, and Mehlich 3. *Commun. Soil Sci. Plant Anal.* **2006**, *37*, 2289–2297. [\[CrossRef\]](#)
31. Takáč, P.; Szabová, T.; Kozáková, L.; Benková, M. Heavy metals and their bioavailability from soils in the long-term polluted Central Spiš region of SR. *Plant Soil Environ.* **2009**, *55*, 167–172. [\[CrossRef\]](#)
32. Senila, M.; Levei, E.A.; Senila, L.R. Assessment of Metals Bioavailability to Vegetables Under Field Conditions Using DGT, Single extractions and multivariate statistics. *BMC Chem.* **2012**, *6*, 119. [\[CrossRef\]](#) [\[PubMed\]](#)

33. Smoleń, S.; Sady, W.; Ledwożyw-Smoleń, I. Quantitative Relations Between the Content of Selected Trace Elements in Soil Extracted with 0.03 M CH₃COOH or 1 M HCl and Its Total Concentration in Carrot Storage Roots. *Acta Sci. Pol. Hortorum Cultus* **2010**, *9*, 3–12. Available online: <https://doaj.org/article/f7895ba69ee94ed39e602f6247dc79ad> (accessed on 28 July 2026).
34. The Government of the Republic of Serbia. *Regulation on Limit Values of Polluting, Harmful and Dangerous Substances in Soil*; Official Gazette No. 30/2018 and No. 64/2019; Public Enterprise Official Gazette: Belgrade, Serbia, 2019.

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