applied sciences

MDPI

Article

Forms of Copper in the Aspect of Anthropogenic Changes in the Profiles of Horticultural Soils in the Cities of South-Eastern Poland

Iwona Makuch-Pietraś [1,*] and Anna Wójcikowska-Kapusta [2]

[1] Department of Nature Conservation and Landscape Ecology, Institute of Agricultural Science, Land Management and Environmental Protection, University of Rzeszów, 35-601 Rzeszów, Poland
[2] Institute of Soil Science, Engineering and Environmental Science, University of Life Science in Lublin, 20-069 Lublin, Poland; anna.kapusta@up.lublin.pl
* Correspondence: makuchiw@ur.edu.pl; Tel.: +48-177855007

Abstract: The aim of the research was to show the changes taking place in soils as a result of the influence of anthropogenic factors in the form of intensive horticulture and pollution within the city. It was made on the basis of the distribution of individual fractions as well as available and total Cu forms in the profiles of garden soils located at houses and in the family allotment gardens in six cities in south-eastern Poland. The research took into account the granulometric composition according to which the cities were divided into two groups. The pollution assessment was based on the concentration indicator, Igeo, and indicators taking into account the forms available for plants: C_{av}/C_t and BF. There was no copper contamination with regard to legislation act and Igeo. The role of organic matter as an important component in copper in the humus horizons of soils in long-term horticultural cultivation has been considered. The content of all forms of copper was higher in humus horizon which also indicated the anthropogenic changes. Among the two groups of soils, a greater impact of the treatments used in horticulture on those made of sands was found in relation to the silty ones.

Keywords: BCR method; copper; garden soil; indices of pollution and concentration in soil

Citation: Makuch-Pietraś, I.; Wójcikowska-Kapusta, A. Forms of Copper in the Aspect of Anthropogenic Changes in the Profiles of Horticultural Soils in the Cities of South-Eastern Poland. *Appl. Sci.* **2021**, *11*, 9018. https://doi.org/10.3390/app11199018

Academic Editors: Bruno Lemière and Karen Hudson-Edwards

Received: 21 August 2021
Accepted: 24 September 2021
Published: 28 September 2021

1. Introduction

Among the soils in the area of anthropogenic impact of urbanization pressure as well as modification by use, there are soils developed in home and allotment gardens. Due to their location within cities, they are part of green areas, used by the owners for growing vegetables, which is the reason for modifying the soil profile [1–3]. The effect of these changes is the modification of humus horizon into a much deeper in the soil profile, which is characterized by a well-developed large amount of organic substance, characterized by an extensive sorption complex and far-reaching possibilities of retaining not only desirable but also toxic substances [4,5]. This induced many scientists to study the content of heavy metals in horticultural soils [2,5–8]. Due to location of the gardens, they are also treated as urban areas, and most research focuses on agglomerations where the impact of anthropopressure is significant. However, it is worth paying attention to smaller cities, where the impact of urbanization occurs, but to a lesser extent. Hence, there was a need to conduct research in the area of the eastern-southern city of Poland, especially as they represent primarily agricultural areas and so far have been ignored in the literature on the subject.

An important aspect of the research is to show the combination of two anthropogenic factors influencing the state of the natural environment in cities. Horticultural use contributes not only to the modification of soil-forming processes, but also changes in the concentration and forms of heavy metals in soils. In determining these changes are helpful the pollution indicators widely discussed in the literature, such as Igeo or the concentration coefficient, reflecting the distribution of heavy metals in the profile. Moreover, it is worth noting that in the literature, there are few publications describing the problem of metal decomposition in the profile with the use of indicators, where data showing the geochemical background are used, which is more practical than using reference values. Typically, the reference values based on literature data are used, which do not fully reflect the natural geochemical status of a given location [9,10]. The indicators presented in the paper are based on the results obtained from the entire profiles, which is an additional value of the research, especially new aspect of research in cities smaller than agglomerations.

The study used the analysis of the BCR sequential extraction procedure, which is of great importance in presenting the fractional distribution of metals and indicating the content of bioavailable forms. This is important from the perspective of man and biocenosis [11,12]. However, this analysis may reveal the consequences of the soil-forming processes taking place, caused by an anthropogenic factor, which is horticulture. The fraction related to the organic substance is in this case an indicator of the connection of anthropogenic factors and the path of contamination movement. In the case of the presented work, an example is copper.

With the objective of contributing information about the anthropogenic sources such as the horticultural use and urban pressure on soils, the following aims of the research were formulated: (i) estimation of Cu content in soils with different particle composition from urban gardens, in comparison with soils from arable fields located outside city limits, using various contamination indices and of bioavailable forms of copper, (ii) determination of the distribution of Cu in the soil profile, in particular with emphasis on organic matter-bound forms, by means of the BCR sequential extraction procedure [11,12].

2. Materials and Methods

2.1. Sampling Site

The study site was described in the earlier article of authors [13]. The research was conducted in south-eastern Poland (Figure 1). Firstly, potential heavy metal contamination was a criterion for the selection of the cities, which are located mainly in agricultural region, with a poorly developed industrial infrastructure. Secondly, two groups of soils were distinguished according to the particle size distribution. There were six cities selected. In each town the survey was conducted, the selection of one allotment garden in a complex of Family Allotment Gardens, one domestic garden at a detached house, and a control site (arable field) outside the city limits was made. An interview with owners were the base to select both the allotments and domestic gardens with at least 20-years horticultural activity selected criterion. High crop culture were an important element in the choice of the gardens represented by the use of only organic fertilizers, often produced by the owner. In comparison to horticulture cultivation, the crop field was selected also after an interview with the owner. Arable land was subjected to extensive cultivation by crop rotation. There were located outside the city, without high-traffic transportation routes nearby. Sand and loamy sand represented sandy soils as a group of light soils which were sampled in Biała Podlaska, Lubartów, and Tarnobrzeg. Soils sampled in Lublin, Przemyśl, and Zamość was represented mostly by a group of medium soils, made from silt, with the particle size distribution of silt loam [13]. Podzolic, brunic, and gleying types were represented in sandy soils, whereas the medium silty soils were luvisols [13,14].

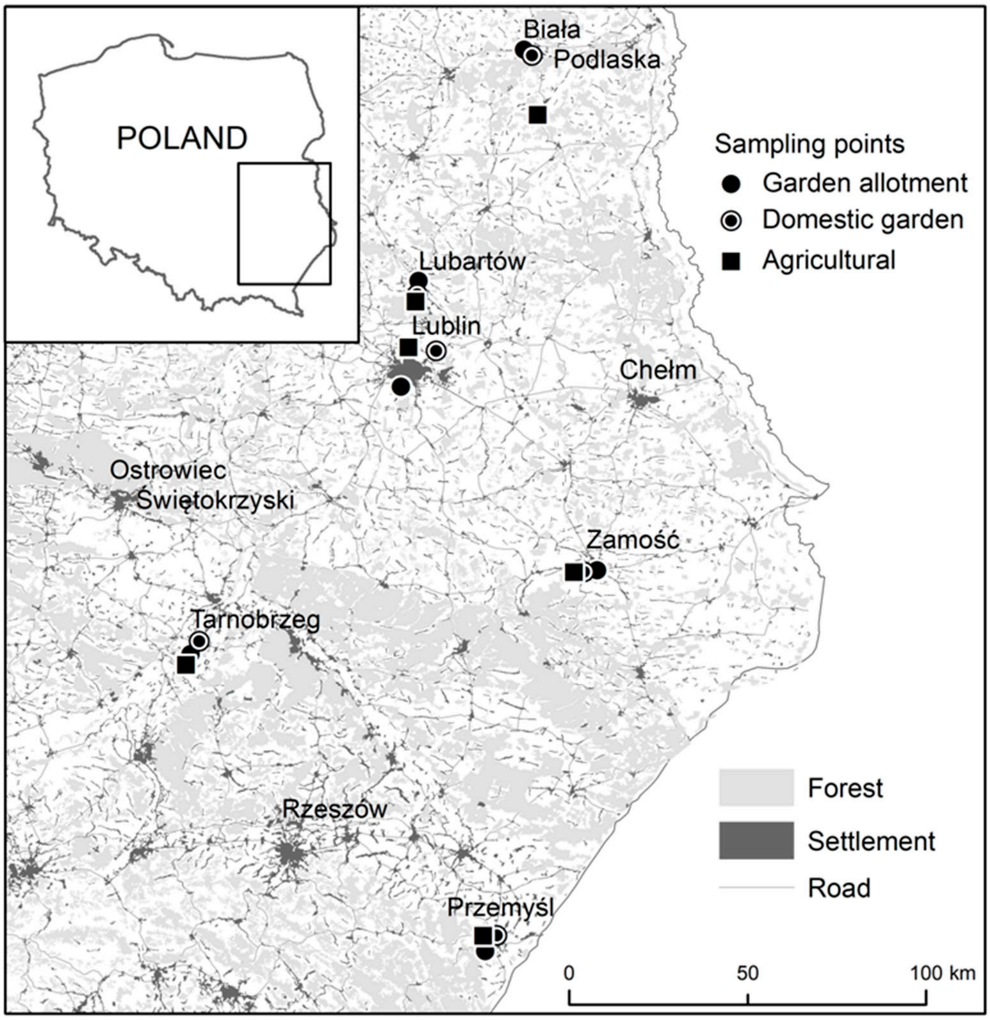

Figure 1. Map of sampling in the study area.

2.2. Soil Sampling and Soil Properties

Soil material for analyses was collected from soil profiles in each domestic, allotment garden, and in the arable field. Samples were taken from each genetic horizon composited of several samples. The material was air-dried and then passed through a 2-mm mesh sieve.

Properties were determined in the soil material using the following methods. The particle size distribution was determined by means of the Bouycous and Cassagrande areometric method, modified by Prószyński. Soil fractions and formations were identified according to PTGleb. [15]. Soil pH was determined potentiometrically in water and in a 1 M KCl solution. Organic carbon content was measured using the Tiurin method and the total nitrogen content was determined by the Kjeldahl method. The hydrolytic acidity was determined by the Kappen method. The sorption capacity was calculated as CEC extracted with ammonium acetate at pH = 7.0 [16]. All samples were analyzed in triplicate, and all results of content were considered as the average value of three measurements made in repeatability conditions.

2.3. Heavy Metal Determination and Sequential Extraction Procedure

Total copper content was determined by extraction using a mixture of concentrated acids (nitric and perchloric acid 1:1). The weight of 0.5 g of soil and 20 mL of mixture was used. It was diluted to 25 mL after mineralization. The sequential extraction procedure proposed by BCR was used to demonstrate the relationship between copper content and organic matter caused by intensive horticultural use [11,12]. The content of four fractions was determined and the scheme of the procedure is presented in Table 1. There was 2 g of soil used in this method. In the first and second fraction, 20 mL of extraction solvents was added and shaken for 16 h. Organic fraction was started with adding 5 mL of H_2O_2 and stayed for one hour. The next step was boiling in 85 °C for one hour. After that once again was added 5 mL of H_2O_2 still boiling for one hour. The last step was adding 25 mL of extraction solvent and shaken for 16 h. Additionally, a bioavailable form of Cu was determined by the Rinkis method in 0.1 M HCl (soil to solution ratio is 1:1) to assess the potential bioavailability [16]. All forms of the element were measured using the ICP-AES method, using Leeman PS 950 apparatus. Digestion with reagents was analytically pure, and the deionized water was performed in the DKL 20 Fully Automatic Digestion Unit (VELP SCIENTIFICA). The calibration curves and the concentration measurements were performed for each metal separately using the certified single element standards for ICP, manufactured by Inorganic Ventures (Lakewood, CO, USA). All samples were digested and analyzed in triplicate, and the final content was always considered as the average value of three measurements made in repeatability conditions.

Table 1. Scheme of the sequential analysis of metals according to BCR.

Fraction		Extraction Solvent
I	Exchangeable and Acid Soluble	0.11 M CH_3COOH, pH = 2
II	Reducible	0.1 mol·dm^{-3} $NH_2OH \cdot HCl$, pH = 2
III	Organic	30% H_2O_2 + 1 mol·dm^{-3} CH_3COONH_4, pH = 2
IV	Residual	$HNO_3 + HClO_4$

2.4. Indices of Pollution

To indicate the anthropogenic changes of soils, the indices of the distribution and concentration of copper were calculated [9,17]:

$$C_f = \frac{C_s}{C_n}$$

C_s—concentration of the heavy metal.
C_n—background level of heavy metal.

The geoaccumulation index (Igeo) was calculated from the total content of heavy metal determined in each profile horizons in relation to the parent material, with the Formula [18]:

$$I_{geo} = \log_2\left[\frac{C}{1.5\ B}\right]$$

C—concentration of the heavy metal in the horizon.
B—background level of heavy metal.

The following classes were distinguished based on the value of the index:

- ≤0: unpolluted.
- 0–1: unpolluted to moderately polluted.
- 1–2: moderately polluted.
- 2–3: moderately to highly polluted.
- 3–4: highly polluted.
- 4–5: highly to extremely highly polluted.
- ≥5: extremely highly polluted.

The ratio of bioavailable forms to the total content of the element was calculated [19].

$$(C_{av}/C_t)\cdot 100$$

C_{av}—content of the bioavailable form of the element.
C_t—total content of the element.

There was calculated the BF value based on the results of the sequential extraction procedure with the Formula [20]:

$$BF = (C_{bio} \cdot 100)/C_{total}$$

where:

C_{bio}—concentrations of bioavailable forms of the metal in the studied soils, i.e., forms contained in fractions I-III of the sequential extraction of soil.
C_{total}—the total concentration of the metal in the studied soil.

2.5. Statistical Analysis

Statistical analyses were carried out to check whether the grouping variables, i.e., particle size distribution and land use, discriminate between the properties and parameters of the soils from surface horizons of profiles. To assess the effect of soil properties on the content and forms of heavy metals, Pearson's correlation coefficients between selected data were calculated. All correlation coefficients results were analyzed in the Statistica 13.3 program at a significance level of $\alpha \leq 0.05$. Principal component analysis (PCA) was made by Canoco 5 software.

3. Results

3.1. Soil Physicochemical Properties

The results were presented in the earlier publication of the authors [13]. Analyzing the mechanical composition, a slight differentiation was found in the group of soils made of sands in horticultural use. In Biała Podlaska, in the gardens there were loamy sand on sand, in Lubartów in the domestic garden-loamy sand on sand, in the allotment garden-loamy sand, and in Tarnobrzeg in the domestic garden-loamy sand and sandy loam, in the allotment garden-loamy sand on sandy loam. Sandy soils used for agriculture in all localities had a mechanical composition of sand (Supplementary Materials Table S1).

The reaction of sandy soils was slightly acidic to neutral in domestic gardens, acidic to neutral in allotment gardens, and strongly acidic in agricultural [21]. The mode of land use also influenced the sorption capacity. The sum of alkaline cations reached the highest values in humus horizons, and its gradual decrease followed with depth, with lower values in arable than in horticultural. However HA was higher in arable than garden soils. Relationship with land use occurred when analyzing the content of C and N, where the mode of land use influenced the greater amount of this component in the humus horizons of garden soils than in agricultural (Supplementary Materials Table S1).

In the case of the second group of silty soils, the profiles in Przemyśl and Zamość, as well as in the allotment garden and the arable field in Lublin were characterized by the silt loam particle size composition. On the other hand, in the domestic garden in Lublin, the mechanical composition of loamy sand was found (Supplementary Materials Table S2).

In silty soils, the reaction qualified all the tested humus horizons as slightly acidic to alkaline [21]. Intensive horticulture did not significantly affect the content and distribution in the profile of the sum of alkaline cations and HA. There were rather no differences between garden and arable land use on the content of C and N, but the amount was the highest in humus horizons (Supplementary Materials Table S2).

3.2. Total Cu Content

The total content of copper in the sandy soils from the domestic gardens was higher than in the samples from the arable fields, whereas high variability of the content of this element was found in the soil from the allotment gardens. The horticulture activity did not influence the copper content, which was similar in the entire profiles. However, a greater amount of copper in the humus horizons and a systematic decrease in its level with depth were observed in the arable soils (Supplementary Materials Table S3).

The total copper content was much higher in the agricultural silty soils than in the sandy soils. Substantially lower differences were observed in the case of the garden soils, especially in the samples from the domestic gardens. The distribution of Cu in the garden soil profiles did not exhibit any changes, while the effect of natural leaching processes was detected in the agricultural soil profiles, which was manifested by a lower amount of copper in the Et horizons and higher Cu content in the Bt horizon (Supplementary Materials Table S4).

3.3. Bioavailable Cu Forms

Regardless of the particle size distribution and land use, the humus horizons in all analyzed soils were characterized by high copper amounts [21]. The highest bioavailable copper content was detected in the humus horizons of the sandy soils, especially in the samples from the domestic and allotment gardens. The level of this Cu form was found to decrease with the profile depth. The highest content of this element was recorded in the humus horizon from the domestic garden in Biała Podlaska (16.8 mg·kg^{-1}) and from the allotment garden in Tarnobrzeg (14.1 mg·kg^{-1}) (Supplementary Materials Table S3). A comparison of samples from the localities with sandy soils to those with silty soils showed similar contents of bioavailable Cu only in the garden samples. In the group of silty soils, the highest bioavailable Cu content, i.e., 25.00 mg·kg^{-1} was determined in the humus horizon of the soil from the domestic garden in Zamość. All humus horizons of the garden soils had a higher level of this element than the arable field soil. (Supplementary Materials Table S4).

3.4. Indices of Pollution

In the sandy soils, the concentration indexes calculated from the ratio of the copper content in the horizon to its content in the background indicated the highest concentration of the element in the topsoil layers. The values of the index ranged from 0.48 to 3.30 and were not influenced by the mode of land use (Supplementary Materials Table S3).

Regardless of the land use, the highest values of the copper concentration index in the silty soil profiles were calculated for the topsoil horizons. There were no differences related to the different modes of land use (Supplementary Materials Table S4).

In the sandy soils, the Igeo index values were very low, regardless of the mode of land use and horizon (0–1.14). Based on the values of this index, the analyzed soils were classified as unpolluted or moderately polluted (Supplementary Materials Table S3). The Igeo values in the silty soils were even lower, ranging from 0.00 to 0.12, and classified them as unpolluted soils (Supplementary Materials Table S4).

The percentage proportion of bioavailable copper in the total content in the sandy soils was the highest (>50%) in the humus horizons of the garden soil but did not exceed 40% in the arable soil (Supplementary Materials Table S3).

The calculated ratio of the bioavailable copper form to its total content in the silty soils had lower values than in the light soils. The highest Cu index values, i.e., 9.59–64.38%, were calculated for the garden soils, whereas the lowest values, i.e., 8.11–25.30%, were calculated for the arable soil. The index values declined with depth in a majority of the studied profiles (Supplementary Materials Table S4).

The BF index for copper in the sandy soils was characterized by very low values: 0.00–41.41, with the highest values in the topsoil horizons. As shown by the values of the index, large amounts of bioavailable Cu were detected in the domestic garden soil from Biała Podlaska and in the soil profiles from Tarnobrzeg (Supplementary Materials Table S3).

The BF values for the silty soils were slightly higher, i.e., 3.73–57.49, compared to the light soils. There were no significant differences related to the mode of land use or between the soil profile layers (Supplementary Materials Table S4).

3.5. Sequential Extraction of Cu

Interestingly, the light soils had no content of the most bioavailable copper fraction I. Additionally, no Cu fraction II bound to iron and manganese oxides was found in the arable soil samples from Biała Podlaska, Lubartów, and Tarnobrzeg. In the garden soils from Tarnobrzeg, copper fraction II was present in the entire profile of the domestic garden soil and in the humus horizon of the allotment garden soil. The content of this fraction was in the range of 0.08–1.49 mg·kg^{-1} (Supplementary Materials Table S3), which accounted for 0.33 to 5.79% (Figure 2).

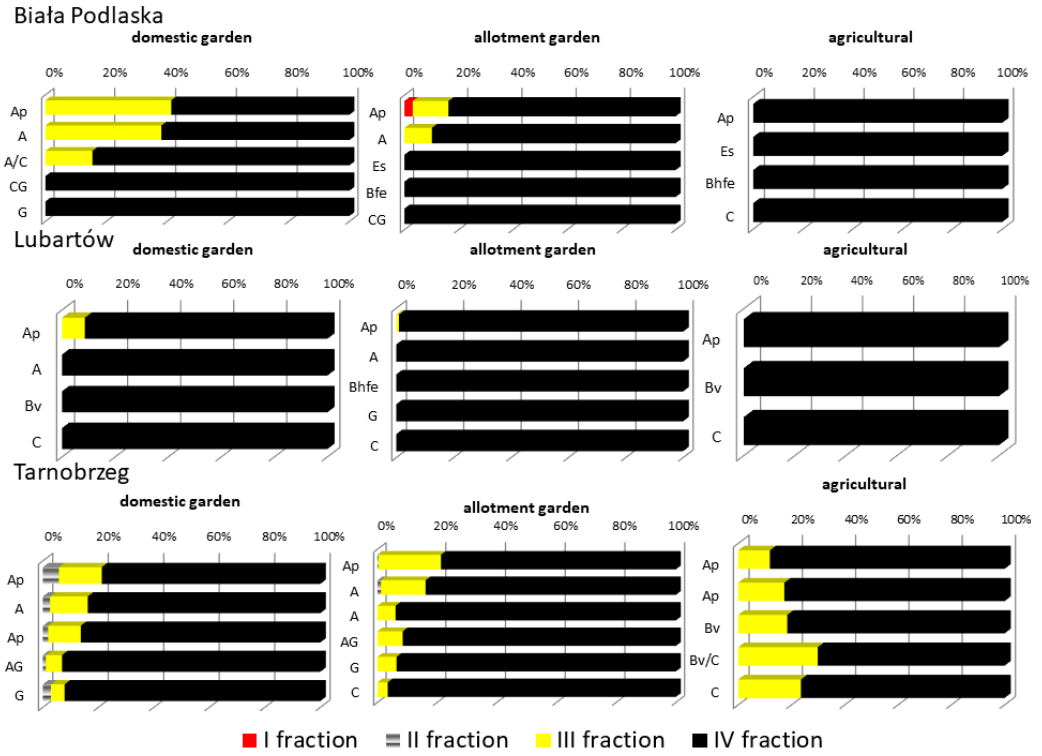

Figure 2. Percentage content of Cu fractions in sandy soils.

In the sandy soils, humus-bound copper fraction III was detected only in the humus horizons of the garden soils from Biała Podlaska (the highest content: 11.69 mg·kg^{-1}) and Lubartów-0.87 and 0.16 mg·kg^{-1} (Supplementary Materials Table S3). In Tarnobrzeg, regardless of the mode of land use, the humus-associated fraction was present in the entire profiles and ranged from 1.12 to 5.08 mg·kg^{-1} (Supplementary Materials Table S3), constituting from 0% to 41.41% of the total copper content (Figure 2).

The residual Cu fraction was the largest of all the fractions determined in the study. In the sandy garden soils, it was in the range of 5.60–38.74 mg·kg^{-1} (Supplementary Materials Table S3), which accounted for 58.59–100% of the total copper content (Figure 2). In turn, a narrower range of 2.02–10.58 mg·kg^{-1} (Supplementary Materials Table S3), which corresponded to 70.14–100% of the total copper content, was detected in the arable soils (Figure 2). In terms of the land use, the content of the residual copper fraction decreased with depth in the arable soils, while no such relationships were noted in the case of the garden soils (Supplementary Materials Table S3).

The content of water-soluble copper fraction I in the silty soils ranged from 0.00 to 7.06 mg·kg^{-1} (Supplementary Materials Table S4) and its percentage proportion in the total content, regardless of the mode of land use, was in the range of 0.00–15.29% (Figure 3). This was the smallest fraction of all those analyzed in this study. The soil sampled in Zamość exhibited an outstanding profile with the highest content of fraction I, which was found to vary greatly with a tendency towards higher contents in the parent material. The humus horizons exhibited high levels of this fraction as well (Figure 3).

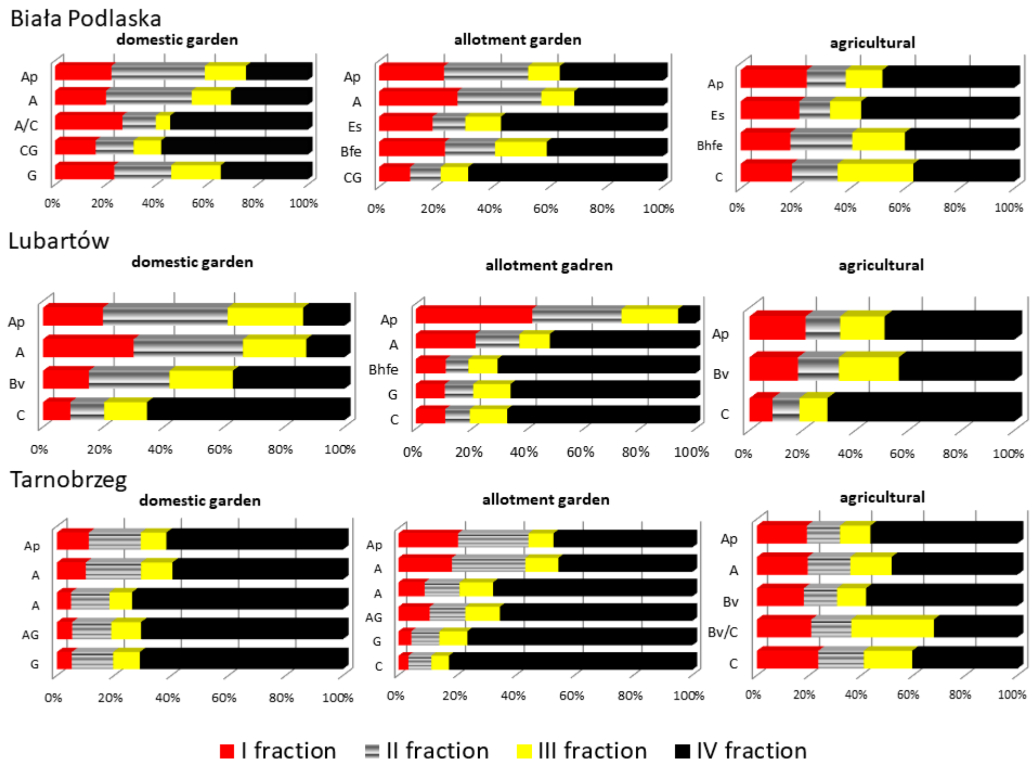

Figure 3. Percentage content of Cu fractions in silty soils.

Regardless of the mode of land use, the content of the copper fraction II bound to iron and manganese oxides in the soils ranged from 0.10 to 4.21 mg·kg^{-1} (Supplementary Materials Table S4), and its percentage proportion in the total content was in the range from 0.24 to 23.04% (Figure 3). The analysis of the content of this fraction in the analyzed cities revealed its highest levels in all genetic horizons in the soils sampled in Zamość, irrespective of the mode of land use. It was impossible to assess whether the humus horizons had a greater proportion of this fraction; moreover, its distribution in the profile was highly variable. The difference in the content of copper fraction II between the field and garden soils was unclear (Figure 3).

Regardless of the mode of land use, the content of humus-bound copper fraction III ranged from 0.91 to 9.42 mg·kg^{-1} (Supplementary Materials Table S4), which accounted for 2.17–45.92% of the total content (Figure 3). It was impossible to show unequivocally whether the content of this fraction was higher in the garden soil profiles, especially in the topsoil layer, as was the case of the sandy soils (Figure 3, Supplementary Materials Table S4).

The percentage proportion of the residual fraction in the total Cu content in the silty soils ranged from 34.56% to 96.27%, which was lower than that in the sandy soils (Figure 3). Its content was in the range of 3.00–47.98 mg·kg^{-1} (Supplementary Materials Table S4). In terms of the study sites, the largest proportion of this fraction was detected in the profiles of the domestic and allotment garden soils sampled in Przemyśl. The content of the residual fraction is determined by the other fractions; hence, its proportion indicates copper forms that are bioavailable or can be mobilized. The profiles of soils sampled in Zamość and in the domestic garden in Lublin were characterized by the highest variability of the Cu fraction composition and a lower level and percentage content of fraction IV (Figure 3, Supplementary Materials Table S4).

3.6. Statistical Analysis

Among the copper forms in the sandy soils, the most significant correlations were found for fractions III and IV mainly with the organic carbon content (r = 0.802 at $p < 0.01$ and r = −0.788 at $p < 0.05$, respectively), the total content (r = 0.823 and r = −0.865 at $p < 0.01$), and the bioavailable form (r = 0.865 and r = −0.878 at $p < 0.01$) (Table 2). In the case of the residual fraction, there was a significant correlation with pH measured in water (r = −0.668 at $p < 0.005$). The most mobile fractions did not show any significant correlations, except from the correlation of fraction II with the silt fraction content (r = 0.936 at $p < 0.001$). Weaker statistically significant relationships were found between the bioavailable copper form and properties that may influence its mobility: pH reaction (r = 0.858 and 0.865 at $p < 0.01$) and organic carbon content (r = 0.734 at $p < 0.05$). Moreover, this form was characterized by a very high correlation coefficient (r = 0.936 at $p < 0.001$) with the total Cu content. Noteworthy, no significant correlations were found for the indicators of the mobile forms. In turn, the C_a/C_t and BF indices were positively correlated with parameters of the bioavailability of the elements (r = 0.772 and 0.715 and 0.668 at $p < 0.05$) and the organic matter content (r = 0.681 and r = 0.788 at $p < 0.05$). Furthermore, the correlation analysis revealed a significant correlation between the BF index and the content of total and bioavailable Cu (r = 0.865 and r = 0.878 at $p < 0.01$) (Table 2).

Table 2. Values of Pearson's correlation coefficients of copper forms and indices with the physico-chemical properties of sandy soils.

Properties of Studied Soil	Cu Total	Cu Avail.	pH H_2O	pH KCl	C Org	<0.002
Cu Total	1000	0.936 *	0.748 ***	0.782	0,575	0.253
C_f	−0.247	−0.195	−0.352	−0,452	0.075	−0.533
Cu Available	0.936 *	1	0.858 **	0.865 **	0.734 ***	0.114
C_a/C_t	0.311	0.603	0.772 ***	0.715 ***	0.681 ***	−0.043
Igeo	−0.171	−0.146	−0.357	−0,459	0.023	−0.483
I Fraction	−0.023	−0.013	0.206	0.212	0.19	−0.243
II Fraction	0.461	0.264	0.392	0.404	−0.046	0.936 *
III Fraction	0.823 **	0.865 **	0.613	0.665	0.802 **	−0.067
IV Fraction	−0.865 **	−0.878 **	−0.668 ***	−0.721	−0.788 ***	−0.050
BF	0.865 **	0.878 **	0.668 ***	0.721	0.788 ***	0.05

Significance level: * −0.001; ** −0.01; *** −0.5.

In the silty soils, there were statistically significant positive correlations of the bioavailable Cu form with the C_f (r = 0.714 at $p < 0.05$), C_a/C_t (r = 0.755 at $p < 0.05$), and Igeo (r = 0.912 at $p < 0.001$) indices and with the organic carbon content (r = 0.721 at $p < 0.05$). Although there were no significant relationships between the total and bioavailable copper content, the C_a/C_t ratio was negatively correlated with the content of the silt fraction (r = 0.774 at $p < 0.05$) (Table 3).

The results of the PCA analysis of the parameters of the Cu content in the soils are presented in Figure 4 and Table 4. The particle size distribution was the most important variable discriminating the content of copper. A majority of points marked with lowercase Arabic letters (si, sa) were located on the opposite sides of the first component axis, which explains over 40.18% of the variance. Unfortunately, there were no regularities in relation to the mode of land use (do, al, ga, ag), as the results showed high heterogeneity. Except for BF, all indices described in the present study were negatively correlated with the basic physicochemical properties (pH or silt content) and with the content of the most bioavailable Cu fractions I and II or the total copper content. A negative correlation was also noted between the BF index indicating the proportion of mobile forms and the residual fraction content. Importantly, there was a positive correlation between the organic carbon content and the content of fraction III. Fractions I and II correlated positively with the parameters of the soil conditions, i.e., pH and the silt fraction content, as shown mainly by the analysis of the silty soils. As shown in the figure, the light soils exhibited higher values of Cu indices, whereas higher total content of the element was found in the medium soils.

Table 3. Values of Pearson's correlation coefficients of copper forms and indices with the physicochemical properties of silty soils.

Properties of Studied Soil	Cu Total	Cu Avail.	pH H_2O	pH KCl	C Org	<0.002
Cu total	1	0.333	0.301	0.158	0.471	0.656
C_f	−0.053	0.714 ***	0.022	0.048	0.36	−0.406
Cu Available	0.333	1	0.279	0.29	0.721 ***	−0.349
C_a/C_t	−0.328	0.755 ***	−0.029	0.077	0.348	−0.774 ***
Igeo	0.181	0.912 *	0.316	0.028	0.482	−0.631
I Fraction	0.392	0.303	0.004	0.215	0.482	0.052
II Fraction	−0.093	0.537	−0.000	0.206	0.434	−0.391
III Fraction	−0.645	0.378	−0.139	−0.068	0.024	−0.639
IV Fraction	0.319	−0.520	0.095	−0.090	−0.317	0.525
BF	−0.319	0.52	−0.095	0.09	0.317	−0.525

Significance level: * −0.001; ** −0.01; *** −0.5.

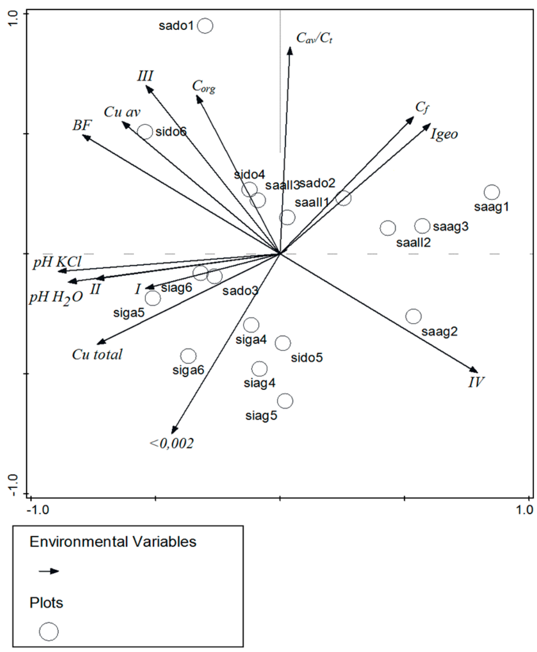

Figure 4. Principal component analysis (PCA) of two indices for the copper content and parameters.

Table 4. Summary of the Cu results in PCA.

Statistic	Axis 1	Axis 2	Axis 3	Axis 4
Eigenvalues	0.4018	0.2613	0.0955	0.0760
Explained Variation (Cumulative)	40.18	66.31	75.86	83.46

4. Discussion

The literature describing the problem of soil contamination with heavy metals in gardens presents the opinion that these are soils contaminated by substances from neighboring houses, roads, urban, and possibly industrial, areas. Copper is one of the most common heavy metals, and its form in soils may be influenced by such physicochemical properties as: pH, content of organic matter, calcium carbonate, clay fraction. It is worth emphasizing that soils under horticultural use as compared to cultivated ones may be characterized by a higher content of organic matter, which predisposes them to retain heavy metals [5]. In the presented studies were higher content in humus horizons of C, N, and sorption capacity and some changes in the reaction.

Taking into account the reaction of the analyzed soils and the proportion of the silt fraction, the total content of copper indicated natural levels of the element [22,23], with the exception of the allotment garden and arable field in Przemyśl and the domestic garden in Zamość. The silty soils exhibited higher total Cu content than that in the sandy soils, which was similar in all types of land use. While its distribution in the garden soil profiles did not show any regularity, the arable soils exhibited a lower Cu level in the Et horizon and substantially higher content of the element in the Bt horizon, which indicates the dominance of natural soil-forming processes over anthropogenic factors. Investigations conducted by many authors have demonstrated a significant relationship of copper contents with the level of floatable parts and soil type, which was confirmed by the differences observed in the soils analyzed in this study [24–33]. Nevertheless, the location of the site may significantly determine the copper content, as suggested by Hursthouse et al. [34]. The mode of land use differentiated the results. The profiles of the garden sandy soils had an evenly distributed two-fold higher level of copper than the arable soils. In turn, accumulation of this component and its systematic decline along the profile depth were observed in the humus horizons of the arable soils. The distribution of the total Cu content is reflected in concentration indices: the highest values were calculated for the humus horizons, irrespective of the mode of land use, and the sandy soils were characterized by higher values. In turn, in the group of the silty soils, a high index was calculated for the Bt horizon in the arable soils. The absence of differences in the copper content between silty soil horizons was confirmed by Gorlach et al. [35]. The concentration of copper in the Ap horizon may be associated with copper binding to organic matter, which has been reported by many authors [1,28,33,36–39]. As underlined by Kabała et al. [40], the location of allotment gardens and cultivation treatments promote higher concentration of, e.g., Cu in the topsoil layers, compared to agricultural soils. In addition to the concentration index, the Igeo index presented here not only showed the high levels of the analyzed element in the soils, but also indicated anthropogenic effects. As reported by many authors, calculation of the Igeo index facilitates determination of the source of copper concentration, e.g., in garden soils [41–43].

Additionally, to demonstrate the relationship of copper with organic matter, a sequential analysis was performed using the BCR method. Very few of the numerous publications on the application of BCR sequential analysis describe the use of this method in analysis of horticultural soils. Regardless of the mode of land use, the proportion of the copper fraction in the sandy soils was as follows: fraction IV > fraction III > fraction II > fraction I; however, no water-soluble, exchangeable, and carbonate-bound fraction I was detected. Furthermore, there was no fraction bound to iron and manganese oxides in the agricultural soils. Higher content of humus-bound fraction III was determined in the humus horizons of the sandy soils, especially in the garden soils, which proves that the mode of land use plays an essential role in its distribution. In the silty soils the mode of land use exerted no impact on the content of copper fractions I, II, and IV. Organic matter-bound copper fraction III predominated in the humus horizons of the garden soils, but there was no such relation found in the arable soils.

Compared to the present results, Moćko and Wacławek [44] reported the dominance of the humus-bound copper fraction and lower content of the residual fraction in the garden soils from Opole. Given the similarity of the humus horizon, the result is worth comparing with the arable chernozems from Kujawy characterized by a high proportion of the humus-bound fraction, which confirms the high affinity of copper to organic matter [18]. Although the arable soils served as a control, their content of the copper fractions is worth emphasizing. In their investigations of the forms of elements in Chinese arable soils, Chao et al. [45] showed very similar findings, i.e., the highest proportion of residual and organic matter-bound fractions and the lowest amounts of mobile fractions. Increased content of mobile fractions (I and II) may be caused by, e.g., the proximity of industrial plants, as demonstrated in studies of cultivated soils in Finland. Residual copper was the most abundant fraction. Moreover, the content of the organic copper fraction positively correlated with organic matter [46].

Due to the location of the analyzed horticultural soils, it is worth comparing the results with other investigations of urban soils. In a study conducted in Naples, Italy, Imperato et al. [38] carried out sequential analysis and found a high affinity of copper for organic matter, which was proved by the high proportion of fraction III. In analyses of the content of toxic forms of metals in urban soils from five European cities, Davidson et al. [37] found the dominance of fractions bound to iron and manganese oxides as well as fractions III and IV. As reported by Dąbkowska-Naskręt et al. [47], urban soils from city parks were characterized by a higher proportion of bioavailable fractions.

The calculation of the BF index reflecting the bioavailability of elements is highly important. More bioavailable forms were detected in silty soils and the same relation was stated for C_{av}/C_t indices. The copper mobility shown in the present study is comparable to that determined for soils from Kielce [20]. Some sites with the sandy soils were characterized by lower values of the indicators, i.e., below 20%. The parent material of the soils subjected to horticultural treatments exhibited substantially lower copper content than the humus horizons.

5. Conclusions

The vast majority of the studied soils had a natural copper content. The distribution of Cu in the profiles indicated a greater concentration in the humus horizons and this was reflected in the concentration coefficient and the Igeo index, which also indicated no contamination. However, the concentration of copper in the surface levels has confirmed that its content could have been affected by the way it was used in combination with its location in the city. Thus, the total copper content was higher in garden soils than in cultivated soils, as indicated by the concentration indices. The study also showed that the concentration of copper was higher in soils made of sands than of silt, which has proved that these are the formations that fully reflect the processes of transforming their properties as a result of use.

Based on the performed sequential extraction analysis, it was found that the last fraction was dominant in both researched soil groups. Copper was an element with a negligible content of bioavailable fractions in soils made of sands, as evidenced by its zero or very low BF index. In the soils made from silt, only fraction I was characterized by low values. It should be noted that due to the special properties and shape of the soil profiles used for horticulture, the fraction associated with the organic substance was the second largest in soils made of sand, which allows concluding that this is the group of soils most susceptible to high cultivation culture. The affinity of copper and its bioavailable forms in light soils is also confirmed by the performed statistical analyzes. In soils made of silt, fraction III was the only fraction whose content varied depending on the use.

Summing up, the analysis of copper distribution in soil profiles based on geochemical indices and BCR analysis have proved the influence of anthropogenic factors. The granulometric composition had a significant influence on the formation of the soil-forming processes taking place, as well as the copper content.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/app11199018/s1, Table S1: Content of the forms and values of Cu pollution indices in sandy soils, Table S2: Content of the forms and values of Cu pollution indices in silty soils, Table S3: Content of the forms and values of Cu pollution indices in sandy soils, Table S4: Content of the forms and values of Cu pollution indices in silty soils.

Author Contributions: Conceptualization, I.M.-P. and A.W.-K.; methodology, I.M.-P. and A.W.-K.; software, I.M.-P.; validation, I.M.-P. and A.W.-K.; formal analysis, I.M.-P.; investigation, I.M.-P. and A.W.-K.; resources, I.M.-P. and A.W.-K.; data curation, I.M.-P. and A.W.-K.; writing—original draft preparation, I.M.-P. and A.W.-K.; writing—review and editing, I.M.-P. and A.W.-K.; visualization,

I.M.-P.; supervision, I.M.-P.; project administration, I.M.-P.; funding acquisition, A.W.-K. Both authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request.

Acknowledgments: The authors gratefully acknowledge the support of Alicja Strzałka, Jerzy Michalczuk and Bernadetta Ortyl for help and willingness.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Burghardt, W.; Schneider, T. Bulk density and content, density and stock of carbon, nitrogen and heavy metals in vegetable patches and lawns of allotments gardens in the northwestern Ruhr area, Germany. *J. Soils Sediments* **2018**, *18*, 407–417. [CrossRef]
2. Leitão, E.; Cameira, M.R.; Costa, H.D.; Pacheco, J.M.; Henriques, M.J.; Martins, L.L.; Mourato, M.P. Environmental quality in urban allotment gardens: Atmospheric deposition, soil, water and vegetable assessment at Lisbon city. *Water Air Soil Pollut.* **2018**, *229*, 31. [CrossRef]
3. Morillo, E.; Romero, A.S.; Madrid, L.; Villaverde, J.; Maqueda, C. Characterization and sources of PAHs and potentially toxic metals in urban environments of Sevilla (Southern Spain). *Water Air Soil Pollut.* **2008**, *187*, 41–51. [CrossRef]
4. Charzyński, P.; Bednarek, R.; Hudańska, P.; Świtoniak, M. Issues related to classification of garden soils from the urban area of Toruń, Poland. *Soil Sci. Plant Nutr.* **2018**, *64*, 132–137. [CrossRef]
5. Alloway, B.J. Contamination of soils in domestic gardens and allotments: A brief overview. *Land Contam. Reclam.* **2004**, *12*, 179–187. [CrossRef]
6. Bechet, B.; Joimel, S.; Jean-Soro, L.; Hursthouse, A.; Agboola, A.; Leitão, T.E.; Costa, H.; Cameira, M.R.; Le Guern, C.; Schwartz, C.; et al. Spatial variability of trace elements in allotment gardens of four European cities: Assessments at city, garden, and plot scale. *J. Soils Sediments* **2018**, *18*, 391–406. [CrossRef]
7. Bretzel, F.; Calderisi, M.; Scatena, M.; Pini, R. Soil quality is key for planning and managing urban allotments intended for the sustainable production of home-consumption vegetables. *Environ. Sci. Pollut. Res.* **2016**, *23*, 17753–17760. [CrossRef]
8. Giusti, L. Heavy metals in urban soils of Bristol (UK). Initial screening for contaminated land. *J. Soils Sediments* **2011**, *11*, 1385–1398. [CrossRef]
9. Weissmannová, H.D.; Pavlovský, J. Indices of soil contamination by heavy metals—methodology of calculation for pollution assessment (minireview). *Environ. Monit. Assess.* **2017**, *189*, 616. [CrossRef]
10. Barbieri, M. The importance of enrichment factor (EF) and geoaccumulation index (Igeo) to evaluate the soil contamination. *J. Geol. Geophys.* **2016**, *5*, 237. [CrossRef]
11. Thomas, R.P.; Ure, A.M.; Davidson, C.M.; Littlejohn, D. Three stage sequential extraction Procedure for the determination of metals in river sediments. *Anal. Chem. Acta* **1994**, *286*, 423–429. [CrossRef]
12. Ure, A.M.; Quevauviller, P.H.; Muntau, H.; Griepink, B. Speciation of heavy metals in soils and sediments. An account of the improvement and harmonization of extraction techniques undertaken under the auspices of the BCR of the Commission of the European Communitie. *Int. J. Environ. Anal. Chem.* **1993**, *51*, 135–151.
13. Makuch-Pietraś, I.; Wójcikowska-Kapusta, A. Differences in the content of Zn fractions in the profiles of soils from allotment and domestic gardens in south-eastern Poland. *Land* **2021**, *10*, 886. [CrossRef]
14. Soil Science Society of Poland, Commission on Soil Genesis, Classification and Cartography. *Polish Soil Classification*; Wydawnictwo Uniwersytetu Przyrodniczego we Wrocławiu, Polskie Towarzystwo Gleboznawcze: Warszawa, Poland, 2019.
15. Polish Standard. *Soil and Mineral Soil Materials—Sampling and Determination of Particle Size Distribution*; PN-R-04032; Polish Committee for Standardization: Warszawa, Poland, 1998.
16. Ostrowska, A.; Gawlinski, S.; Szczubiałka, Z. *Methods of Analysis and Evaluation of Properties of Soils and Plants*; Institute of Environmental Protection: Warsaw, Poland, 1991.
17. Weissmannová, H.D.; Pavlovský, J.; Chovanec, P. Heavy metal contaminations of urban soils in Ostrava, Czech Republic: Assessment of metal pollution and using principal component analysis. *Int. J. Environ. Res.* **2015**, *9*, 683–696.
18. Kowalska, J.; Mazurek, R.; Gąsiorek, M.; Setlak, M.; Zaleski, T.; Waroszewski, J. Soil pollution indices conditioned by medieval metallurgical activity—A case study from Krakow (Poland). *Environ. Pollut.* **2016**, *218*, 1023–1036. [CrossRef]
19. Dąbkowska–Naskręt, H.; Kędzia, W. Mobilność miedzi w uprawnych czarnych ziemiach kujawskich. *Zesz Naukowe Komitetu Człowiek i Środowisko* **1996**, *14*, 51–56.
20. Bielicka-Giełdoń, A.; Ryłko, E.; Żamojć, K. Distribution, bioavailability and fractionation of metallic elements in allotment garden soils using the BCR sequential extraction procedure. *Pol. J. Environ. Stud.* **2013**, *22*, 1013–1021.
21. Nawozowe, Z.; Cz, I. *Liczby Graniczne do Wyceny Zawartości w Glebach Makro-i Mikroelementów*; Seria P(14); IUNG Puławy: Puławy, Poland, 1990.

22. Rozporządzenie Ministra Środowiska z Dnia 1 Września 2016 r. w Sprawie Sposobu Prowadzenia Oceny Zanieczyszczenia Powierzchni Ziemi. Available online: http://isap.sejm.gov.pl/isap.nsf/DocDetails.xsp?id=WDU20160001395 (accessed on 22 August 2021).
23. Kabata-Pendias, A.; Pendias, H. *Biogeochemistry of Trace Elements*; PWN: Warsaw, Poland, 1999.
24. Chojnicki, J.; Czarnowska, K. The changes of the contents of total and readily soluble phosphorus and Zn, Cu, Pb, Cd in agricultural soils under intensive cultivation. *Soil Sci. Ann.* **1993**, *44*, 99–111.
25. Czarnowska, K. Total content of heavy metals in parent rocks as reference background levels of soils. *Soil Sci. Ann.* **1996**, *47*, 43–50.
26. Czarnowska, K.; Gworek, B. Spatial distribution of heavy metals in soils and soil pH in Warsaw area. *Pol. Ecol. Stud.* **1983**, *9*, 85–95.
27. Grzebisz, W.; Cieśla, L.; Komisarek, J.; Potarzycki, J. Geochemical assessment of heavy metals pollution of urban soils. *Pol. J. Environ. Stud.* **2002**, *11*, 493.
28. Kabata–Pendias, A. Zawartość metali ciężkich w glebach uprawnych Polski. *Pamiętnik Puławski* **1981**, *74*, 101–111.
29. Klimowicz, Z.; Melke, J. The content of heavy metals in soils in the vicinity of traffic roads using chosen stretches of road as examples. *Soil Sci. Ann.* **2000**, *51*, 36–45.
30. Terelak, H.; Piotrowska, M.; Motowicka–Terelak, T.; Stuczyński, T.; Budzyńska, K. Zawartość metali ciężkich i siarki w glebach użytków rolnych Polski oraz ich zanieczyszczenie tymi składnikami. *Zeszyty Problemowe Postępów Nauk Rolniczych* **1995**, *418*, 45–59.
31. Terelak, H.; Tujaka, A.; Motowicka–Terelak, T. Trace element content (Cd, Cu, Ni, Pb, Zn) in farm—Land soils in Poland. *Arch. Ochr. Środ.* **2001**, *27*, 159–174.
32. Terelak, H.; Tujaka, A. Występowanie pierwiastków śladowych w glebach użytków rolnych województwa podkarpackiego. *Zeszyty Problemowe Postępów Nauk Rolniczych* **2003**, *493*, 245–252.
33. Terelak, H.; Tujaka, A.; Pietruch, C. Cooper in the surface layer of the farmland soils in Poland. *Pol. J. Soil Sci.* **2003**, *36*, 137–143.
34. Hursthouse, A.; Tognarelli, D.; Tucker, P.; Marsan, F.A.; Martini, C.; Madrid, L.; Madrid, F.; Diaz-Barrientos, E. Metal content of surface soils in parks and allotments from three European cities: Initial pilot study results. *Land Contam. Reclam.* **2004**, *12*, 189–196. [CrossRef]
35. Gorlach, E.; Brydak, K.; Gambuś, F. Distribution of heavy metals in soil profiles of the Cracow region. *Pol. J. Soil Sci.* **1993**, *26*, 97–104.
36. Bretzel, F.; Calderisi, M. Metal contamination in urban soils of coastal Tuscany (Italy). *Environ. Monit. Assess.* **2006**, *118*, 319–335. [CrossRef]
37. Davidson, C.M.; Urquhart, G.J.; Ajmone–Marsan, F.; Biasioli, M.; Costa Duarte, A.; Diaz–Barrientos, E.; Grčman, H.; Hossack, I.; Hursthouse, A.; Madrid, L.; et al. Fractionation of potentially toxic elements in urban soils from five European cities by means of a harmonised sequential procedure. *Anal. Chim. Acta* **2006**, *565*, 63–72. [CrossRef]
38. Imperato, M.; Adamo, P.; Naimo, D.; Arienzo, M.; Stanzione, D.; Violante, P. Spatial distribution of heavy metals in urban soils of Naples city (Italy). *Environ. Pollut.* **2003**, *124*, 247–256. [CrossRef]
39. Römkens, P.; Salomons, W. Cd, Cu and Zn solubility in arable and forest soils: Consequences of land use changes for metal mobility and risk assessment. *Soil Sci.* **1998**, *163*, 859–871. [CrossRef]
40. Kabała, C.; Chodak, T.; Szerszeń, L.; Karczewska, A.; Szopka, K.; Fratczak, U. Factors influencing the concentration of heavy metals in soils of allotment gardens in the city of Wrocław. *Fresenius Environ. Bull.* **2009**, *18*, 622–630.
41. Ciupa, T.; Suligowski, R.; Kozłowski, R. Trace metals in surface soils under different land uses in Kielce city, south-central Poland. *Environ. Earth Sci.* **2020**, *79*, 14. [CrossRef]
42. Świercz, A.; Smorzewska, E. Variations in the zinc and lead content in surface layers of urban soils in Kielce (Poland) with regard to land use. *J. Elem.* **2015**, *20*, 449–461.
43. Świercz, A.; Zajęcka, E. Accumulation of heavy metals in the urban soils of the city of Skarżysko-Kamienna (Poland) with regard to land use. *Carpath. J. Earth Environ.* **2018**, *13*, 249–266. [CrossRef]
44. Moćko, A.; Wacławek, W. Three-step extraction procedure for determination of heavy metals availability to vegetables. *Anal. Bioanal. Chem.* **2004**, *380*, 813–817. [CrossRef]
45. Chao, W.; Xiao–Chen, L.; Li–Min, Z.; Pei–Fang, W.; Zhi–Yong, G. Pb, Cu, Zn and Ni concentration in vegetables in relation to their extractable fractions in soils in suburban areas of Nanjing, China. *Pol. J. Environ. Stud.* **2007**, *16*, 199–207.
46. Kaasalainen, M.; Yli-Halla, M. Use of sequential extraction to assess metal partitioning in soils. *Environ. Pollut.* **2003**, *126*, 225–233. [CrossRef]
47. Dąbkowska-Naskręt, H.; Różański, S.; Bartkowiak, A. Forms and mobility of trace elements in soils of park areas from the city of Bydgoszcz, north Poland. *Soil Sci. Ann.* **2016**, *67*, 73–78. [CrossRef]