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Differences in the Content of Zn Fractions in the Profiles of Soils from Allotment and Domestic Gardens in South-Eastern Poland

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Abstract: The aim of the research was to show the distribution of fractions as well as bioavailability and the total forms of Zn in the profiles of soils from domestic gardens and family allotment gardens in six cities in south-eastern Poland. Results found that the level of Zn total form varied in the ranges from A horizon: 12.75–154.75 mg·kg^{-1} in sandy soils and 18.20–104.00 mg·kg^{-1} in silty soils. Accumulation of metals was assessed using concentration indices, Igeo, and the C_{av}/C_t and BF indices of bioavailable forms. The analysis took into account the role of organic matter as an important component in binding the analyzed metals in soil horizons subjected to long-term horticultural cultivation. In the two groups of sandy and silty soils distinguished according to their particle size distribution, horticultural treatments were found to exert a greater impact on sandy soils. Additionally, higher contents of the examined element were stated in the humus horizons, as indicated by the high values of concentration and Igeo indices showing high Zn pollution in the soils. The content of bioavailable zinc forms was significantly high, especially in soils with a higher metal content.

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

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1. Introduction

Allotment gardens are one of the most interesting types of urban greenery, along with domestic gardens, which serve similar functions in detached housing estates. In addition to their recreational function, they give owners the opportunity to grow their own vegetables and fruit [1,2]. Large-scale multi-year investigations have proved heavy metal pollution as a problem that may affect these areas due to their location within city limits. However, most studies mainly focus on large cities or centers located in highly industrialized areas [3–9] where soils are actually contaminated with heavy metals. In the case of smaller cities or located in less industrialized areas, it is difficult to find items describing a case study. This is an indication to analyze the soils of allotment gardens in terms of heavy metal content in areas with less urbanization pressure than agglomerations. The problem was also found in south-eastern Poland, which represented mostly the agricultural area.

Additionally, attention should be paid to the specific properties, structure, and long-term use of gardens, which contribute to the transition of natural soils into anthropogenically transformed ones characteristic of a long-cultivated hortisol horizon [10]. The effects of such changes include increased organic matter content, changes in the sorption complex, and an improved soil pH value [11]. Due to the high impact of urban and industrial pollution, the topsoil may contain higher metal concentrations [2,11–14]. The distribution of metals in the profile may vary depending on its structure. An important role in the metal distribution is played by the well-developed deeper humus horizon with a large amount of organic matter and a more extensive sorption complex. Another differentiating property is the particle size distribution of the soil. Based on the above information, as well as the huge popularity of both home and allotment gardens, the experiment for the article was developed. An important aspect of this experiment is the separation of two groups based on soil composition.

To show differences between soil types and divergences in their organic matter content, not only the total content but also metal fractions are worth determining, using an appropriate sequential extraction such as BCR. Furthermore, simple methods based on widely used indices of contaminant concentrations and soil pollution can help to demonstrate the differences between the anthropogenic and natural sources of elements [15], which is extremely important for garden owners producing vegetables intended for consumption [16].

The aspects discussed above became a reason to try to consider the problem of heavy metals content in one work, which is a new contribution to the literature on the subject.

For proper assessment of the contamination risks associated with the horticultural use of urban soils in cities of south-eastern Poland, the following research objectives were formulated: (i) estimation of Zn content in soils from urban gardens, in comparison with soils from arable fields located outside city limits, using various contamination indices, (ii) estimation of bioavailable forms through fractionation of metals and determination of bioavailable forms, by means of the Rinkis method, (iii) determination of the distribution of trace elements in the soil profile, with particular emphasis on organic matter-bound forms, by means of the sequential extraction BCR procedure [17,18].

2. Materials and Methods

2.1. Study Site

The research was conducted in the south-east of Poland. The general climatic conditions are characterized by an average temperature of around 9 °C and precipitation of 600 mm [19]. There are some differences between cities in terms of physiography and geology. Biała Podlaska is situated on the Łuków Plain, which is a flat, sandy area in the outflow zone of the glacial-river waters of the Warcia glaciation. Lubartów is located in the region of Lubartów Heights. This area is a denuded moraine surface with gravel inselbergs. Tarnobrzeg is a city located in the Vistula Lowland, which is part of the Sandomierz Basin. The valley is filled with quaternary river sediments with a thickness of several meters. Next to the flood terrace, there is a higher sandy terrace and a terrace covered with loess. Lublin is located on the Świdnik Plateau, which is part of the Lublin Upland. It is built of a thick series of loess resting on the upper cretaceous layers, degraded moraine, glaciofluvial sands, and gravels. Przemyśl is part of the Przemyśl Foothills, which is the outer part of the Carpathian Mountains, built of East-Carpathian flysch. Zamość lies in the Zamość Basin area, which is an extensive denudation depression, formed in less resistant upper cretaceous marls and chalk [20].

2.2. Sampling Site

Six cities (Figure 1) located in south-eastern Poland were selected for the study. A survey was conducted to find appropriate study sites in each town. The survey enabled 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. Both the allotments and domestic gardens were selected based on an interview with owners with at least 20-years of horticultural activity in the selected criterion. A similar criterion was used for the crop field. An important element in the choice of the gardens was the mode of horticultural cultivation, that is, the use of only organic fertilizers, often produced by the owner, representing high crop culture. The crop field was selected after an interview with the owner, whose arable land was subjected to extensive cultivation by crop rotation. Moreover, the arable field was located outside the city, with no high-traffic transportation routes nearby. Potential heavy metal contamination was a criterion for the selection of the cities. The south-east of Poland is mainly an agricultural region, with a poorly developed industrial infrastructure.

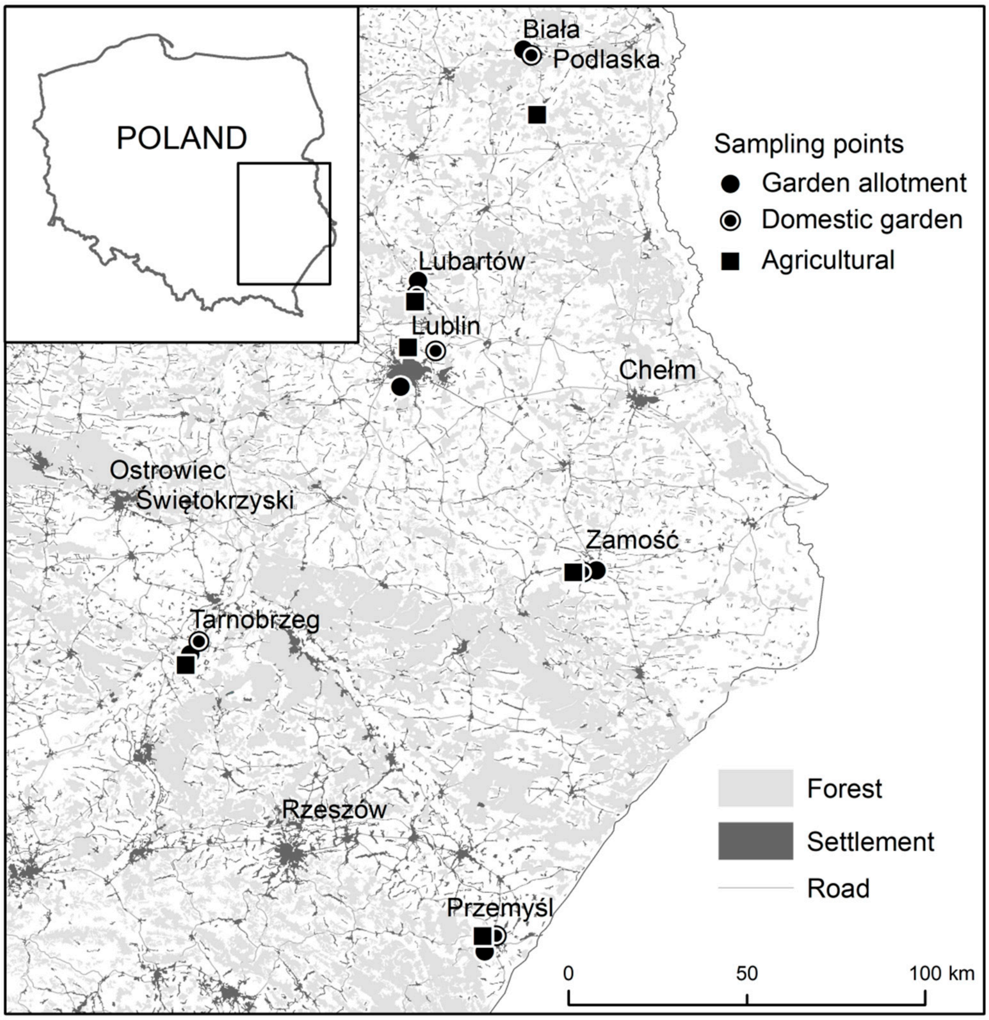

Figure 1. Map of sampling in the study area.

Two groups of soils were distinguished according to the particle size distribution from six cities. One group comprised sandy soils group of light soils. These sand and loamy sand soils were sampled in Biała Podlaska, Lubartów, and Tarnobrzeg (Table S1). The second group was represented by soils from the group of medium soils, made from silt, mostly with the particle size distribution of silt loam, sampled in Lublin, Przemyśl, and Zamość (Table S2). The light sandy soils sampled from the analyzed cities represent podzolic, brunic, and gleying types, whereas the medium silty soils are luvisols [21]. Soil classification and properties are presented in Supporting Materials.

2.3. Soil Sampling and Basic Soil Properties

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

Basic physicochemical properties were determined in the soil material. The particle size distribution was determined by means of the Bouyoucos and Casagrande areometric method, modified by Prószyński. Soil fractions and formations were identified according to PTGleb. [22]. Soil pH was determined potentiometrically in water and in a 1 M KCl solution. The content of organic matter was measured using the Tiurin method and the total nitrogen content was determined by the Kjeldahl method. The sorption capacity of the soils was calculated as CEC extracted with ammonium acetate at pH = 7.0, and the hydrolytic acidity was determined by the Kappen method [23]. All samples were analyzed in triplicate, and the final content was always considered as the average value of three measurements made in repeatability conditions.

2.4. Heavy Metal Determination and Sequential Extraction Procedure

The total copper and zinc content in the soil samples was determined by extraction using a mixture of concentrated acids (nitric and perchloric acid 1:1). To demonstrate the relationship between zinc contents and organic matter in the soils subjected to intensive horticultural use, the sequential extraction procedure proposed by BCR [17,18] was applied and the content of four fractions was determined. The scheme of the procedure is presented in Table 1. Additionally, to assess the potential bioavailability of zinc, bioavailable forms of this element were determined by the Rinkis method in 0.1 M HCl [23]. All forms of the element were determined by the ICP-AES method, using Leeman PS 950 apparatus. Digestion was performed in the DKL 20 Fully Automatic Digestion Unit (VELP SCIENTIFICA). The reagents used in the analyses were analytically pure, and the water was deionized. 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, NJ, 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		Extracion 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	$HNO_3 + HClO_4$

2.5. Indices of Pollution

Based on the results, the indices of the distribution and concentration of zinc in the analyzed soils were calculated [15,24]:

$$C_f = \frac{Cs}{Cn} \tag{1}$$

C_s—concentration of the heavy metal;

C_n—background level of heavy metal.

The geoacumulation index (Igeo) was calculated from the total content of heavy metal determined in the profile horizons in relation to the parent material, using the following formula [25]:

$$I_{geo} = \log_2 \left[\frac{C}{1.5\ B} \right] \tag{2}$$

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 Zn forms to the total content of these elements was calculated [26].

$$(C_{av}/C_t)\cdot 100 \quad (3)$$

C_{av}—content of the bioavailable form of the element;
C_t—total content of the element.
Based on the results of the sequential extraction procedure, the BF value was calculated using the following formula [27]:

$$BF = (C_{bio}\cdot 100)/C_{total} \quad (4)$$

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.

2.6. Statistical Analysis

For the topsoil levels, statistical analyses were carried out to check whether the grouping variables, that is, particle size distribution and land use, discriminate between the properties and parameters of the soils. To assess the effect of soil properties on the content and forms of heavy metal, Pearson's correlation coefficients between selected data were calculated. The results were analyzed in the Statistica 13.3 program at a significance level of $\alpha \leq 0.05$. Additionally, principal component analysis was performed using Canoco 5 software.

3. Results

3.1. Basic Soil Properties

The mode of land use in relation to the light soils was a crucial determinant of such properties as pH, sorption capacity with its components, or organic carbon content. The physicochemical properties of the humus horizons were more favorable in the horticultural samples, compared to the arable soil samples; however, no such relationships were found in the medium soils (Tables S1 and S2).

3.2. Zn Content

3.2.1. Total Zn Content

All topsoil layers of the sandy soils exhibited a higher total zinc level than their parent material, indicating a potential impact of the location and land use. The highest content was determined in the soil from the domestic garden in Biała Podlaska and from both types of gardens in Tarnobrzeg (Table S3).

Regardless of the mode of land use, all medium soils were characterized by higher total zinc contents in the humus horizons, compared to that in the parent material. In some study sites, substantially higher Zn accumulation was observed in the surface layer of the allotment soil in Przemyśl and in the soil from the domestic garden and arable field in Zamość (Table S4). With regard to the study sites with the sandy soils, the distribution of the zinc content in their profiles was more variable and the profiles differed from each other, but no specific pattern was observed (Tables S3 and S4).

3.2.2. Bioavailable Zn Forms

The humus horizons in the sandy soils sampled from the domestic gardens were characterized by high amounts of zinc soluble in 1 mol $HCl\cdot dm^{-3}$, with the highest content, that is, 114.5 and 115.2 $mg\cdot kg^{-1}$, determined in the soil from the domestic garden in Biała Podlaska. In terms of the threshold values, the humus horizons of the sandy soils were characterized by high zinc content, with the exception of the arable field soil in Biała Podlaska. In the group of medium soils, high zinc contents were detected in the domestic garden soil in Przemyśl as well as the allotment garden and arable field soil in Zamość. The other soils exhibited a moderate abundance of this component [28]. The content of bioavailable zinc declined with the profile depth in all soils. In terms of the mode of land use, the profiles of the horticultural soils were characterized by a higher level of this element (Table S3).

In the case of the silty soils, the highest content of zinc soluble in 1 mol HCl·dm^{-3} was exhibited by the humus horizons in the garden soils, and the values decreased proportionally to the profile depth. In turn, the humus horizons of the arable field soils contained substantially lower contents of bioavailable Zn, likewise the other genetic horizons in the profiles (Table S4).

3.2.3. Indices of Pollution

Regardless of the mode of land use, the values of the tested zinc C_f index ranged from 0.63 to 17.34 in the sandy soils. A substantial decrease in the index value was noticed in the case of the garden soil profiles, whereas smaller differences between these values were found for the agricultural soils (Table S3).

The silty soil profiles differed substantially in the values of the zinc concentration index, depending on the mode of land use. The highest values of this indicator were found in the soil profiles from the domestic gardens (0.62–11.30), whereas the allotment soil samples were characterized by its lowest values (0.48–2.45). The zinc concentration index in the arable soils ranged from 0.80 to 4.00, and its value decreased with depth (Table S4).

High Igeo values for zinc in the light soils were calculated only in the case of the topsoil layers, especially in the domestic garden in Biała Podlaska (the highest value: 3.53), which indicates high pollution of the soils. The values in the other soils ranged between 0.00 and 0.80 and classified them as unpolluted (Table S3).

In the group of the silty soils, high values of the Igeo index were obtained in the case of the domestic garden soil from Zamość (1.39–2.91) classified as moderately polluted and in the Ap horizon of the arable soil (1.42) representing the same pollution class. The other profiles exhibited index values in the range from 0.00 to 0.90 and represented the unpolluted soil class (Table S4).

The humus horizons of the silty garden soils exhibited the highest values of the ratio of the bioavailable zinc form to its total content (over 60), whereas lower values were reported for the Ap horizons of the arable soil (up to 40). Regardless of the mode of land use, the solubility of zinc declined with depth (Table S3).

The Ap horizons of the silty soils were characterized by high values of the ratio of the bioavailable zinc form to the total content (even above 100 in the domestic garden in Lublin). Zinc solubility decreased with depth in a majority of the soil profiles (Table S4).

The BF index in the group of light soils was lower in the arable soils. In most profiles, it decreased with depth, which proves the accumulation of bioavailable forms in the topsoil horizons and indicates an important role that may be played by humus in garden soils (Table S3). No such tendencies were found for the silty soils. The BF index values were similar in the entire profile and slightly higher in the case of the garden soils (Table S4).

3.2.4. Sequential Extraction of Zn

The content of water-soluble and exchangeable zinc fraction I in the sandy soils was in the range of 0.96–32.11 mg·kg^{-1} (Table S3). The fraction is important due to its bioavailability; hence, humus horizons should contain its optimal amounts. The topsoil horizons of the garden soils were characterized by greater amounts of this fraction in comparison with the top layers of the arable soils. The soils from the domestic garden in Biała Podlaska exhibited the highest content of this fraction. The content of exchangeable and water-soluble zinc declined in soil samples from sites subjected to both modes of land use (Figure 2, Table S3).

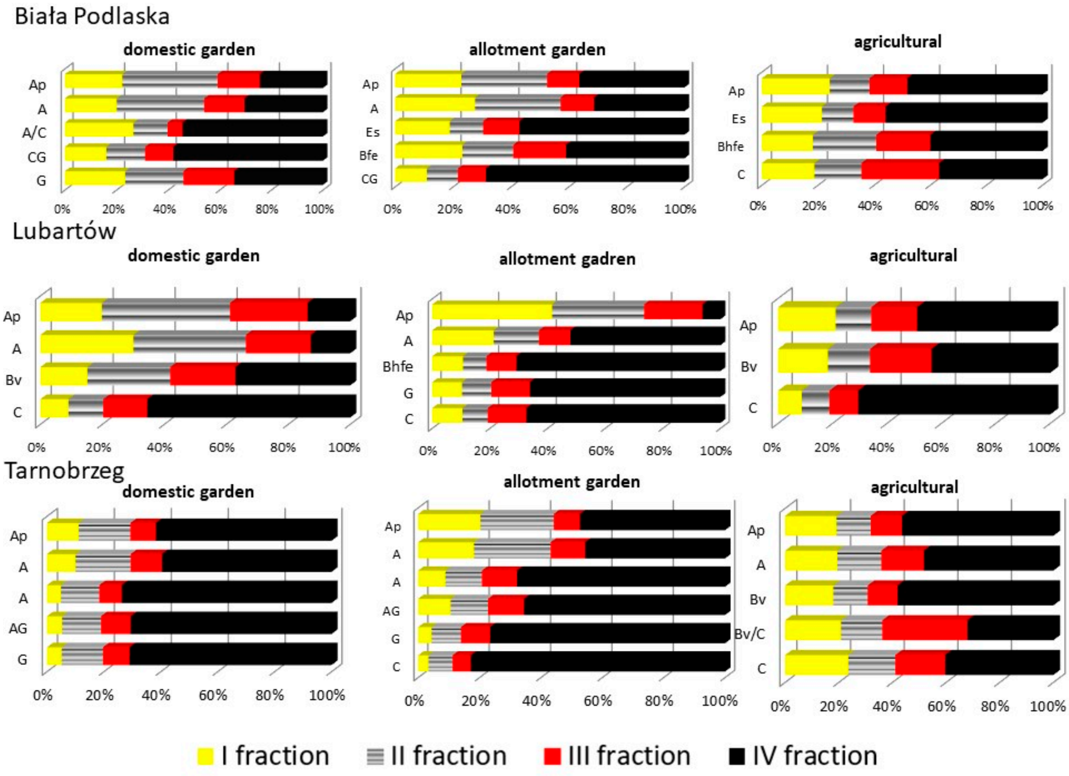

Figure 2. Percentage content of Zn fractions in sandy soils.

The percentage proportion of the zinc fraction bound to iron and manganese oxides in the light soils ranged from 7.85 to 41.38% of the total content (Figure 2), which was in the range of 1.09–53.24 mg·kg^{-1} (Table S3). In the group of garden soils, the humus horizons from the domestic garden in Biała Podlaska had the highest levels of this form of zinc, and this trend was also observed in the other profiles of the garden soils. The topsoil layers in the arable soils exhibited lower contents of zinc fraction II (Figure 2, Table S3).

The content of Zn fraction III in the sandy soils ranged from 1.44 to 24.06 mg·kg^{-1} (Table S3), which accounted for 5.69–27.67% of the total content (Figure 2). The humus-associated fraction is the best indicator in sequential extraction, showing the relationship between heavy metal contamination and high organic matter content. The humus horizons in the garden soil profiles exhibited a higher level of humus-associated zinc fraction III than the deeper horizons. As in the case of the fractions discussed above, the highest content was determined in the humus horizons of the domestic garden soil from Biała Podlaska. The arable soils contained substantially smaller amounts of this Zn fraction; however, there was a similar trend as in the case of the horticultural soil (Figure 2, Table S3).

The content of residual fraction IV in the light soils was in the range of 1.17–47.04 mg·kg^{-1} (Table S3), with the percentage proportion in the total content varying in a wide range of 6.21–82.82% (Figure 2). The residual fraction in the humus horizons of the garden soils represented a lower percentage than the other fractions, especially in two study sites, that is, Biała Podlaska and Tarnobrzeg, probably due to the greater proportion of the humus-associated fraction. In comparison with the humus horizon, the parent material exhibited a greater proportion of the residual Zn fraction, except for the arable soils sampled in Biała Podlaska and Tarnobrzeg (Figure 2). The content of fraction IV in most profiles declined with depth (Table S3).

The percentage proportion of zinc fraction I in the total content in the silty soils ranged from 0.62 to 27.22% (Figure 3) and its content was in the range of 0.33–5.95 mg·kg^{-1} (Table S4). The content of this zinc fraction decreased with depth in the soils from both types of land use. The mode of land use did not have a clear effect on the content of this fraction (Figure 3, Table S4).

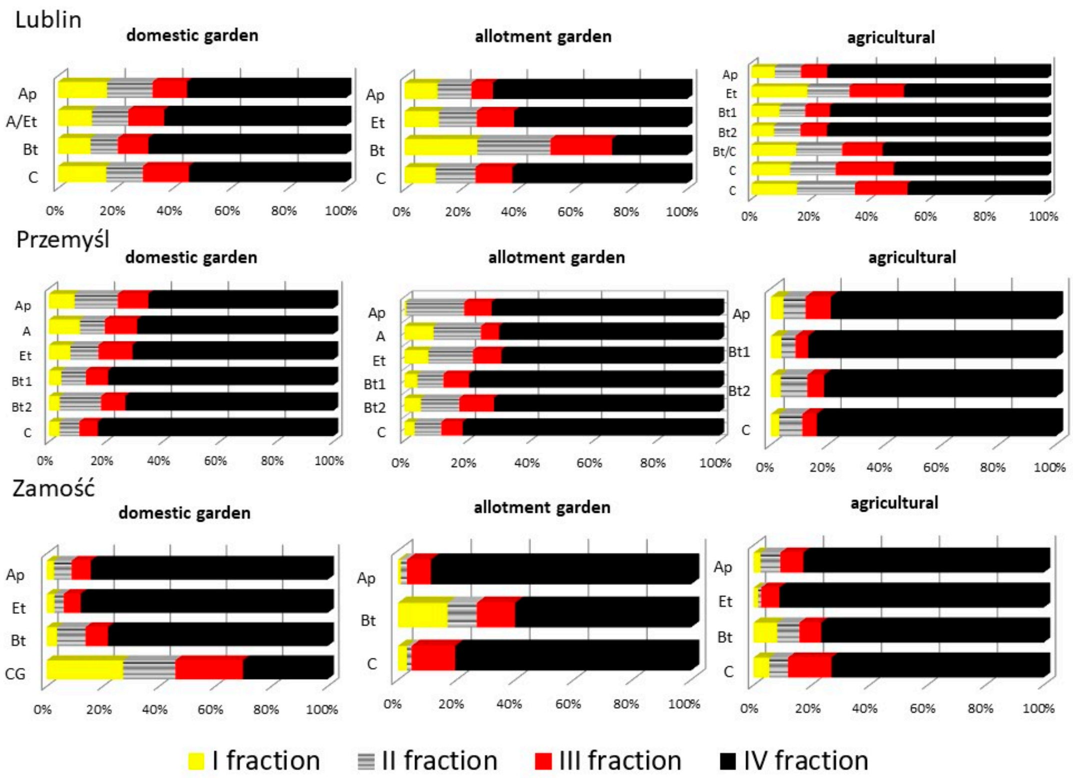

Figure 3. Percentage content of Zn fractions in silty soils.

The percentage of zinc fraction II bound to iron and manganese oxides ranged from 1.57 to 25.94% in the garden soils from 1.03 to 19.64% in the agricultural soils (Figure 3). Its content was in the range of 0.29–11.02 mg·kg^{-1} (Table S4). In both types of land use, the content of the zinc fraction bound to iron and manganese oxides in the silty soil profiles was found to vary and was mainly determined by the soil formation process (Table S4).

Regardless of the land use, the content of zinc fraction III was in the range of 1.54–7.05 mg·kg^{-1} (Table S4), which represented from 4.41% to 24.04% (Figure 3). In contrast to the light soils, the content of this fraction in the humus horizons was not substantially higher than that in the other genetic horizons. There was also no effect of the mode of land use on the content of the humus-bound fraction in the analyzed soils (Table S4).

In the medium soils, the content of the residual zinc fraction in the humus horizons was similar and higher than in the deeper horizons, regardless of the mode of land use. As in the case of the total zinc content, the humus horizon in the domestic garden soil in Zamość contained the highest amounts of the residual form of this element (Table S4). Regardless of the type of land use, the level of this fraction was in the range of 1.97–87.68 mg·kg^{-1} (Table S4). The percentage proportion of residual zinc in the total content was slightly higher in the arable soils (47.31–91.09%) than in the garden soils (30.14–88.84%) (Figure 3).

3.3. Statistical Analysis

In the sandy soils, the organic carbon content was significantly correlated with the zinc content indices: C_f (r = 0.860 at $p < 0.01$), C_a/C_t (r = 0.689 at $p < 0.05$), and Igeo (r = 0.890 at $p < 0.01$). It was also correlated with the total Zn content, bioavailable forms, and fraction II of this element. Significant correlations were also found for the total content and bioavailable form with C_f (r = 0.934 and 0.965 at $p < 0.001$) and Igeo (r = 0.915 and 0.954 at $p < 0.001$). There was also a statistically significant correlation between the total content and the bioavailable zinc form (r = 0.982 at $p < 0.001$) and between fraction II and pH measured in water (r = 0.669 at $p < 0.05$) (Table 2).

Table 2. Values of Pearson's correlation coefficients of zinc forms and indices with the physicochemical properties of sandy soils.

Properties of Studied Soil	Zn Total	Zn Avail.	pH H_2O	pH KCl	Crop	<0.002
Zn total	1.000	0.982 *	0.616	0.627	0.879 **	0.009
C_f	0.934 *	0.965 *	0.381	0.370	0.860 **	−0.259
Zn available	0.982 *	1.000	0.599	0.595	0.929 *	−0.111
C_a/C_t	0.385	0.509	0.644	0.595	0.689 ***	−0.189
Igeo	0.915 *	0.954 *	0.389	0.392	0.890 **	−0.292
I fraction	−0.226	−0.081	−0.121	−0.206	−0.029	−0.551
II fraction	0.470	0.582	0.669 ***	0.647	0.784 ***	−0.196
III fraction	−0.035	0.111	−0.070	−0.114	0.241	−0.197
IV fraction	−0.158	−0.323	−0.304	−0.243	−0.494	0.395
BF	0.158	0.323	0.304	0.243	0.494	−0.395

Significance level: *—0.001; **—0.01; ***—0.05.

In comparison to the sandy soils, the organic matter content in the medium soils had no significant effect on the content of zinc, although the total and bioavailable forms exhibited a positive correlation (r = 0.825 at $p < 0.01$ and r = 0.741 at $p < 0.05$, respectively). Additionally, these forms were characterized by a significantly high coefficient of correlations with each other (r = 0.942 at $p < 0.001$) and with C_f (r = 0.909 and 0.962, respectively at $p < 0.001$) and Igeo (r = 0.886 at $p < 0$ 01 and 0.915 at $p < 0.001$). The correlation analysis revealed only one statistically significant correlation between the silt fraction content and C_a/C_t (r = 0.855 at $p < 0.01$) (Table 3).

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

Properties of Studied Soil	Zn Total	Zn Avail.	pH H_2O	pH KCl	Crop	<0.002
Zn total	1.000	0.942 *	0.206	0.197	0.825 **	−0.135
C_f	0.909 *	0.962 *	0.287	0.272	0.638	−0.356
Zn available	0.942 *	1.000	0.190	0.233	0.741 ***	−0.422
C_a/C_t	0.377	0.648	−0.102	0.094	0.285	−0.855 **
Igeo	0.886 **	0.915 *	0.305	0.334	0.636	−0.328
I fraction	−0.611	−0.352	−0.218	−0.152	−0.539	−0.577
II fraction	−0.220	−0.132	−0.334	−0.098	0.042	−0.480
III fraction	−0.616	−0.521	−0.713 *	−0.613	−0.386	−0.302
IV fraction	0.525	0.330	0.391	0.222	0.320	0.592
BF	−0.525	−0.330	−0.391	−0.222	−0.320	−0.592

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

The PCA results for the parameters of soil Zn are presented in Table 4 and Figure 4. The first component, which explains 34.90% of the total variance, clearly discriminated most of the parameters of soil physicochemical properties and zinc content. Moreover, the content of total zinc and its bioavailable form, the C_f and C_a/C_t indices, and the Corg content were discriminated by the second component, although to a lesser extent. These variables are located close to each other and have the same direction, which indicates their positive and strong correlation. Among the analyzed forms of zinc, residual fraction IV exhibited an opposite direction and sense of the vector, which indicated a negative correlation with the other parameters and a low effect of the physicochemical properties on this form of the element. The BF index expressing the mobility of Zn forms was positively correlated with fractions I and II, which were characterized by the highest bioavailability in soil. In turn, fraction III was negatively correlated with these parameters and positively correlated with the reaction and content of the silt fraction, which allows the conclusion that it is dependent on these parameters. The analyzed soil types form two groups: the medium soils are located closer to the first principal component, while the light soils are more closely related to the second principal component. In the sandy soils, there is a lesser effect of the components on the agricultural land use, which forms a group located closer to the axis of the second variable axis. No similar relationships were found in the case of the silty soils.

Table 4. Summary of the Zn results in PCA.

Statistic	Axis 1	Axis 2	Axis 3	Axis 4
Eigenvalues	0.3490	0.3196	0.0977	0.0942
Explained variation (cumulative)	34.90	66.86	76.63	86.05

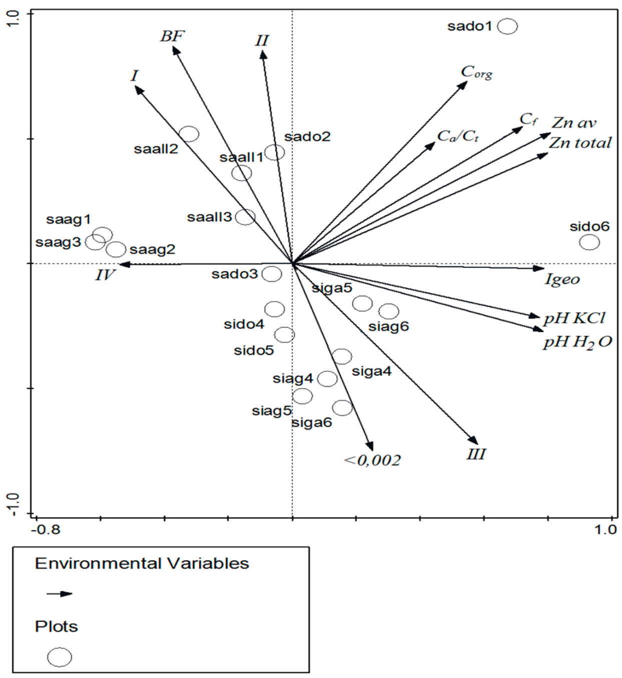

Figure 4. Principal component analysis (PCA) of two indices for the zinc content and parameters.

4. Discussion

As indicated by literature reports on the problem of soil contamination with heavy metals in gardens, it is generally believed that such sites are contaminated by substances from neighboring houses, roads, and urban or industrial areas [11]. As shown by the author, zinc is one of the most common contaminants, and their form present in soils is influenced by, for example, soil physicochemical properties such as pH, organic matter content, calcium carbonate, and silt fraction. Moreover, it is worth emphasizing that horticultural soils may exhibit higher contents of organic matter than arable soils, which promotes the migration of heavy metals [11].

Pollution assessment has been carried out in the humus horizons of the sandy and silty soils which were characterized with natural zinc contents (except for the domestic garden in Biała Podlaska and the domestic garden in Zamość) [29,30]. This differentiation indicates the possibility of local changes in the accumulation of heavy metals.

The total zinc content decreased with the profile depth in all light and silty soils. This differentiation indicates the possibility of local changes in the accumulation of heavy metals by Gorlach et al. [31] Kabata-Pendias [32], and Kawałko and Chodak [33]. This tendency was reflected in the high zinc concentration indices in the topsoil layers. As suggested by Świercz and Smorzewska [34], high values of this index may be related to many anthropogenic factors and geological backgrounds. In the case of soils located in the area of the influence of the city, the anthropogenic factor becomes very significant. The second used index was Igeo which was characterized by quite high values in the humus horizons and similar results were reported by Ciupa et al. [35], Świercz and Smorzewska [34], and Świercz and Zajęcka [36]. This has been a confirmation of the concentration ratio used earlier. In the case of soils where horticulture is used, land use may be an additional factor influencing the Zn content. In terms of the mode of land use, the zinc content was higher in the horticultural than agricultural soils only in the group of the sandy soils. These results were in agreement with those reported by Kelly and Thornton [37], who found accumulation of this element in intensively cultivated soils. Similar conclusions were formed by Kabała et al. [38], who compared soils from horticultural and agricultural land use. Additionally, the zinc content was positively correlated with organic matter, which was also demonstrated by many authors [1,39–46]. From the literature on the problem of heavy metals in garden soils, it is difficult to find items describing the differences between types, or mechanical groups. Whereas in the arable soils, were stated substantial differences in the total zinc content between the soil types. This was also confirmed by many authors in their analyses of the content of this element in various cultivated soils [32,39,42,46–51].

An interesting aspect of the work is the sequential analysis, showing the diversity of forms associated with the organic substance, as well as mobile fractions, which result from a greater accumulation of Zn. The surface horizon of the soils made of sands was characterized by a higher content of mobile fractions, although the fraction associated with the organic substance was lower. The residual fraction dominated in the surface horizons of soils made of silt, regardless of the way of use. Attention was drawn to the distribution of fractions in the deeper levels of the profile, which reflected the natural soil formation process. These results are supported by many literature positions. Similarly, Moćko and Wacławek [52] reported the dominance of the residual zinc fraction and the organic matter-bound fraction in garden soils from Opole, whereas mobile fractions II and I represented the lowest proportion. In China, soils where vegetables were grown exhibited the dominance of the organic matter-bound fraction, whereas the proportion of the exchangeable and residual fractions was highly variable. The content of mobile fractions (I and II) may vary depending on the conditions prevailing in soils [53]. In arable soils, Herencia et al. [54] showed constant amounts of the residual fraction in different fertilization systems. After the application of compost, the sum of fractions I, II, and III and the amount of the organic matter-bound fraction were found to increase. These results prove the high affinity of zinc for the organic carbon content. Industries may be another determinant of the content of mobile zinc fractions, as confirmed by Kaasalainen and Yli-Halla [55] in their investigations of arable soils of Finland. In the case of soils of south-eastern Poland, it could be stated that the lowest proportion of the Zn fractions, especially fractions I and II, in the analyzed soils may be associated with the limited impact of the industry-related factor. In turn, the aspect of the urbanization impact should be emphasized. As reported by Imperato et al. [56], urban soils were characterized by a smaller share of individual fractions in the total zinc content. The organic fraction was the smallest of all mobile fractions, compared to the residual fraction. As reported by other researchers, urban soils were characterized by the highest amounts of mobile fractions in contrast to arable and garden soils [57,58].

Similar conclusions were formulated by Dąbkowska-Naskręt et al. [59] in their study of urban soils from city parks, which were characterized by the highly variable mobility of Zn. The BF index is a very interesting example of reflecting the mobility of heavy metals. The BF index reported by Bielicka-Giełdoń et al. [27] had a value of 50–70% and was more comparable with the light soils, where it reached as high as 90% in the topsoil layer. The bioavailability of zinc in the analyzed medium soils significantly decreased and was below 40% also in the humus horizons. This indicates strong dependence of zinc mobility on the mineral part of soils.

5. Conclusions

Based on research, it was found that the vast majority of the analyzed soils had natural zinc levels. Sites selected for the study were cities with a potentially lower degree of urban pressure, however, at several research points, there was an increased content of the investigated metal.

Moreover, the accumulation of zinc in profiles was reflected by the concentration index, which was higher in the humus horizons, which indicates the influence of the land use combined with the location of the researched sites, which was confirmed by the higher total content in garden soils than in cultivated soils. Moreover, the concentration indices were higher in the sandy than silty soils. The Igeo index was similar, which exhibited quite high values in the humus horizons, and in some points classified the soil as even highly polluted in some study sites (Biała Podlaska—domestic garden; Zamość—domestic garden and arable field), which was confirmed by the comparison of the total content with permissible soil contamination with heavy metals. Based on the above information, it can be concluded that the location of the soil had an important role, and the humus level developed during horticulture may contribute to the accumulation of heavy metals.

To show the connection of soil organic matter formed by the horticulture with Zn content, the sequential extraction was used to distinguished fractions with the best bioavailability, through fractions accumulated in humus, to the residual fraction. The residual fraction of Zn dominated in both soil groups. The horticultural use effect of the soil was associated with greater accumulation of zinc in the humus horizons, in particular in the light soils, which was confirmed by the statistically significant correlations with the organic carbon content.

Generally, the availability of zinc determined on the basis of the BF index was highly influenced by the particle size distribution, especially in the case of light soils, where the BF values were higher in the humus horizons. This allows a conclusion that horticultural production in urban areas requires more attention in the case of sandy soils, as they may contribute to further migration of heavy metals.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/land10090886/s1, Table S1: Basic physicochemical properties of sandy soils, Table S2: Basic physicochemical properties of silty soils, Table S3: Content of the forms and values of Zn pollution indices in sandy soils, Table S4: Content of the forms and values of Zn pollution indices in silty soils.

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