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Accumulation of Heavy Metal Ions from Urban Soil in Spontaneous Flora

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Abstract: This study aimed to analyse the bioaccumulation of heavy metal ions in plants of spontaneous flora. An urban area was established from which soil samples were taken and analyses were performed on the content of heavy metal ions. The soil samples were collected from Iasi's urban area to determine the heavy metal concentrations, obtain maps of sensitive land, and determine the content of heavy metals in spontaneous flora and transfer these into an aqueous extract. The investigation of heavy metal ion levels in certain plants revealed the following: (i) all plants from the *Brassicaceae* accumulate heavy metals, and *B. juncea* has a great ability to accumulate and transfer Cu, Cr(VI), Cd, Ni, Pb, and Zn towards the shoots; (ii) heavy metals (Fe, Cu, Cr, Mn, Zn) were present in variable concentrations, with mint and nettle being notable for their increased level of iron and thyme, and rattle for its zinc levels; (iii) toxic metals (Pb, Cd, Ni) are present in low concentrations in plants as well as in infusions, except for in primula and plantain, which do not have high levels of Pb and Cd. The results showed that values exceeded the maximum recommended values in areas with industrial pollution. Taking into account the potential for the bioaccumulation of heavy metal ions by plants from spontaneous flora and their use as medicinal plants, it is recommended, based on the studies conducted, to harvest and use plants from soils that do not contain heavy metal ions.

Keywords: soil contamination; heavy metals; medicinal plants; herbs; chemical composition

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1. Introduction

The chemical composition of soil is extremely diverse, and soils contain practically all known chemicals [1]. Organic-mineral soil constituents are characterised by organic complexes with metal ions (Fe^{2+}, Cu^{2+}, Mn^{2+}) and associations formed between clays and humic and non-humic organic substances [2–4]. The pollutants released into all soils reach a distance of between 20 and 50 km. Soils support large amounts of pollutants from sludge from wastewater treatment plants, sludge from ports, waste from farms, etc. Waste from different industrial activities causes soil pollution with organic and inorganic compounds [5–7]. Due to their high toxicity and long-term stability in the environment, the accumulation of heavy metals in soil, and consequently in spontaneous flora, is a significant environmental problem [8]. Through ingesting food, breathing in particles, inhaling particles, and absorption through the skin, the bioaccumulation of heavy metals may enhance the dangers to human health [9,10]. Heavy metals are highly toxic to living organisms [7]. Above a specific point, toxic consequences occur, whereas below that point, some elements (Co, Cu, Fe, Ni, and Zn) may even be necessary building blocks for proteins involved in different metabolic pathways [11]. Heavy metal pollution is a global problem that is now of great interest for both industrial sites and for protected natural areas [12–14].

Heavy metal pollution is caused primarily by the metallurgical and ferrous industries, which release large amounts of dust into the atmosphere, and also by solid-fuel boilers, cement factories, road transport, waste dumps, and tailing deposits [15–17].

In Romania, heavy metals represented by oxides and gases pollute industrial areas around cities such as Baia Mare [18], Zlatna [19], and Copşa Mică [20,21]. In Baia Mare and Zlatna, pollution is mainly caused by lead [18], and it is caused by cadmium, zinc, lead, and copper in Copşa Mică [20]. In Copşa Mică, economic activities with a metallurgical and chemical profile determined soil pollution with heavy metals on more than 8000 ha, of which 1500 ha were found with cadmium, 422 ha were found with zinc, 335 ha were found with lead, and 32 ha were found with copper [21]. After 1990, metallurgical activities were drastically reduced and even stopped. However, the locals cultivate these lands, a fact that may affect their health [21].

In the last two decades, the concentration of lead in the human body in some areas has increased 200-fold, even exceeding the recommended concentration. Regarding the studied area, the main sites contaminated with heavy metals and hydrocarbons in the Iasi area are represented by the lands on which the Arcelor Mittal plant is located, as well as in the location of the former non-compliant municipal waste deposit at Tomesti (15.3 ha), which is located 8 km from the city of Iasi [22,23]. The deposit was closed in 2015 as part of the "Integrated Waste Management System" project, in which measures were adopted to ensure good soil quality and protect the health of the population and the environment.

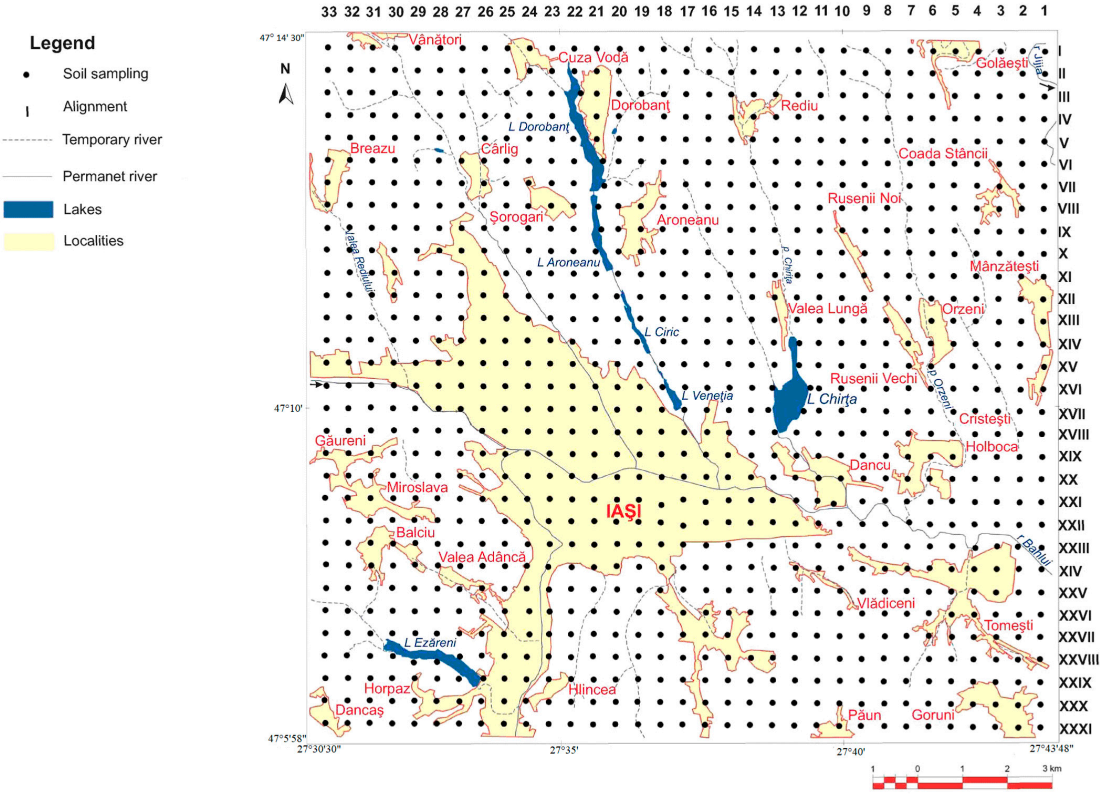
Heavy metals can enter the soil or plants from fertilisers, supplements, and pesticides used in food production, or from gases released into the atmosphere from industry and by combustion [24]. Worldwide, a large number of plants that can bioaccumulate heavy metal ions from the soil have been tested both in the laboratory and in field conditions [25–29]. Currently, there are over 400 recognized species of plants that hyperaccumulate metals. Some species and genotypes can grow on lands that contain increased concentrations of heavy metals, and they hyperaccumulate metals that either occur there naturally or are there due to human activity [30,31]. Heavy metal pollution has particularly strong effects on land [32]; therefore, it is useful to know the content of heavy metals in urban lands to accurately establish their pollution levels. Several studies have reported soil contamination by heavy metals released due to industrial activities, especially in urban areas [33,34], and these raise dangers to human health [35,36]. Negative health effects on the population living in an area with contaminated soils have been observed.

Different studies have been conducted on the heavy metals in urban soils [23,37], but there is an absence of a link between soil pollution and heavy metal content in different plants. In this regard, soil samples were collected from the Iasi urban area for the following reasons: (1) to explore the characteristics of soil and heavy metal concentrations, (2) to generate maps of heavy metals in the studied areas, and (3) to determine the content of heavy metals in spontaneous flora. This study analysed, for the first time in an urban area, the possibility of bioaccumulation of heavy metal ions in plants from spontaneous flora. The findings demonstrated that plants grown in industrially polluted soils contain significant amounts of heavy metals that are transferred in aqueous media.

The water-soluble fractions of bioaccumulated heavy metals present toxicity risks, because the studied plants are used for herbal and medicinal teas and in different modern and traditional foods as aromatic herbs. In the studied area, Cr, Cu, Ni, Pb, and Zn are enriched in the soil samples; however, their content is below the potential human exposure limits. If levels of heavy metal cations are low risk for individual health, the presence of multiple cations exceeded the acceptable limit.

2. Materials and Methods

The study area was 16 km^2 and included the built-up area of Iasi and its surroundings (Figure 1a). The population numbers almost 400,000 inhabitants, with a density of about 150 inhabitants/km^2. Geochemical distribution maps of potentially polluting heavy elements were constructed using GIS methods for interpolating discrete data. For graphical representation, the ESRI ArcGIS Desktop platform was used [38]. A map of land use is presented in Figure 1b.



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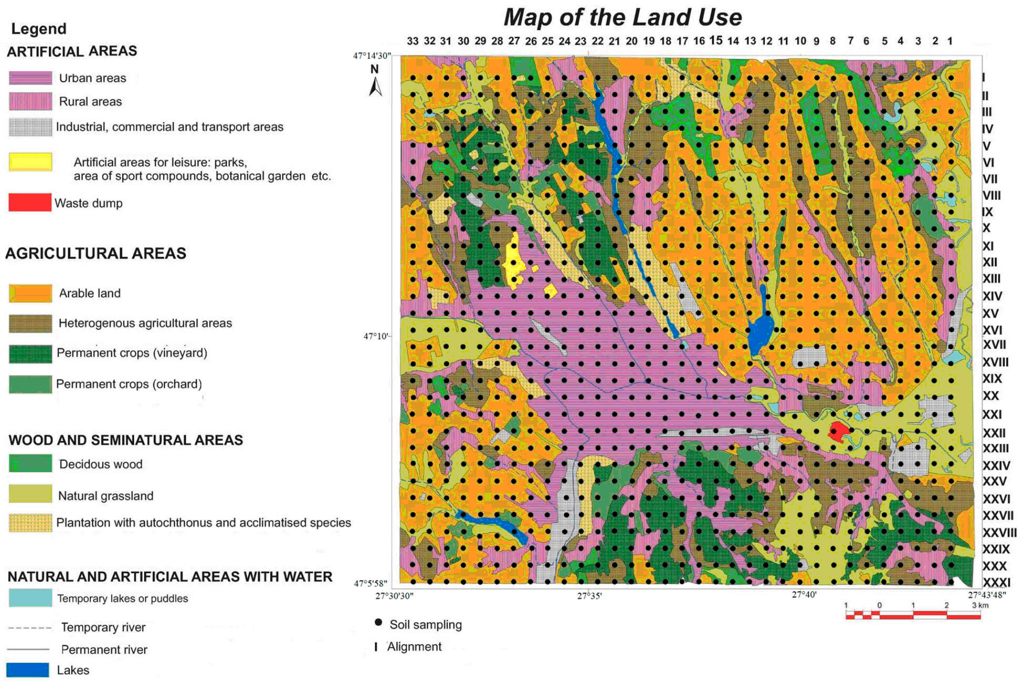

(**b**)

Figure 1. (**a**) Sample collection grid from the study area (16 km^2) including the built-up area of Iasi and its surroundings (1030 soil samples were taken at a depth of 0–25 cm from a network of 500 m); (**b**) land use.

2.1. Soil Sample Preparation

The level of contamination was assessed based on the collection and analysis of 1030 soil samples, collected at a depth of 0–25 cm, from the city of Iasi and the neighbouring areas, within a radius of 500 m. The collected soil samples were naturally dried at room temperature (20 °C). After this, the soil samples were ground with an agate mortar, sieved, and stored in polypropylene containers as samples for analysis.

The method described in the literature to determine the net concentration of heavy metals in soil was used to undertake acidic extraction [39]. A 250 cm^3 glass vessel containing 10.0 g of soil sample was mixed with 50 cm^3 of diluted nitric acid (1:1), and the mixture was then homogenised. The glass was covered and boiled for 10 min on low heat. The mixture was cooled to room temperature, then 10 cm^3 of hydrogen peroxide was added dropwise under stirring. The glass content was heated and boiled under weak heating for 10 min, then cooled and filtered on a G4 filter funnel into a volumetric flask with a capacity of 100 cm^3. The precipitate was mineralised with nitric acid following the described procedure, and finally, the volume of the filtrate was diluted to 100 cm^3 with bidistilled water. Sample analysis was performed via atomic absorption spectroscopy using an iCE 3400 AAS Spectrometer (Thermo Fisher Scientific, Waltham, MA, USA), and fluorescence spectrometry RX was carried out with an EDXRF (Thermo Fisher Scientific™ Niton™ XL3t XRF-Analyzer, Waltham, MA, USA). Soil samples were stored in glass containers for further study and during further processing. Specifically, the plants were rinsed with deionised water and dried first in the shade and then in an oven at 110 °C for 2–4 h. The dried and ground samples were subsequently stored in bottles for further study. During all of these steps, necessary measures were taken to avoid any loss or contamination of the samples with heavy metals.

2.2. Spontaneous Flora Sample Preparation

A furnace was used to heat 1 g of ground plant material (shoots) for 5 h at 550 °C. After cooling under desiccating conditions, the crucible contents were added, and 2.5 mL 6M HNO_3 was added to dissolve the samples. The necessary glassware was thoroughly cleaned using regular soap and tap water before being submerged in an acid bath (30% nitric acid) and dried in a fume hood. Glassware was washed with deionised water. The sample solution was filtered, diluted to a total volume of 20 mL, and analysed with an atomic absorption spectrophotometer. In the laboratory, the soil content of the heavy metals Cd, Cr, Cu, Hg, Ni, Pb, and Zn was determined. For some of these heavy metals, maps of their accumulation distribution in soil were made. The determination of heavy metals in plants was carried out via UV/VIS and atomic absorption spectrophotometry [40]. After harvesting, the plants were washed with distilled water, dried at room temperature, and then processed by wet digestion (conc. HNO_3).

2.3. Methods for Heavy Metals' Determination from Aqueous Extract

The aqueous extracts were obtained by infusing the dried plants (1.00 g) with 100 mL of drinking water (Timisesti-Iasi source). The resulting infusions using all 11 plants from spontaneous flora were analysed by atomic absorption spectrophotometry to evaluate their content of the following elements: Cu, Cr, Cd, Pb, Fe, Mn, Zn, and Ni.

Principle of operation: With the specific reagent and analysis purity, the heavy metals form a substance of a certain colour through which, depending on the nature of the lamp, a light beam is transmitted. The device measures the absorbance at a certain wavelength and determines the concentration of the desired substance in the solution [41,42]. The absorption of light by a coloured substance is crossed by a beam of light. It is translated with the formula:

$$A = lg\frac{I_o}{I} = -lgT = \varepsilon \cdot b \cdot C \quad (1)$$

where I and I_o represent light intensity, A—absorbance, C—concentration (mg L^{-1}), *T*—transmittance, *b*—the thickness of the absorbent layer traversed (centimetres), and ε—extension coefficient.

Reagent and method blanks, duplicates, and standard reference materials were used in the quality assurance and control of chemical analyses. The reference materials were from CPA Chem. Ltd., Stara Zagora, Bulgaria. Standard solutions were used for calibration; when necessary, digested soil solutions were diluted by a factor of 10 to fit the calibration range.

Each element underwent calibration using a linear regression result (R^2) of 0.999. The least amount of random and systematic error was possible. To have trust in the precision, repeatability, and dependability of the results, after calibration curves were developed, all of the tests were run twice.

To find the relevance of the analytical results, standard statistical procedures were applied: the arithmetic mean of the measurements, absolute error, mean deviation, and standard deviation were applied; a propagation technique was applied to eliminate unreliable data error [43,44].

The legislation that established the permissive value of heavy metals content is Council Directive 86/278/EEC for Protection of the Environment (European Communities Council 1986) and the Romanian Regulation of Allowable Quantities of Hazardous and Harmful Substance in Soil (Order of the Ministry of Waters, Forests, and Environmental Protection No. 756/3 November 1997). According to the Romanian legislation, the intervention thresholds for soils with less sensitive use are 10 mg kg^{-1} Cd, 600 mg kg^{-1} Cr, 1500 mg kg^{-1} Zn, 500 mg kg^{-1} Cu, 4000 mg kg^{-1} Mn, 1000 mg kg^{-1} Pb, 500 mg kg^{-1} Ni, and 250 mg kg^{-1} Co [45]. As for the content of heavy metals in plants, it is regulated in the documents of the European Commission. For example, the maximum cadmium content allowed in non-leafy Brassica is 0.04 mg/kg wet weight, and in leafy Brassica, it is 0.1 mg/kg wet weight [46].

3. Results and Discussion

3.1. Heavy Metal Concentrations in Soils

Soils from the north part of the studied area were formed in excessive temperate climate conditions through an intense bioaccumulation process, and chernozems were dominant in the area. The chemical characteristics of the soil, such as organic carbon content, pH, oxide forms, carbonates, and some physical properties such as clay content, might influence the concentration of chemical elements [47]. The soil content of the heavy metals Cr, Cu, Ni, Pb, and Zn was analysed, determined, and interpreted [48–52].

Chromium is recognized to have lithophile geochemical affinity [53]; the maximum recommended value for total Cr content in soil is 30 mg kg^{-1}. The alert threshold (AT) for sensitive land (SL) use is 100 mg kg^{-1}, and for less sensitive land (LSL), it is 300 mg kg^{-1}. The distribution of Cr in the investigated soils appeared to be very close to the natural state, because 99.32% of the samples showed values within the normal range, whereas those that exceeded the alert threshold represented only 0.68% of samples, and those that exceeded the intervention threshold (IT) represented 0.48% of samples (Figure 2).

Copper has a chalcophile affinity that leads to its association in some minerals and ores with other heavy metals such as Pb, Zn, Mo, Ag, and Ni [54]. In the topsoil, a good correlation exists between Cu and Al, Ni, Cr, Mn, and Zn. The maximum recommended value for the total content of Cu in soil is 20 mg kg^{-1}. The AT for SL is 100 mg kg^{-1}, and for LSL, it is 250 mg kg^{-1}. The IT is at 200 mg kg^{-1} for SL and 500 mg kg^{-1} for LSL (Figure 3).

In the study area, the natural distribution of Cu contained values that not only exceeded the threshold value (5.73% of samples) but also the IT (1.94% of samples). These values determine the geochemical halos in chernozem soils located outside the southern part of Iasi city.

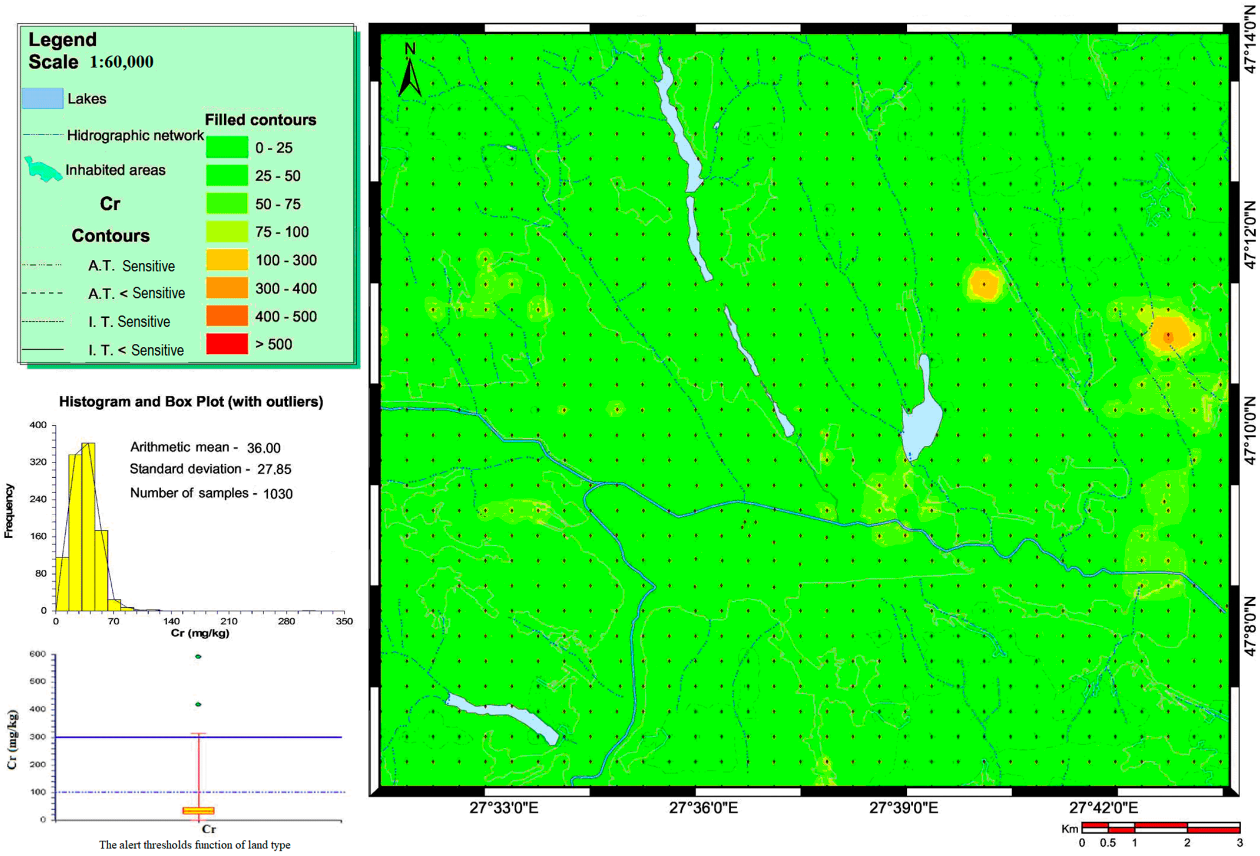

Figure 2. Map of Cr distribution in the analysed soil (mg kg^{-1}).

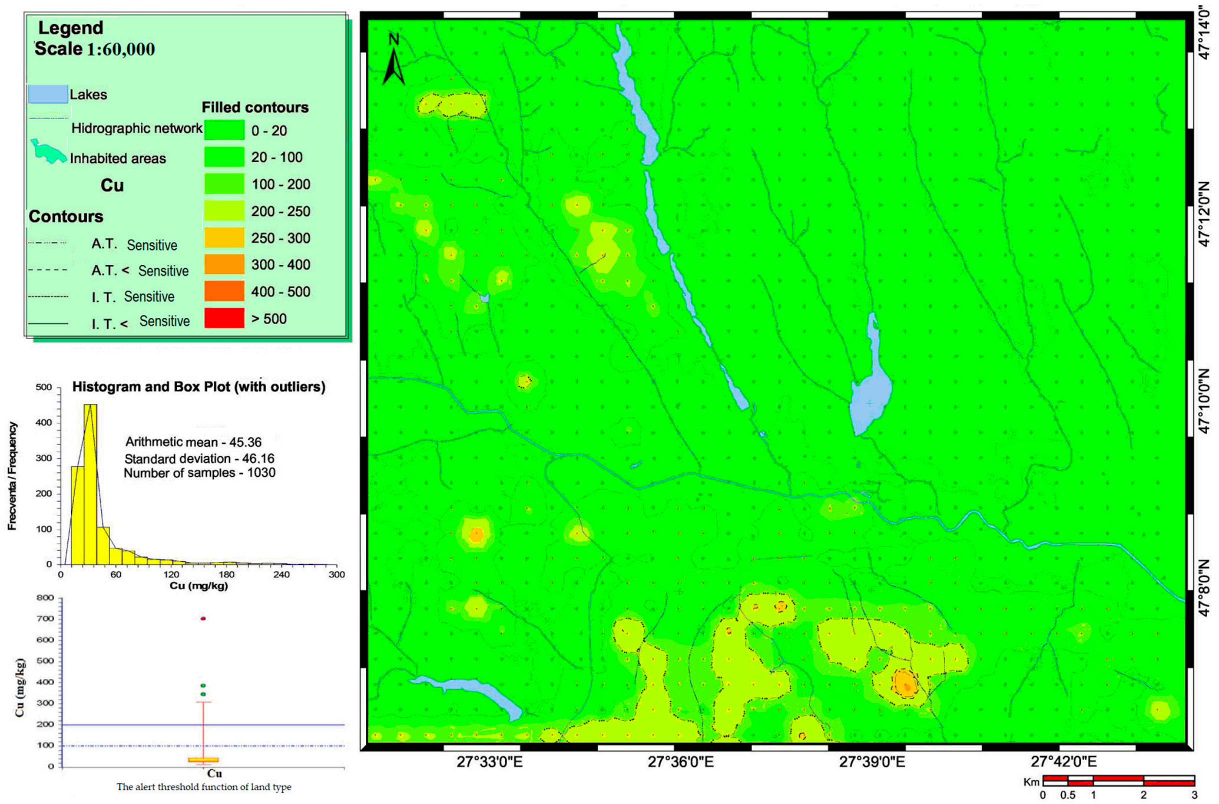

Figure 3. Map of Cu distribution in the analysed soil (mg kg^{-1}).

Nickel has a chalcophile geochemical affinity, the latter explaining the association of Ni with Co, Cu, and Pt in some sulphide ores [55]. The maximum limit for total Ni content in soil is 20 mg kg^{-1}. The AT for SL use is 75 mg kg^{-1}, and for LSL use, it is 200 mg kg^{-1}. The IT is 150 mg kg^{-1} for SL and 500 mg kg^{-1} for LSL. Throughout the studied soil profiles, the Ni content is presented in Figure 4. Samples for which the Ni content exceeded the alert threshold have a punctuated arrangement in the investigated area, an arrangement that is spatially related to the occurrence of chernozems.

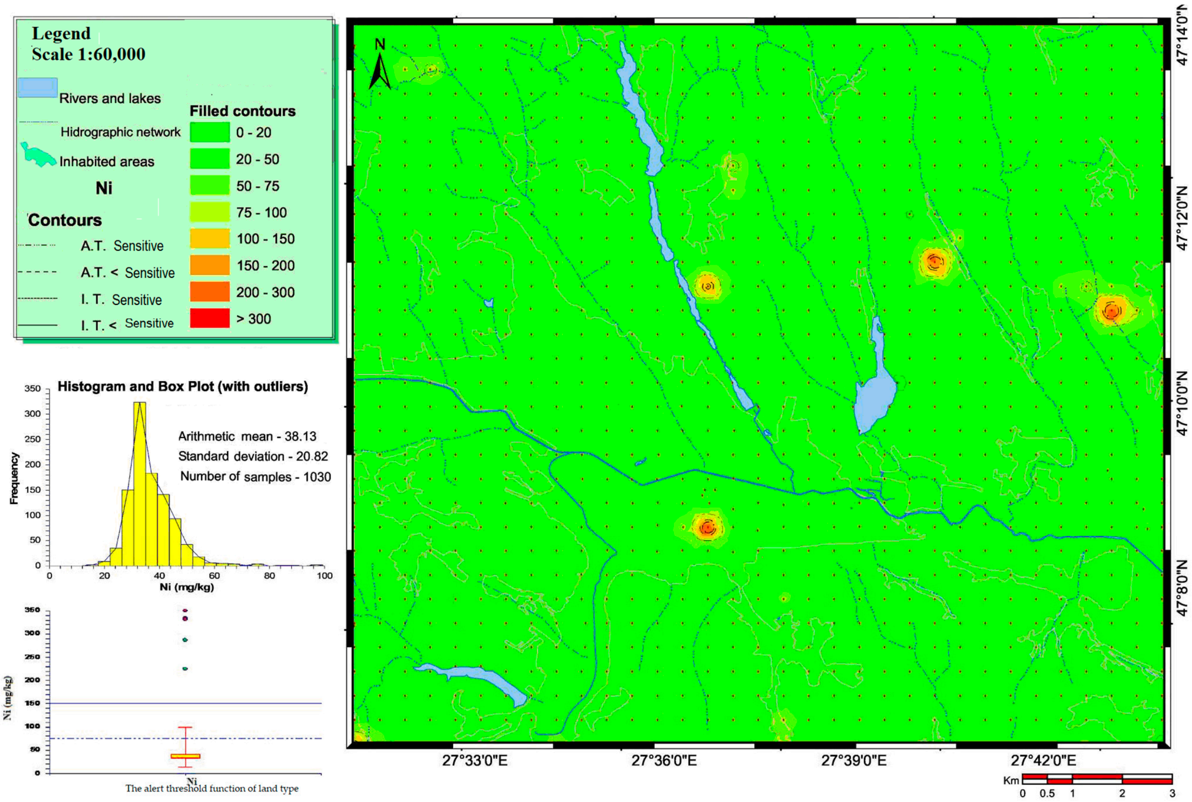

Figure 4. Map of Ni distribution in the analysed soil (mg kg^{-1}).

Lead has a geochemical affinity for chalcophiles [56], which explains why it is found in sulphide ores with Fe, Zn, Cu, Sb, and Ag. The maximum limit for total Pb content in soil is 20 mg kg^{-1}. The AT for SL is 50 mg kg^{-1}, and for LSL land, it is 250 mg kg^{-1}. The IT is 100 mg kg^{-1} for sensitive land and 1000 mg kg^{-1} for less sensitive land. The Pb content determined in the study area varied within a fairly wide range, from 4.5 to 1995.4 mg kg^{-1} (Figure 5).

Furthermore, 92.52% of the analysed samples had a Pb content ranging within normal limits; only 5.73% of samples had Pb content higher than the alert limit, and 1.75% of samples exceeded the IT.

Zinc interacts with several heavy metals, including Cu, Pb, Ag, Au, Sb, As, and Se, in certain sulphide ores [57]. The maximum recommended limit for the total Zn content in soil is 100 mg kg^{-1}. The AT for SL is 300 mg kg^{-1}, and for LSL, it is 700 mg kg^{-1}. The IT is 600 mg kg^{-1} for SL and 1500 mg kg^{-1} for LSL. Since zinc is a necessary nutrient for most plants, algae in rivers and lakes may absorb most of the dissolved zinc in water. However, excessive zinc in soils can be hazardous to many plant species. The Zn content determined for soils from Iasi city and its surroundings varied widely (10.1–5624 mg kg^{-1}), with a majority of samples (96.5%) in which the content did not exceed normal values for soils. Samples with a Zn content that exceeded the AT (2.04%) and were higher than the IT (1.46%) belonged to soils in the urban areas with a southern exposure. Differences in the Zn content spatially overlapped mostly with those of Pb, suggesting that they were generated by the same common pollutant sources (Figure 6). In the study area, soil pollution was characterised by the presence of three heavy metals, Pb, Zn and Cu, above the recommended limits.

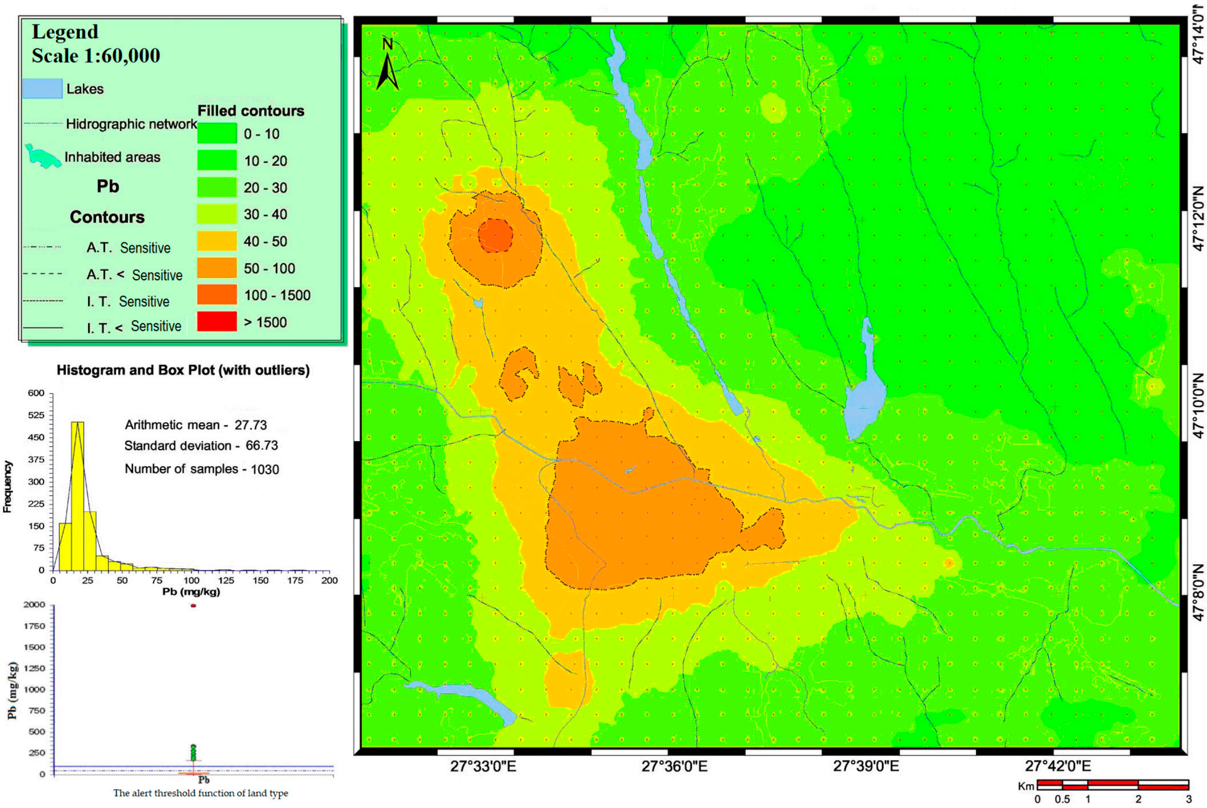

Figure 5. Map of Pb distribution in the analysed soil (mg kg^{-1}).

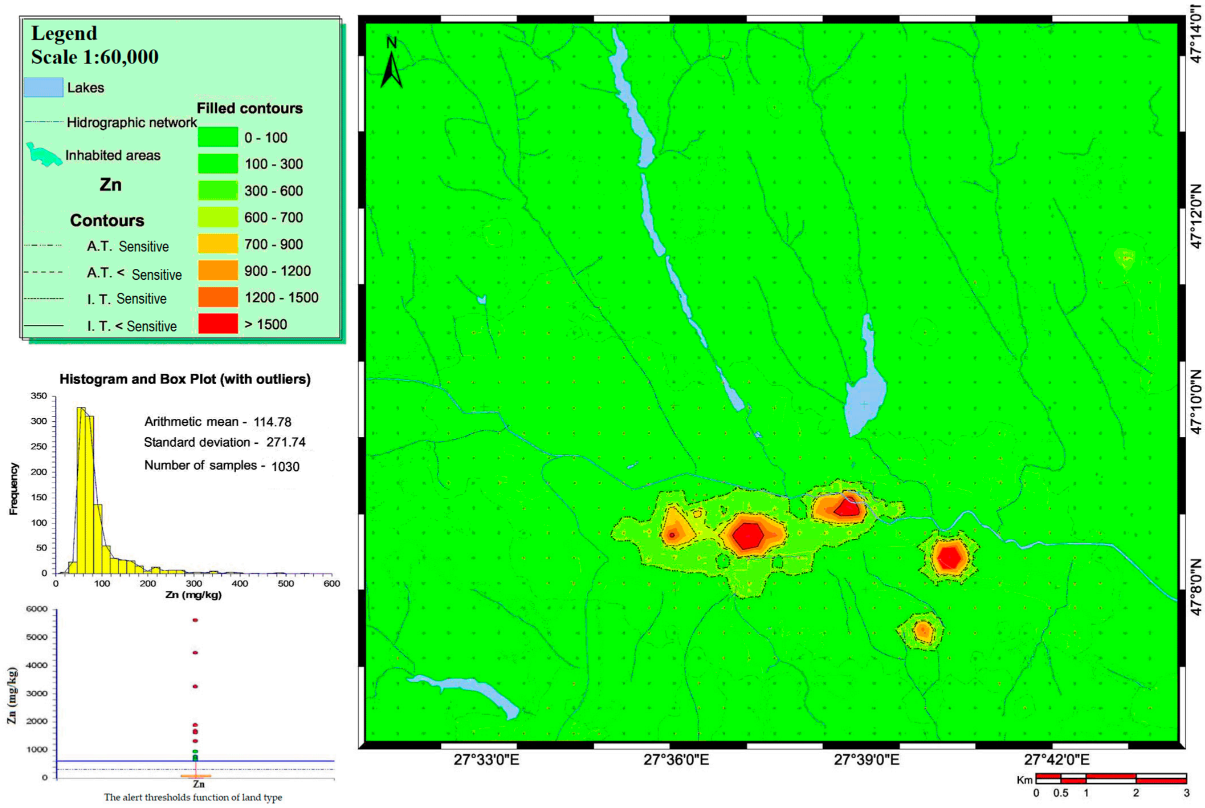

Figure 6. Map of Zn distribution in the analysed soil (mg kg^{-1}).

We can conclude that heavy-metal pollution in Iasi was caused primarily by solid fuel boilers and road transport. For Zn, three genera and 20 species of plants are known to show hyperaccumulation. This group also includes the *Thlaspi* genus, which is known for hyperaccumulating different types of metals. For example, *T. caerulescens* accumulates Cd, Ni, Pb, and Zn; *T. geosingense* accumulates Ni and Zn; *T. ochroleucum* accumulates Ni and Zn; and *T. rotundifolium* accumulates Ni, Pb, and Zn.

3.2. Concentrations of Heavy Metals in Plants from the Spontaneous Flora

Many hyperaccumulators belong to Brassicaceae and are capable of accumulating large amounts of heavy metal ions [58]. Kumar et al. [59] analysed several Brassicaceae species with rapid growth, such as Indian mustard, black mustard, turnip, rape, and kale, for their ability to tolerate and accumulate metals. All plants from *Brassicaceae* accumulate metals, but *B. juncea* specifically has a great capacity to accumulate and transfer Cu, Cr(VI), Cd, Ni, Pb, and Zn to the shoots. The main families of metal-hyperaccumulator plants are *Asteraceae*, *Brassicaceae*, *Caryophyllaceae*, *Cyperareae*, *Fabaceae*, *Lamiaceae*, *Poaceae*, *Violaceae*, and *Euphorbiaceae* [60]. The plants from Brassicaceae are the most numerous, comprising 11 genera and 87 species. A hyperaccumulator is defined as a plant that phytoaccumulates a minimum of 0.01% Cd and As, or a minimum of 0.1% Co, Cu, Cr, Zn, or Pb, or 1% Mn and Ni. The investigation of heavy metal ion levels in certain plants revealed the following: (i) All species from the Brassicaceae accumulate metals. From these, *B. juncea* has a great ability to accumulate and transfer Cu, Cr(VI), Cd, Ni, Pb, and Zn. (ii) Heavy metals (Fe, Cu, Cr, Mn, Zn) are present in variable concentrations, with mint and nettle having a notably increased level of iron and thyme, and rattle a higher level of zinc. (iii) Toxic metals (Pb, Cd, Ni) are present at low concentrations in plants as well as in infusions, except in primula and plantain, which do not have high levels of Pb and Cd.

In this study, 11 plants of spontaneous flora were collected from 2018–2019 from areas in which the existence of heavy metal ions was determined: mint (*Folium menthae*), chamomile (*Flores chamonillae*), yarrow (*Flores miellefolii*), field thyme (*Herba cichorii*), nettle (*Folium urticae*), dandelion (*Folium taraxaci*), celandine (*Herba chelidonii*), plantain (*Folium plantaginis*), primula (*Flores primulae*), shepherd's purse (*Herba bursae pastoris*), and rattle (*Herba hyperici*). Analytical data revealed that of the five herbs used in nutrition, mint and nettle contained the highest amounts of iron of 80.52 ± 5.06 μg g^{-1} dry matter (DM) and 49.62 ± 3.82 μg g^{-1}, respectively. Zinc was present in higher concentrations in field thyme (967.71 ± 6.28 μg g^{-1}) and rattle (811.09 ± 9.69 μg g^{-1}), and the maximum manganese content was found in rattle (55.66 ± 5.15 μg g^{-1}). Chromium and copper were detected at lower concentrations (Table 1).

Table 1. Mineral elements in the studied plants (μg g^{-1}).

Heavy Metals Ions	Iron	Chromium	Copper	Manganese	Zinc
Folium urticae	49.62 ± 3.82	2.19 ± 0.13	6.74 ± 0.45	14.98 ± 0.49	30.40 ± 4.12
Folium taraxaci	31.11 ± 1.41	5.21 ± 0.42	2.78 ± 0.11	14.33 ± 0.34	49.35 ± 2.01
Herba cichorii	22.08 ± 1.63	10.44 ± 0.80	2.09 ± 0.24	20.54 ± 1.78	967.61 ± 6.28
Herba hyperici	10.23 ± 1.27	1.84 ± 0.82	3.31 ± 0.61	55.66 ± 5.15	811.09 ± 9.69
Folium menthae	80.52 ± 5.06	2.67 ± 0.84	4.15 ± 0.31	25.67 ± 0.96	309.63 ± 45.1
Min	8.96	1.02	1.85	13.99	26.28
Max	85.58	11.25	4.46	60.81	973.28
Mean	38.712	4.47	3.814	26.236	433.616
Standard deviation	27.44327	3.5897	1.80067	17.0806	26.35

3.3. Concentrations of Heavy Metals in Aqueous Extract

In the aqueous extracts obtained from plantain and primula, no Pb or Cd were found. The rest of the extracts contained Pb, Cd, and Ni in concentrations between 0.0014–0.0283 mg L^{-1}. The water used for the preparation of plant extracts contained only iron in low concentrations (0.0073 mg L^{-1}).

The content of heavy metals in aqueous extract is presented in Figure 7.

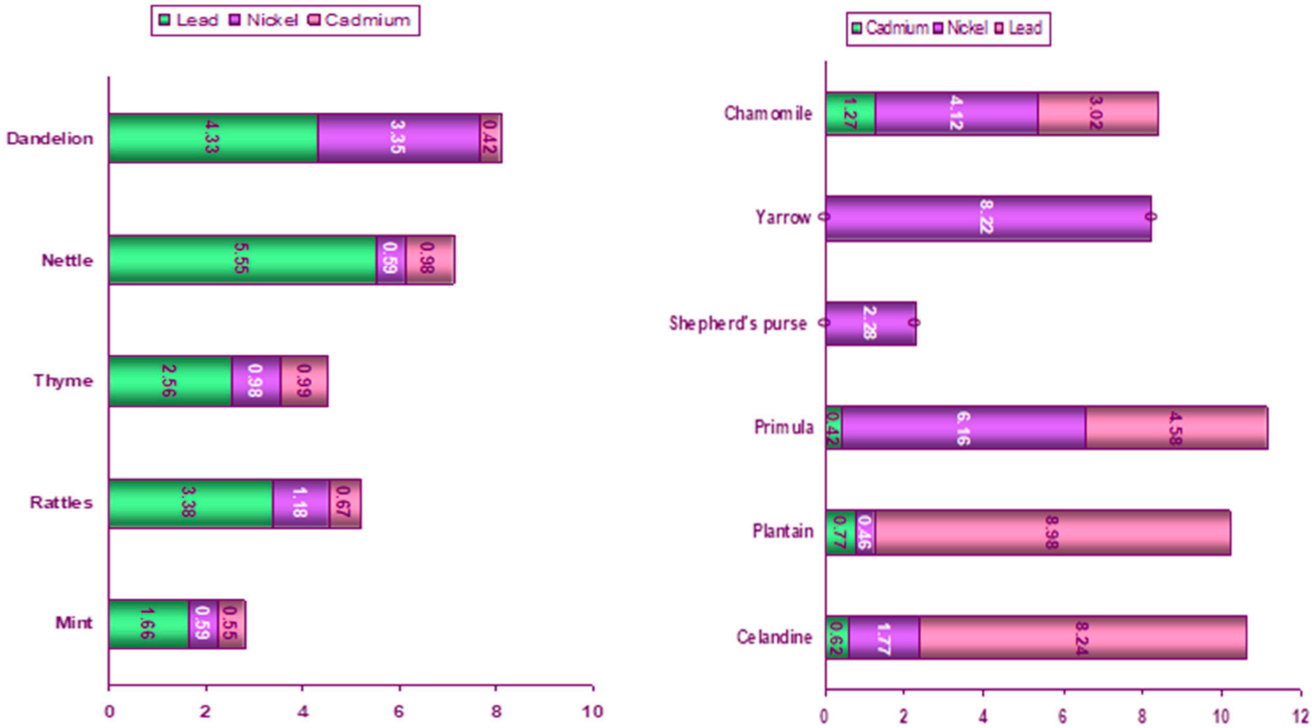

Figure 7. The content of heavy metals in aqueous extract of analysed herbs.

From Figure 7, it can be seen that each herb accumulates and can solubilise other heavy metals. For example, in aqueous extract of nettle, dandelion, celandine, and plantain, heigh concentrations of lead (between 3.38 and 8.89 mg L^{-1}), were found, and in aqueous extract of yarrow and primula, nickel was found. The results are in accordance with the literature [61].

4. Conclusions

In urban residential areas, the soil can be polluted by a wide range of pollutants, resulting from industrial sources and human activities.

Beyond the potential toxicity of contaminated soil to human health through direct contact, contact through inhalation or through the plants from spontaneous flora is very important.

The results of the present investigation revealed that the concentrations of heavy metals (Cu, Cr(VI), Cd, Ni, Pb, and Zn) found in soil samples taken from Iasi, Romania suggest high levels of Pb and Zn, above the alert thresholds in limited areas, as required by Romanian legislation.

The investigation of heavy metal levels in some plants revealed the following:

- The presence of heavy metals (Fe, Cu, Cr, Mn, Zn) was detected in variable concentrations, with mint and nettle being notable for their increased level of iron and thyme and rattle for an increased level of zinc;
- Potentially toxic metals (Pb, Cd, Ni) are present at low concentrations in plants as well as in infusions, except in primula and plantain, which do not contain Pb and Cd.

In order to avoid contamination and potentially negative effects on the environment and on human health, it is crucial to analyse and monitor the amounts of heavy metals in soil and in plants from spontaneous flora suitable for consumption. The obtained information should be helpful in recommending the implementation of remediation strategies and in getting heavy metal contamination in soil and plants from spontaneous flora under control.

Taking into account the potential for the accumulation of heavy metal ions by plants from the spontaneous flora in the area and these same plants' use in medicine and based on the studies conducted, it is recommended to harvest and use the plants from soils that do not contain heavy metal ions, considering the expansion of inhabited areas in the studied metropolitan area.

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Data Availability Statement: The data presented in this study are available on request from the corresponding author.

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

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