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Heavy Metals in the Cultivated Soils of Central and Western Serbia

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Abstract: Concern over the harmful impacts of heavy metal pollution in soil has increased dramatically on a global scale. For the sake of environmental preservation, accurate estimates of the heavy metal concentrations in soil are essential. This study provides valuable data regarding heavy metal concentrations in soil collected from field crops production area in Central and Western Serbia. Five wider localities in the zones of Central and Western Serbia were selected for the collection of soil samples. Based on our research, focused on determining the total contents of heavy metals in the soil and the degree of pollution in the environment caused by their behavior, distribution, and origin, it can be concluded that there is pronounced variability in relation to localities. Heavy metal contents were mostly within the same ranges as those in similar soils from Europe and around the world. Any pollution control system must include heavy metal monitoring, including the methodical collection of data on the concentrations of heavy metals in a particular environment. Before environmental degradation occurs, it is crucial to set pollution limits and implement efficient monitoring procedures.

Keywords: heavy metals; soil contamination; Central and Western Serbia

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1. Introduction

Soil in the central and western parts of the Republic of Serbia is facing numerous pressures, including the expansion of urban zones, pollution from agriculture and industry, erosion, low crop diversification, and extreme weather events associated with climate change [1].

From chemical, physiological, and ecological points of view, heavy metals form a heterogeneous group of elements. The concentrations of toxic metals are different depending on the geological base, the type of soil, the geographical area, and climatic factors [2]. The distribution and availability of potentially toxic elements in the soil depend on a large number of biotic and abiotic factors, the most common of which are the geomorphological and geochemical characteristics of the parent substrate of the soil, weather characteristics, soil texture and structure, soil pH reactions, oxidation–reduction processes, cationic exchange capacity (CEC), content of organic matter, soil microorganisms, etc. [3–7]. Their behavior in the soil and availability to plants, in addition to their concentrations, are also influenced by the physico-chemical properties of the soil. Research has shown that there are correlations between the toxic metal content of the soil and the pH of the soil; the content of the clay fraction; the cation adsorption capacity; the character of organic matter; Fe, Mn, and Al oxides; and the redox potential [8]. Numerous mechanisms occur in the soil that affect the destinations of hazardous metals, including volatilization, sorption by microbiota, occlusion, diffusion, dissolution, uptake, migration, and binding with organic matter [9]. According to research, pedogenesis processes concentrate Ag, As, Cd, Cu, Hg, Pb, S, Bi, and Zn in the surface soil layer, whereas Al, Fe, Ga, Mg, Ni, Sc, Ti, V, and Zn are found in the lower strata of the soil profile, where they typically attach to deposits of clay and hydrated oxides. Insufficient time for pedogenesis processes to relocate and distribute harmful metals to deeper soil layers is one of the main causes of the high concentrations of toxic metals seen in the surface layers of polluted soils in recent times [10,11]. Due to intensive technological and industrial development, large amounts of harmful and toxic substances enter the environment in various ways. Among these substances, there is a significant share of heavy metals, which, due to their indestructibility, toxicity, and biogeochemical circulation, represent a major problem for the environment [12,13]. Environmental protection experts face significant difficulty when it comes to heavy metal pollution in soil. In addition to causing morphological variation and abnormal growth in plants, HMs in soil have been shown to cause severe health-related effects in humans, including cancer, anemia, impaired kidney function, and skin lesions [14–16]. Determining the levels of the heavy metals in soil is of great importance, in order to study the potential level of environmental pollution in more detail, the mechanisms of movement and binding of heavy metals, and their mobility and potential bioavailability [17].

The objectives of this study were to determine the levels of the heavy metals iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), nickel (Ni), and lead (Pb) in the agricultural soils of Central and Western Serbia.

2. Materials and Methods

2.1. Study Sites and Sample Collection

The study area, located in Central and Western Serbia, consisted of five localities (Gruža: 43°54′0″ N, 20°46′0″ E; Kragujevac: 44°01′0″ N, 20°55′0″ E; Kraljevo: 43°43′33″ N, 20°41′22″ E; Čačak: 43°53′29″ N, 20°20′59″ E; and Užice: 43°51′31″ N, 19°50′56″ E), from which 100 soil samples were collected at surface (0–30 cm) depth for one year, between December 2020 and December 2021, considering that the surface layers of soil (up to 30 cm) are exposed to the highest degrees of accumulation of most heavy metals and metalloids (Figure 1).

Figure 1. Map of the study area: Central and Western Serbia, and the distribution of soil sampling points.

2.2. Soil Sampling and Chemical Analysis

Tests of soil samples included the following: pH in H_2O and 1M KCl was determined using the SRPS ISO 10390:2007 potentiometric method; $CaCO_3$ (%)—the SRPS ISO 10693:2005 volumetric method; organic matter (%)—calculated from organic carbon (C) with CNS Analyzer (http://www.statsoft.com, accessed on 10 July 2024); total nitrogen (%)—CNS Analyzer; available phosphorus (P_2O_5)—AL method, spectrophotometrically; available potassium—K_2O-AL method, flame photometrically. The contents of heavy metals in all analyzed samples were determined using inductively coupled plasma–optical emission spectroscopy (ICP-OES, Thermo Scientific, Cambridge, UK) iCAP 6000 series with an optical system (Eschelet grid) and CID detector with provided cooling of the camera at −45 °C. An inductively coupled plasma–optical emission spectrometer was used to determine the concentrations of several heavy metals (including Fe, Mn, Zn, Cu, Ni, and Pb) that were present in the digested solution [18,19].

2.3. Statistical Analysis

Principal component analysis (PCA) simplifies the interpretation of patterns in data by highlighting variables that exhibit similar behaviors. In this study, PCA was applied to analyze 100 samples from five locations in Central and Western Serbia, focusing on research variables such as chemical parameters and heavy metal content in soil samples. The results are presented in biplots, providing a clear visualization of the relationships among these variables. The data analysis was conducted using StatSoft Statistica 12 (StatSoft Inc., Tulsa, OK, USA) and R software, version 4.0.2 (64-bit) http://www.statsoft.com, accessed on 10 July 2024.

3. Results

3.1. Chemical Properties and Levels of Heavy Metals in Soils

Experimentally obtained chemical parameters and heavy metal contents (pH, as well as the contents of P_2O_5, K_2O, N, organic matter, Fe, Mn, Zn, Cu, Ni, Pb, Cd, and Cr) in soil samples from 100 sites in the regions of Central and Western Serbia are presented in Supplementary Table S1. According to the results, the pH levels (H_2O) ranged from 4.30 to 7.61. Most samples fell within the range of 5 to 6, indicating acidic soil. The pH (KCl) ranged from 3.73 to 6.89, generally showing increased acidity compared to pH (H_2O). The nutrient contents were also investigated for the samples presented in Supplementary Table S1. The P_2O_5 content ranged from 0.3 to 85 mg 100 g^{-1}, with high variability in soil P content across samples. The K_2O content ranged from 16.4 to 60 mg 100 g^{-1}, indicating adequate to high K_2O levels for plant growth. The nitrogen content ranged from 0.10% to 0.44%, indicating low to moderate N levels. The organic matter content ranged from 1.83% to 7.69%. Higher organic matter was generally found in samples from Užice, indicating potentially richer soil compared to other locations. The Fe content ranged from 1.8 to 126 µg g^{-1}, indicating high variation across samples. Manganese levels also varied significantly (from 4.6 to 136 µg g^{-1}), with some soils being very rich in Mn. Zn concentrations were generally low (0.44 to 10 µg/g), with a few samples showing higher values. Cu levels varied between 0.52 and 15.8 µg g^{-1}, with higher values indicating potential contamination or rich natural deposits. Ni concentrations were generally low to moderate, ranging from 0.76 to 13.56 µg g^{-1}. Pb levels were mostly low, ranging from 0 to 5.7 µg g^{-1}, indicating minimal contamination. The Cd level was uniformly low (0.1 µg g^{-1}) across all samples, indicating a consistent presence at low levels. Most Cr values were zero, suggesting negligible Cr content in the soil. The location of Gruža was characterized by pH values suggesting moderately acidic to neutral soil, high variability in P_2O_5 and K_2O contents, and generally moderate organic matter content. The soil samples from Kragujevac were more acidic compared to those from Gruža and showed higher levels of Fe and Mn in some samples. The soil samples from Kraljevo were more acidic, with some very high organic matter content. These samples showed high variability in Fe and Mn contents, and some samples had high levels of Pb and Zn. The soil samples from Čačak were predominantly acidic. Many samples had high levels of iron and organic matter, along with very high levels of Zn and Pb. The soil samples from Užice were generally more neutral, with consistently high organic matter content and higher levels of Mn and Fe. Some samples also showed very high Zn and Pb contents.

3.2. Chemometric Results

An unrooted tree diagram was generated using R software version 4.0.2 (64-bit) with the "ape" package (Analysis of Phylogenetics and Evolution). This tool was employed to graphically represent the chemical parameters and heavy metal contents in soil data, as assessed through cluster analysis. The experimental results were first organized into a matrix, followed by a hierarchical cluster analysis. The distance matrix was calculated using the Euclidean method, and the cluster analysis was conducted using the "complete" linkage method. Sample similarities are depicted by the proximity of branches, as shown in Figure 2. The samples are identified using the numerical values provided in Supplementary Table S1.

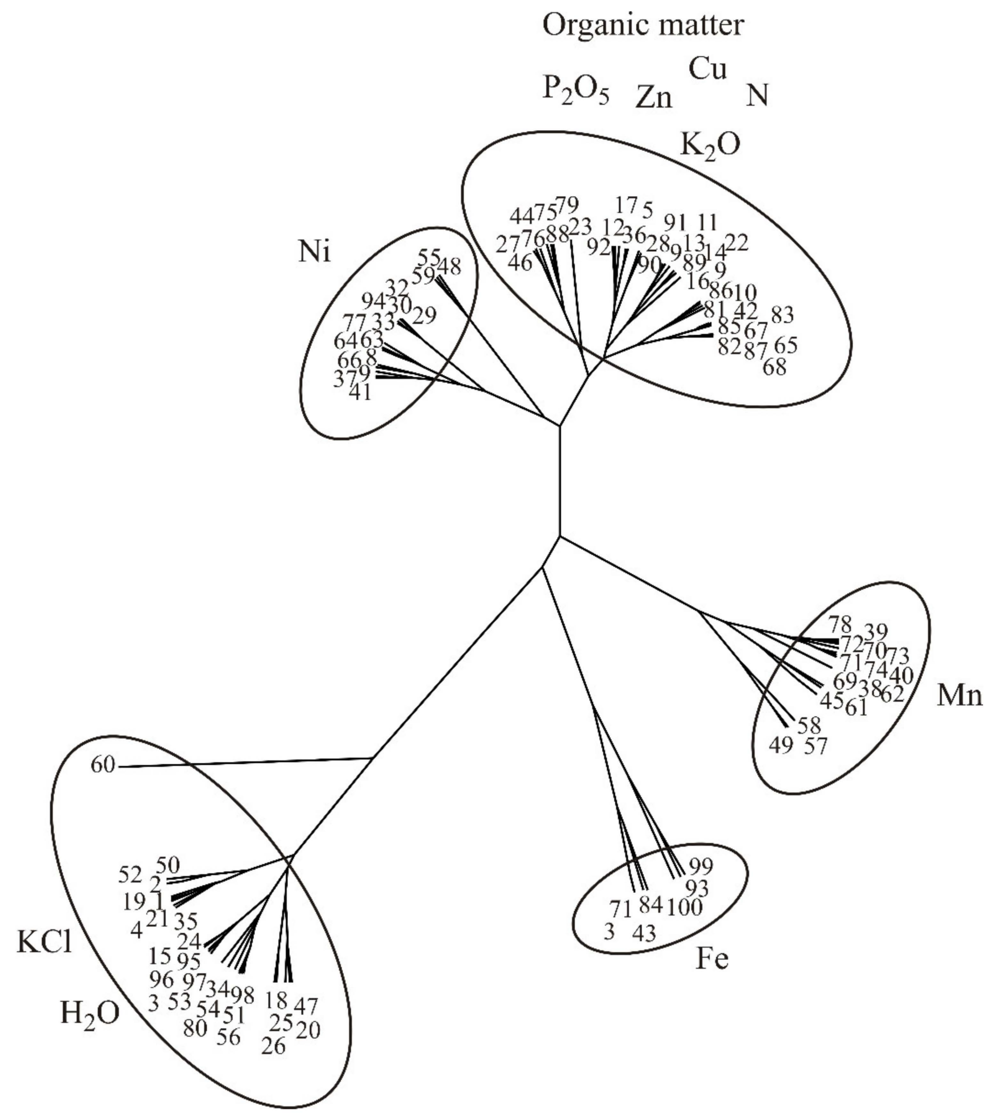

Figure 2. The unrooted phylogenetic tree based on chemical parameters and heavy metal content in the soil data. The samples were labeled according to numerical values shown in Supplementary Table S1.

Several clusters were observed; Cluster 1 gathered samples having increased organic matter, N, K_2O, P_2O_5, Zn, and Cu contents, while Cluster 2 was established based on samples having increased Ni content. Cluster 3 consisted of samples with elevated Mn content, while the Cluster 4 included samples with higher levels of KCl and H_2O. Cluster 5 was characterized by samples with increased Fe content. Statistically significant correlations ($p < 0.001$) were identified between several chemical parameters and heavy metal contents in the samples, as illustrated in Figure 2, in which the colors of the circles represent their correlation coefficients, while their sizes reflect the *p*-values of the correlations. The highest positive correlations were found between H_2O content and KCl content ($r = 0.963$), K_2O and P_2O_5 contents ($r = 0.346$), and N and organic matter contents ($r = 0.469$). Fe content was negatively correlated to the contents of H_2O and KCl ($r = -0.712$ and $r = -0.737$, respectively), while Mn content was negatively correlated to those of H_2O and KCl ($r = -0.694$ and $r= -0.6597$, respectively). Fe and Mn contents were positively correlated ($r = 0.396$). Zn content was positively correlated to the contents of P_2O_5 and K_2O ($r = 0.409$ and $r = 0.407$, respectively), while Cu content was positively correlated to P_2O_5 and Zn contents ($r = 0.392$ and $r = 0.447$, respectively). Ni content was positively correlated to the content of organic matter ($r = 0.372$) and negatively correlated to the contents of H_2O and KCl ($r = -0.379$ and $r = -0.368$). Pb content was negatively correlated to H_2O content ($r = -0.361$) (Figure 3).

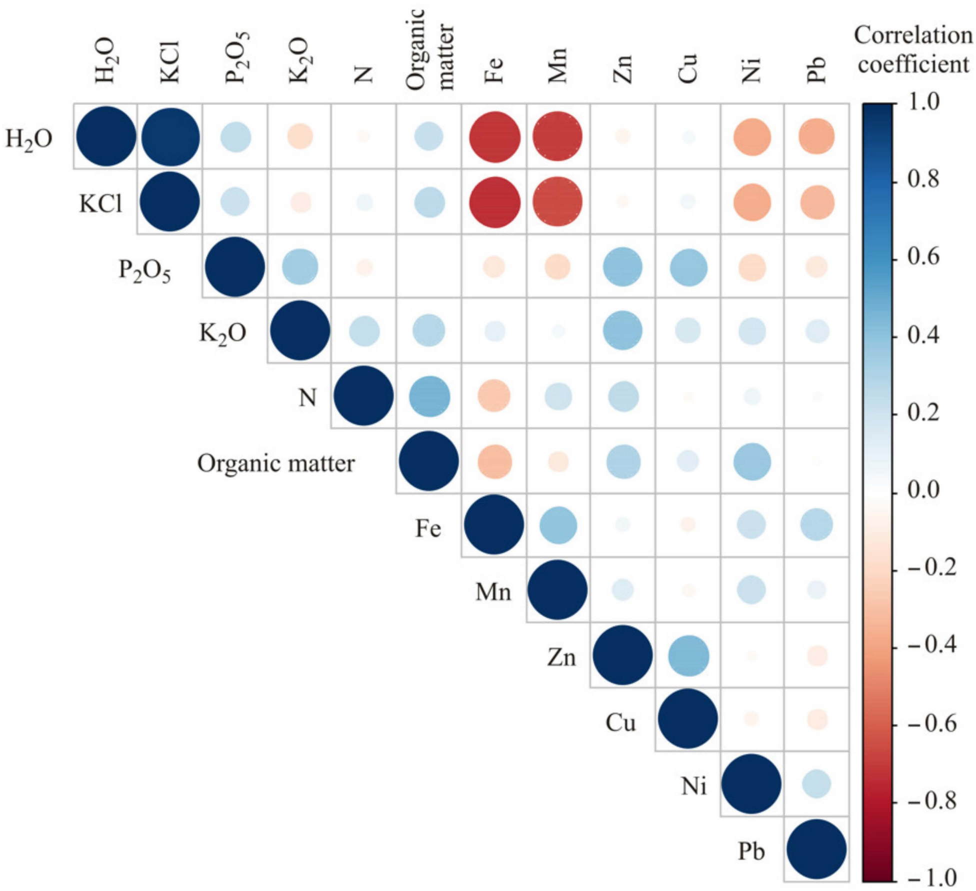

Figure 3. Color correlation graph between chemical parameters and heavy metal contents in the soil samples.

The principal component analysis (PCA) of the chemical parameters and heavy metal contents in the samples revealed that the first three principal components accounted for 63.0% of the total variance within the 12-parameter factor space (including H_2O, KCl, P_2O_5, K_2O, N, organic matter, Fe, Mn, Zn, Cu, Ni, and Pb contents). According to the PCA results, Fe content, which contributed 17.7% to the total variance, and Mn content, contributing 14.3%, had positive influences on the first principal component (PC1). In contrast, the contents of H_2O and KCl, contributing 25.9% and 25.5% respectively, had negative impacts on the calculation of PC1.

The contents of P_2O_5 (9.3% of the total variance, based on correlations), K_2O (21.4%), N (11.1%), organic matter (15.6%), Zn (26.5%), and Cu (11.2%) showed positive influences on the second principal component (PC2). The contents of P_2O_5 (20.4% of the total variance, based on correlations) and Cu (13.6%) showed positive influences on the third principal component (PC3) calculation, while the contents of N (18.3%), organic matter (21.1%), and Ni (13.1%) exerted negative influences to PC3, as shown in Figure 4. The samples were labeled with the numerical values provided in Supplementary Table S1.

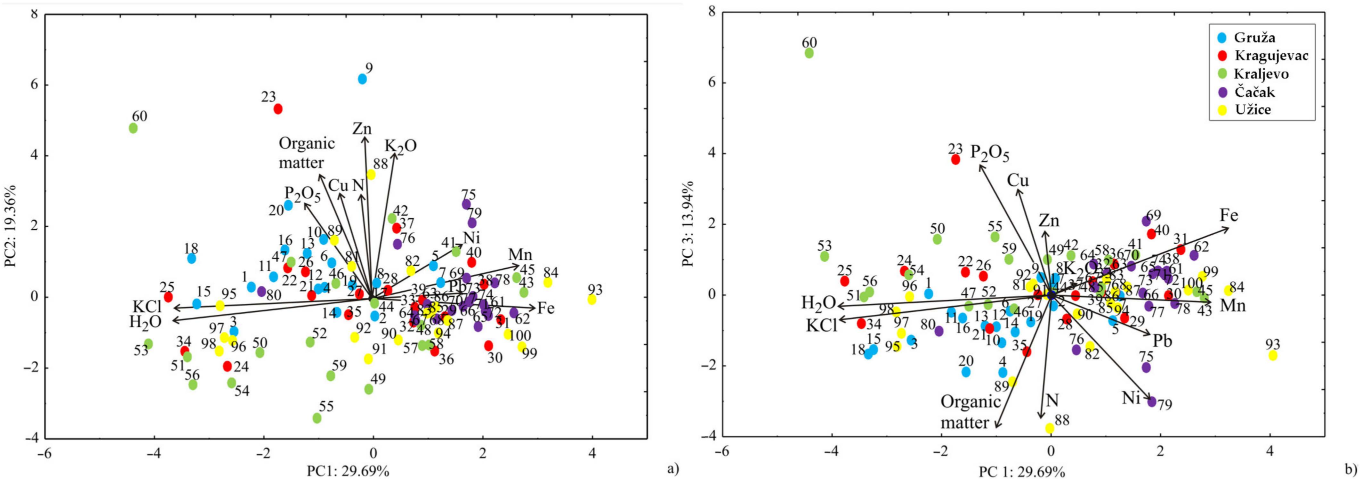

Figure 4. PCA ordination of chemical parameters and heavy metal contents in the soil samples is presented as follows: (**a**) projection in the PC1-PC2 plane, and (**b**) projection in the PC1-PC3 plane. The samples are labeled with the numerical values provided in Supplementary Table S1.

4. Discussion

Currently, agriculture is fighting to adapt to climate change and provide wholesome food for the world's expanding population on dwindling amounts of arable land. At the same time, the negative impacts of human activities, including agriculture, on the environment have to be minimized [17,19]. Soil characteristics such as humidity, total contents of essential elements (carbon, nitrogen, and phosphorus), soil pH reaction, cation exchange capacity, and other parameters are of great significance for the development of many ecological processes, such as carbon reserve deposition, nitrogen mineralization, decomposition of organic matter, water purification, etc. [20–22]. While heavy metals are generally present in the soil in sufficient quantities, they are predominantly in their insoluble forms, which limits their availability to plants, so Zn and Cu are usually absorbed in clay particles, $CaCO_3$, or organic matter, while Fe is most often found in the form of hydroxide [23,24]. The elements Cu, Mn, Ni, and Zn are essential for the functioning of living organisms, but in large concentrations, they can be toxic and have negative effects on the environment. On the other hand, As, Cd, Cr, Pb, and Hg are considered toxic even in low concentrations [25]. Previous research indicates that heavy metals and metalloids most often accumulate in the surface soil layers, and their contents can be several times higher in deeper layers and in reference values for a specific area [26,27]. The total content, solubility, and availability parameters of the examined elements depend, to a significant degree, on the composition of the parent substrate, the soil texture, the content of organic matter, and soil pH reactions [28].

In the regions of Central and Western Serbia, due to the diversity of the geological substrate, climatic characteristics, biodiversity, topographical and hydrological conditions, and anthropogenic influences, different types of soil have formed. The dominant soil types have slightly acidic or acidic reactions, are carbonate-free or slightly carbonated, are slightly humus to humus, have very low or low contents of easily accessible phosphorus, and have optimal or high contents of easily accessible potassium [29].

In terms of acidity, soil pH represents one of the most important chemical characteristics, on which many other physical, chemical, and biological properties depend. The value of pH significantly affects the amounts, types, and contents of organic matter, Fe and Al oxides, and cation sorption, which increases with increasing pH [30]. Also, pH affects the dissolution and deposition processes and the redox potential, and represents a limiting factor in terms of the bioavailability and mobility of essential and potentially toxic elements [31]. It is known that, in the range from neutral to low pH values, most elements become more mobile and, therefore, bioavailable [32]; however, exceptions occur with As, Mo, Se, V, and Cr, whose bioavailability and mobility actually increase in slightly alkaline environments [33]. A decisive factor could be high pH values, which affect the availability of nutrients in the soil, primarily phosphorus, as well as the essential micronutrients Fe, Mn, Zn, and C [31,34]. The amounts of $CaCO_3$ in the analyzed soil samples varied depending on the location and soil type.

The amount of organic matter (OM) affects soil structure, water retention, water permeability, and aeration. As for its influence on chemical properties, we primarily mean the influence that OM has on the cation exchange capacity (CEC), buffering capacity, and bioavailability of metals [35]. Over the years, there has been a drastic decrease in the content of OM in the soil, as a result of climate change, management systems, erosion, and other degradation processes [36]. On more than half of the total land surface in Southeastern Europe, the content of OM is very low—on average, below 3.4% [37], which is similar to the results obtained in our research. In the analyzed localities, the content of OM in the soil ranged from 0.30% to 5.10%, indicating a trend of decreasing content. The variation in OM content values can be explained by terrain heterogeneity and the presence of multiple soil types, as well as different management practices that lead to large differences in soil organic matter stocks. The amount of nitrogen in the soil directly depends on the amount of OM, so if the content of OM is high, the nitrogen content will be proportionally high [38]. The amount of nitrogen in the tested soil samples ranged from 0.05% to 2.1%. Soils in most tested locations were very poorly supplied with phosphorus. The content of readily available potassium (K_2O) in the soil ranged from 3.51 mg 100 g^{-1} to 38.10 mg 100 g^{-1}.

Iron (Fe) is one of the most abundant elements in nature, and its average content in soil is about 3.5%, or about 30,000 mg kg^{-1} [39]. Manganese (Mn), alongside Al and Fe, is one of the most abundant elements in the lithosphere, and its average content in soil, globally, ranges from 41 to 550 mg kg^{-1} [2]. The average copper content in the world's soils ranges from 2 to 50 mg kg^{-1} [25], and the total content usually depends on the parent soil substrate and the distribution of local and regional characteristics in the soil. In the surface soil layers, copper is most often found in its divalent form, Cr(II), so it is generally very toxic and bioavailable; however, the higher the value of the soil pH reaction, the greater the influence on its mobility, solubility, and availability in the soil [2]. Nickel (Ni), similar to chromium, can be found in all types of soils, ranging from negligible to extremely high concentrations [25], and the average nickel content in soils around the world ranges from 13 to 37 mg kg^{-1} [25]. The content and mobility of nickel in soil is most influenced by pH, so in soils where $pH < 6$, nickel becomes very soluble and toxic; meanwhile, in neutral and weakly alkaline soils, it occurs in the form of hydroxide, with very low mobility and solubility [25]. Certainly, the factors that significantly influence the mobility and availability of Ni are OM, CEC, and the contents of clay particles [2]. The main source of lead (Pb) in soil comes from the parent substrate; however, due to various anthropogenic activities, the surface layers of the soil are additionally enriched with lead [25]. The average content of lead (Pb) in soils, globally, is around 27 mg kg^{-1}, and its content in the soil is greatly influenced by the granulometric composition, i.e., the sizes of the particles to which Pb can bind, as larger amounts of lead are bound to finer particles of clay and colloids [2]. Zinc (Zn) is one of the most prevalent elements, and its content in soil largely depends on the composition of the parent material on which the soil forms. It varies widely, from 10 to 100 mg kg^{-1}, while the average value for world soils is 55 mg kg^{-1} [40]. Many factors affect the solubility of Zn, but also its ability and method of binding to the soil.

The most important of these factors are pH, soil texture, CEC, and organic matter content. The solubility of zinc is highest in an acidic environment, while, with an increase in pH, especially above 6.5, zinc occurs in forms that are very stable and almost inaccessible to plants. The content of Zn in the analyzed samples indicates a large variability, depending on the locality [41]. This has been confirmed in several studies [42,43] and is consistent with the fact that heavy metals are generally adsorbed on organic matter [44], and that organic matter contributes to the accumulation of heavy metals in the soil [45]. Kabata–Pendias et al. [12] conclude that the average content of total Zn in the surface layers of different global soil types in the world ranges from 17 mg kg^{-1} to 125 mg kg^{-1}. The behaviors of heavy metals such as Cd, Cr, Pb, Co, etc. have become a growing concern in ecological research because of the possibility of ecotoxicity, as well as their persistence, bioaccumulation, and biomagnification properties, making them a threat to the water and soil resources' health [46,47].

5. Conclusions

This study provides valuable data regarding heavy metal concentrations in soil collected from field crops in production areas of Central and Western Serbia. Based on this research, and its focus on the total content of heavy metals in the soils of Central and Western Serbia, as well as on determining the degree of pollution in the environment caused by their behavior, distribution, and origin, it can be concluded that there is pronounced variability in relation to localities. Their contents were mostly within the same ranges as those of similar soils from Europe and around the world. Any pollution control system must include heavy metal monitoring, including the methodical collection of data on the concentrations of heavy metals in a particular environment. Before environmental degradation occurs, it is crucial to set pollution limits and implement efficient monitoring procedures.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/agronomy14081836/s1, Table S1: Experimental results.

Author Contributions: Conceptualization, I.D.; methodology, I.D.; software, L.P.; validation, I.D.; formal analysis, I.D. and E.J.H.; investigation, I.D. and M.D.; resources, I.D.; data curation, I.D. and L.K.; writing—original draft preparation, I.D., P.V.V.P., M.S. and L.P.; writing—review and editing, I.D., P.V.V.P., L.P., E.J.H., M.S., M.D. and L.K.; project administration, I.D. and P.V.V.P.; funding acquisition, I.D. and P.V.V.P. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The original contributions presented in the study are included in the article/Supplementary Materials, further inquiries can be directed to the corresponding author.

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