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TEMPORAL AND SPATIAL CHANGES IN METAL CONTENTS OF ARABLE SOILS IN THE BUG RIVER CATCHMENT IN 1995-2015 (POLAND)

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Abstract

The paper presents an analysis of the content and spatial distribution of metals (Fe, Mn, Cu, Co, Ni, Cr, Zn, Pb and Cd) in arable soils sampled from the Bug River catchment in the years: 1995, 2000, 2005, 2010 and 2015. The degree of soil contamination/enrichment in heavy metals (HM) was assessed using I_{geo}*, CF, PLI and local sources of HM were identified using multivariate statistical analysis. The concentration levels of the studied elements were as follows (min-max in* $mg \cdot kg^{-1}$*): Fe = 2300.00-14100.00; Mn = 52.00-428.00; Cu = 1.80-15.30; Co = 0.82-5.23; Ni = 1.80-20.60; Cr = 2.60-25.60; Zn = 15.20-71.70; Pb = 3.90-34.20 and Cd = 0.05-1.04. The analyses showed that all metals are at geochemical background levels, except for a slight enrichment in Cd and Pb. HMs were largely bound by organic matter and iron and manganese oxides. Statistical models (FA and CA) identified two sources of HMs. The first source of pollution was a local industry, communication and precipitation. The second source was related to organic and mineral fertilization and the use of crop protection products.*

***Keywords**: Heavy metals; Arable soils; Spatial distribution; Sources of pollution; Poland; Pollution indexes*

Introduction

Soil is a component of the environment that provides a wide range of services that have become necessary for human functioning. It mitigates the effects of flooding due to its ability to store and retain water and has a high potential to absorb pollutants, simultaneously preventing it from entering other components of the environment. It is also a habitat for organisms that exhibit a predisposition to dispose of hazardous substances. Besides, soil provides a physical base for buildings and serves aesthetic, recreational, and cultural functions [1, 2].

The presence of heavy metals (HMs) in soils is troublesome and a dangerous environmental problem, because of their chemical nature, since they are accumulated within ecosystems and do not degrade, and due to the complexity of the soil matrix [2, 3]. Heavy metals are involved in many complex chemical and biological interactions, among which bioavailability, toxicity, or leaching are uniquely important [4]. Considering their stability and bioaggregation capability, as well as their physiological effects on living organisms at low concentrations, they should be treated as elements of significant harmfulness [5–7]. Their accumulation in soils poses a risk to ecosystem functioning, and the consequences of pollution are an acute concern in the agricultural field. Humans are exposed to HMs through the food chain along the soil-plant-human or soil-plant-animal-human pathway, and also by direct exposure, i.e., contact with skin, mucous

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membranes, or through ingestion [8]. Chronic exposure to HMs poses a threat to human and animal health, the potentially toxic consequences usually become apparent after some time even counted in decades, and the known medical treatments are not able to reverse the health effects of their impact with full effectiveness [2, 7]. It is known, soil, water, and food contaminated with HMs influence the increase of cancer morbidity and mortality [9], but the toxicity of each element depends on its chemical form [6]. On the other hand, some metals, which pose a danger to the environment in elevated concentrations, may be essential for the development and functioning of living organisms. These primarily include zinc and copper [10].

Many studies are available in the literature signaling elevated HM concentrations in agriculturally used soils relative to background concentrations [7, 11, 12], which significantly affect soil quality. It highly determines the quality of groundwater and crops and may be modified by e.g. agrotechnical treatments or the use of irrigation and drainage processes [13]. Intensive agricultural practices associated with the usage of crop protection products and fertilizers contaminate groundwater or soil solution, making HMs readily available to plants. The effects of such phenomenon are severe to remove, so it is outstanding to minimize HMs entry into the soil [11, 14]. Soil acidification by sulfur and nitrogen oxides and changes in agricultural practices, such as the application of some fertilizers, promote the adverse environmental impact of HM by increasing the mobility of metallic compounds and facilitating the uptake of some metals by crops, which is simultaneously associated with increased human exposure [15, 16]. To reliably represent the degree of soil contamination, it is necessary not only to determine the total HMs content but also to assess the anthropogenic besides lithogenic contribution, which is complicated in heavily exploited areas [12]. The presence of HMs in agricultural soils may be justified by the type of bedrock, but the sublime importance should be given to origins associated with human activities. Sources of toxic elements include the use of pesticides, herbicides, chemical fertilizers, including superphosphates and superphosphate-based ones, manure, and sewage sludge, as well as emissions and wear and tear on components of transportation and agricultural machinery. In some regions, extractive industries should also be considered [10, 17, 18].

Determining environmental levels of HMs proves to be extremely useful in identifying areas of potential toxicity due to their contribution to biogeochemical cycles, as well as in resource management, land use planning, and tailoring agricultural practices to local conditions [11, 19]. It is also crucial to assess the soil suitability for agriculture, especially in terms of its use for food production, to prevent potential impacts on human health [6, 7].

This study aimed to characterize spatial and temporal changes of HMs content in arable soils in the Bug River catchment for 25 years. Arable soils, due to their direct relationship with the food chain, may be considered a key pathway through humans come into direct contact with most pollutants, including HMs. Heavy metals are highly bound in the soil; therefore, despite their emissions reduction, the problem of risks associated with previous accumulation remains valid. Also, intensive agricultural practices in conjunction with the usage of pesticides and fertilizers cause soil contamination by HMs, which, because they are readily available to plants, may also pose a measurable risk to human health. The results of predictions for HMs present in soil may illustrate specific trends and help determine the location of contamination and the directions of HMs spread, which is a broader result that may provide more informed and sustainable soil management. Ideally, there should be a golden mean between promoted economic development, the changing needs of the population, and necessary soil conservation, so performing soil surveys seems extremely helpful in finding that golden mean.

Considering the points presented above, the Bug River basin seems to be a suitable area to analyze environmental issues. The main objectives of the conducted studies were: (i) to analyze the content and spatial distribution of metals (Fe, Mn, Cu, Co, Ni, Cr, Zn, Pb and Cd) in arable soils sampled from the Bug River catchment area, based on studies performed by the Institute of Soil Science and Plant Cultivation in Puławy in the years: 1995, 2000, 2005, 2010 and 2015; (ii) to assess the degree of soil contamination/enrichment with metals (HMs) using I_{geo}, CF, PLI; (iii) to identify local sources and determinants of HMs content and spatial distribution in soils using multivariate statistical analysis. This research approach may provide basic information for better management of this region in the future.

Experimental part

Study area

The Bug River is the fourth largest river in Poland. It is a typical lowland river with low slopes. The riverbed meanders creating numerous bight and oxbows. The landscape of the river valley is marked by a high level of naturalness. The total length of the Bug River is 772km. Riverhead and the upper section of 185km land in Ukraine. In its middle course, along 363km, the Bug constitutes a natural border between the Republic of Poland and Ukraine (185km) and Belarus (178km). The remaining 224km are on Polish territory, where the Bug flows into the Narew River, on the territory of Zegrze Reservoir. The area of the basin in Poland is 39420km^2. The Polish part of the Bug River basin is located in the Lublin, Podlaskie, and Mazovia Voivodeships. Arable fields dominate in the Bug River basin (50.3%). Meadows and pastures constitute 17.7%, forests cover 23.5% of the catchment area. Table 1 shows the dominant soil types in the catchment area divided into provinces.

Table 1. Soil types occurring in the Bug River catchment

Voivodeship (research point)	Dominant soil groups
Lublin (Sławicinek Stary, Białka, Siedliki, Nadrybie Dwór, Rybie, Józefin, Alojzów, Rogalin, Ulhówek, Polatycze)	Inceptisols, Alfisols, Mollisols
Mazovia (Zawisty Podleśne, Wrotnów, Zdany, Świniarów)	Spodosols, Inceptisols
Podlaskie (Podolany)	Alfisols, Inceptisols

The climate is marked by frequent variability and different weather conditions. The vegetation period is about 200 days long. The average annual precipitation is about 600 mm, while the average annual air temperature is 8°C. Winds are highly variable, but westerly winds predominate. In winter, the winds are mainly easterly.

The catchment area is dominated by cities with small populations. There are only three larger towns: Siedlce (72,858 inhabitants), Chełm (69,016) and Biała Podlaska (55,424). The best-developed industry is the food one. The largest sectors of this industry are bakery, milk, sugar, meat, and fruit and vegetables. The tourist industry is also well developed and is located mainly in places with rich and beautiful landscapes. 14% of the Bug catchment area is under legal protection.

Soil sampling and analytical procedures

The experiment presented in the paper was conducted by the Institute of Soil Science and Plant Cultivation in Puławy on agriculturally used soils [20].

The study analyses the contents of Fe, Mn, Cu, Co, Ni, Cr, Zn, Pb and Cd in the years: 1995, 2000, 2005, 2010 and 2015, in three voivodeships (Lublin, Podlaskie, and Mazovia), located in the basin of the Bug River. The research object is demonstrated in figure 1. The total number of soil samples was 15. Samples for laboratory analyses were collected with a steel soil probe from a depth of 0-20cm from an area of about 100m^2. Plant remains were removed from the soil surface before sampling. The combination of individual samples constituted a bulk sample, representative of the research point. Containers were labeled with the number of the respective research point, sealed, and secured in a technique that prevented loss and contamination of the sample. Upon arrival at the laboratory, the probes were registered and labeled according to the operative system. Then, the samples were air-dried, sieved through a 1.0mm mesh sieve, mixed until homogeneous, and ground in an agate mill, after which they were referred for analysis. Analysis of the studied metals was performed by atomic absorption spectrometry (soil sampled in 1995-2005) or inductively coupled plasma mass spectrometry

(ICP-MS) (soil sampled since 2010) in solution after soil mineralization with royal water. Soil mineralization with nitrohydrochloric acid was performed according to the international standard ISO-11466: Soil quality — Extraction of trace elements soluble in aqua regia. Soil reaction in KCl was determined by potentiometric method [21], organic matter (MO) content was determined by modified Tiurin method [22]. The analyses were performed in an accredited laboratory (number AB 339) of the Institute of Soil Science and Plant Cultivation - State Research Institute [23].

Fig. 1. Location of research points

Soil contamination assessment

Metal content (HMs) testing may be a good indicator of soil contamination or pollution. There are many criteria and ratios used worldwide for assessing soil health. One of the first and now widely used one is the geoaccumulation index (I_{geo}), defined by *G. Müller* [24]. Other ratios proposed later include the CF (contamination factor) and the PLI (pollution load index) [2, 5, 14, 17, 25]. These indicators are sensical tools for processing, analyzing, and transforming raw environmental data into valuable information, and on the grounds of them, polluted areas may be identified for further research and improvement. Most ratios used in pollution assessment refer to background values, which are understood as the concentrations of particular elements present naturally in the environment. The primary role of geochemical background in environmental studies is to determine whether the studied area is subject to anthropogenic impact, whether we are dealing with the effects of pollution or enrichment. The obtained metal contents were compared with the "globally" defined geochemical background with the average element content in the Earth's crust proposed by *K.K.Turekian and K.H. Wedephol* [26] and with the value of geochemical background defined locally for the soils of Poland defined by *K. Czarnowska* [27] (Table 2).

The geochemical index (I_{geo}) is defined using the formula [24]:

$$I_{geo} = \log_2[C_n/(1.5B_n)] \quad (1)$$

where: C_n - measured content of the analyzed metal (mg·kg^{-1}); B_n - the geochemical concentration of the given element proposed by *K.K.Turekian and K.H. Wedephol* [26].

The constant 1.5 is the background matrix correlation coefficient due to lithological variability. I_{geo} values are classified according *to G. Müller* [24] and are divided into seven classes: uncontaminated (Igeo ≤ 0) – class 0; uncontaminated to moderately contaminated ($0 < I_{geo} \leq 1$) – class 1; moderately contaminated ($1 < I_{geo} \leq 2$) – class 2; moderately to heavily contaminated ($1 < Ig_{eo} \leq 2$) – class 3; heavily contaminated ($3 < I_{geo} \leq 4$) – class 4; heavily to extremely contaminated ($4 < I_{geo} \leq 5$) – class 5; extremely contaminated ($5 < I_{geo} \leq 6$) – class 6.

The CF ratio was also calculated and it is the ratio of each metal content to the background value [26]:

$$CF = C_{metal}/C_{background} \ [28]. \quad (2)$$

A four-level scale proposed for the CF ratio was ued: low pollution (CF <1), moderate pollution (1⩽CF <3), considerable pollution (3⩽CF <6), and very high pollution (CF⩾6).

Soil quality was also determined by calculating the pollution load index (PLI) for the elements: Fe, Mn, Cu, Co, Ni, Cr, Zn, Pb and Cd. The ratio is a comprehensive measure of contamination by more than one element. PLI is an experimental formula developed by *D.L. Tomlinson et al.* [29]:

$$PLI = (CF_1 \cdot CF_2 \cdot \ldots \cdot CF_n)^{1/n} \quad (3)$$

where: n is the number of elements analyzed in the sample.

The empirical index provides simple comparisons of average heavy metal contamination at different soil sampling sites. A PLI = 0 indicates perfection, PLI < 1 - no contamination, and PLI > 1 indicates contamination. PLI is a ratio of contaminant load at a sampling site, not the number of elements assessed [30].

Statistical analysis

All statistical analyses were performed using the licensed software Statistica ver. 13.3 for Windows. Mean, minimum, maximum, standard deviation, and coefficient of variation were calculated. Shapiro-Wilk test was used to verify the normality of distribution. The results were considered statistically significant with a probability of error of $p < 0.05$. Spearman's correlation analysis was used to investigate the relationships between metals, multivariate analyses were used to identify the primary sources of elements in the study area [31].

Before performing the statistical multi-factor analysis (FA), the KMO test (Kaiser-Meyer-Olkin) [32] and Bartlett's test [33] were performed for the elemental content of 75 samples.

The KMO value was obtained in the range of 0.55 to 0.60, and Bartlett's test was statistically significant. Multivariate statistical analysis, which is well used to identify metal sources [34, 35], was also applied. Ward's version of cluster analysis (CA) was used to classify metals from different sources but with similar physical and chemical properties [36].

Results and discussion

Metal content in arable soils in the Bug River catchment area

Descriptive statistics for the content of 9 analyzed elements, organic matter (MO), and pH_{KCl} in soil from 15 control and measurement points are presented in Table 2. The factors affecting the bioavailability of metals in soil are organic matter and pH. According to *L. Fernandes et al.* [37] soil with higher organic matter content has higher metal content. The organic matter (MO) content ranged from 0.9-5.79%. MO content in 75% of the samples was in the range of 0.9-2.0%. The most abundant soils in MO were at the measurement point Józefin (average 5.55%).

High pH values promote adsorption and precipitation, while low pH may weaken the bonding strength and hinder metal retention in soil, bottom sediments [38]. Soil pH ranged from 3.4 to 7.7 pH_{KCl}, indicating a significant proportion of acidic and very acidic soils (about 59% of the total samples tested). Slightly more than 17% of samples were with neutral or alkaline pH.

Mean metal contents in arable soils of the Bug River catchment occurred in the following descending order: Fe > Mn > Zn > Pb > Cr > Ni > Cu > Co > Cd. The geochemical background established by *K.K.Turekian and K.H. Wedephol* [26], i.e., the content of elements present in the earth's crust, was used to assess soil contamination. The analyses conducted showed that all metals are at natural levels, except Cd (16%), Pb (4%), and Zn (1.3%). Then, referring to the local background proposed by Czarnowska (1996), the analysis showed exceedances for Cd (60%), Pb (36%), Mn (24%), Zn and Ni (18.6%), Co (5.3%) and Fe and Cu (4%). The elements, that were found in the highest amounts in the soil were Fe and Mn, while Cd was the least, which is largely associated with the geochemical properties of these elements. *L.C. De Andrade et al.,* [39] state that elements such as Fe and Mn are found in abundance in regional soils and come from natural sources such as the earth's crust. Both metals may come from the weathering of rock fragments rich in these elements. The contents of Fe and Mn vary and occur in the studied soil in the range of 2300.00-14100.00 mg $Fe \cdot kg^{-1}$ and 52.00-428.00 mg $Mn \cdot kg^{-1}$. The content of Mn in 76% of the samples is in the range of 52.00-300.00 $mg \cdot kg^{-1}$. The availability of Fe and Mn to plants depends mainly on the soil reaction [40].

In the case of Zn and Pb, the total contents in soils were as follows 15.20-71.7mg $Zn \cdot kg^{-1}$ and 3.90-34.20mg $Pb \cdot kg^{-1}$, with averages in the analyzed years being 23.89±4.33 - 39.26±39.18mg $Zn \cdot kg^{-1}$ and 7.77±2.16 - 11.73±6.72mg $Pb \cdot kg^{-1}$. Zinc is essential for plants, but due to its high mobility in soil, there is a risk of excessive uptake of this element [40]. Lead is one of the toxic metals found in the environment. It has low mobility in soils, but in terms of significant pollution, it is incepted easily by plants from both soil and atmospheric dust [41]. Intensive sorption of Zn and Pb in soils is associated with the content of organic matter, clay minerals, and hydrated Fe and Mn oxides [40]. Road traffic may be a source of Zn and Pb in soils - soils located close to roads with heavy traffic are particularly vulnerable. Many authors indicate that large amounts of Zn are emitted from tire abrasion during vehicle exploitation. *B.S. Rajaram et al*. [42] argued that most vehicles use unleaded gasoline, but the element remains in the environment constantly, especially exposed to heavy traffic.

The present study showed low contents of Cr, Ni, Cu and Co in the surface layers of arable soils, falling within the ranges respectively: 2.60-25.60, 1.80-20.60, 1.80-15.30, 0.82-5.23$mg \cdot kg^{-1}$, and are mainly at natural levels. It is worth emphasizing that the sublime risk from soil chromium is associated with its hexavalent form, while the trivalent one is relatively immobile in the soil, resulting in less potential risk from its presence [43]. Nickel in soil, like most other heavy metals, may be of natural or anthropogenic origin. Its mobility and potential bioavailability are among the lowest among heavy metals [44]. According to *E. Kelepertzis* [45] and *G.Tóth et al.* [46], enrichment of soil in Cr, Ni, and Zn is mainly due to pesticides, phosphate, and inorganic fertilizers usage. Copper is among the substances essential for human health, being part of enzymes involved in major metabolic processes. Copper in soil occurs mainly in combinations with organic matter, clay minerals, and in the form of low-mobile sulfates, sulfides, and carbonates [41]. Elevated amounts of Cu in food may negatively affect human health; however, most crops take up and accumulate Cu only in low quantities [47]. Like Cu and Co is an element needed by humans (it is part of vitamin B_{12}). Noteworthy is that the potential for Co transfer from soil to edible plant parts is quite low [48].

The maximal Cd content was about 6 times higher than the geochemical background, indicating that soils are enriched in Cd and that its origin is anthropogenic. The mean of Cd in the soil of the Bug River catchment during the years fluctuated from 0.14±0.15 to 0.27±0.23mg $\cdot kg^{-1}$, with a range of 0.05-1.04$mg \cdot kg^{-1}$. Sewage sludge, manure, and lime are the causes of Cd enrichment [49, 50]. High levels of this element in agricultural soil are caused by repeated application of phosphorus fertilizer [51, 52]. This element, like Pb, may enter the soil from transportation emissions. Vehicles emit Cd with dust from worn tires [53] and diesel engines [54], which is related to the small diameter of the element's particles and its long residence time in the atmosphere. These particles are readily transported over long distances [55]. Cadmium found in soil is highly mobile. It may be taken up by the root system of plants and transported to aboveground organs [40]. Consumption of crops of plants grown on Cd-contaminated soils poses a high risk to human health. To avert further Cd contamination, soil conservation measures are needed, for instance, controlling the amount of Cd in phosphate fertilizers and the proper manure and liming usage.

Table 2. Basic statistics of metal concentrations, pH, and MO in agricultural soils in the Bug River catchment area

		min-max (mg·kg^{-1})	mean±SD (mg·kg^{-1})	coefficient of variation (%)	geochemical background (mg·kg^{-1})
Fe					
	1995	3100.00-14100.00	6853.33±3686.35	53.79	47200[a] 12900[b]
	2000	2700.00-13300.00	6353.33±3105.88	48.89	
	2005	3000.00-12700.00	6246.67±2870.04	45.95	
	2010	2300.00-10800.00	5366.67±2377.86	44.31	
	2015	2300.00-8000.00	4553.33±1791.41	39.34	
Mn					
	1995	163.00-428.00	269.13±71.63	26.62	850[a] 289.0[b]
	2000	165.00-413.00	264.87±71.87	27.14	
	2005	174.00-398.00	261.73±72.42	27.67	
	2010	67.00-413.00	257.47±91.25	35.44	
	2015	52.00-362.00	217.53±91.50	42.06	
Cu					
	1995	2.00-15.30	5.76±3.74	64.43	45[a] 7.1[b]
	2000	1.80-13.30	5.34±3.42	64.12	
	2005	2.00-12.30	5.37±3.32	61.73	
	2010	1.80-10.60	4.88±2.85	58.40	
	2015	2.10-10.20	4.54±2.42	53.39	
Co					
	1995	0.85-3.95	2.14±0.94	43.80	19[a] 4.0[b]
	2000	0.89-5.07	2.24±1.24	55.14	
	2005	1.13-5.23	2.49±1.26	50.60	
	2010	0.90-4.72	2.32±1.08	46.60	
	2015	0.82-3.83	2.15±0.92	42.58	
Ni					
	1995	2.50-18.80	6.63±4.83	72.75	68[a] 10.2[b]
	2000	2.20-19.20	6.24±4.98	79.84	
	2005	2.60-20.60	6.57±5.04	76.81	
	2010	1.90-11.40	5.00±3.04	60.89	
	2015	1.80-11.00	4.71±2.57	54.46	
Cr					
	1995	3.50-22.80	8.57±5.57	64.98	90[a] 27.0[b]
	2000	3.50-18.80	8.54±4.80	56.26	
	2005	3.80-25.60	8.84±5.82	65.87	
	2010	2.60-14.90	6.35±3.53	55.62	
	2015	2.80-14.10	6.27±3.07	49.03	
Zn					
	1995	16.50-68.30	28.52±16.35	57.35	95[a] 30.0[b]
	2000	15.50-173.00	39.26±39.18	56.61	
	2005	16.90-70.70	28.64±16.92	59.08	
	2010	17.60-31.30	23.89±4.33	18.15	
	2015	15.20-97.30	27.66±20.72	74.90	
Pb					
	1995	3.90-34.10	11.47±6.92	60.32	20[a] 9.8[b]
	2000	5.00-34.20	11.73±6.72	57.30	
	2005	5.70-30.30	11.27±5.51	48.89	
	2010	5.60-16.50	9.42±2.87	30.45	
	2015	4.50-13.20	7.77±2.16	27.73	

	min-max ($mg\cdot kg^{-1}$)	mean±SD ($mg\cdot kg^{-1}$)	coefficient of variation (%)	geochemical background ($mg\cdot kg^{-1}$)
Cd				
1995	0.09-1.04	0.27±0.23	84.71	
2000	0.13-0.84	0.27±0.17	62.71	
2005	0.07-0.78	0.25±0.18	71.45	0.3[a] 0.18[b]
2010	0.07-0.69	0.16±0.14	90.24	
2015	0.05-0.69	0.14±0.15	105.19	
pH_{KCl} (-)				
1995	4-6.9			
2000	3.9-7.2			
2005	4.2-6.8	-	-	-
2010	3.8-7.7			
2015	3.4-7.3			
MO (%)				
1995	1.26-5.75	2.02±1.07	0.53	
2000	1.25-5.68	1.97±1.05	0.53	
2005	1.11-5.05	1.85±0.93	0.50	-
2010	0.90-5.79	1.90±1.13	0.60	
2015	1.11-5.48	2.01±1.07	0.54	

Analyzed metal contents in soils of the Bug River catchment were collated with other authors' findings who conducted studies in Europe, Asia, and Africa (Table 3).

Table 3. Literature values for mean and ranges concentrations (mg/kg) of heavy metals determined in agricultural soils in different areas of the world

Location	Metal concentration (mg·kg)									Reference
	Fe	Mn	Cu	Co	Ni	Cr	Zn	Pb	Cd	
Europe										
Bug River Basin, Poland	5874.67	254.15	5.18	2.27	5.83	7.71	29.59	10.33	0.22	this study
soil monitoring, Poland	9000.00	363.49	10.30	3.93	9.77	10.99	78.79	22.46	0.50	[23]
Czernichów commune, Vistula River Basin, Poland	-	471.5	10.34	-	24.30	40.73	111.1	31.65	1.13	[56]
Soil monitoring, Europe	21700.00	520.00	16.40	10.40	30.70	32.60	60.90	23.90	0.28	[57]
Leipzig–Halle–Bitterfield region, Germany	-	-	27.9	-	20.9	52.4	75.0	40.0	bld	[58]
Ebro River Basin, Spain	-	-	17	-	19	20	57	17	0.41	[59]
Segura River valley, Spain	15274	30	21.6	7.9	23.7	28.3	57.8	19.6	0.38	[60]
Argolida basin, Greece	-	1020.5	74.68	21.99	146.8	83.12	74.88	19.74	0.54	[45]
Probishtip Region, Republic of Macedonia	26940-52130	447-2125	15-94	9-27	20-190	23-364	8-966	30-223	1-3	[61]
Asia										

Location	Metal concentration (mg·kg)									Reference
	Fe	Mn	Cu	Co	Ni	Cr	Zn	Pb	Cd	
Kulsi River Basin, India	2189.38	-	-	2.30	7.26	5.52	22.7	9.41	-	[74]
Telangana, India	-	-	31.2	23.8	13.7	100.6	92.4	18.2	-	[75]
Fuxin, China	-	-	9.31	-	56.01	91.86	120.85	12.22	1.03	[76]
Three Gorges Dam region, China	24100	-	52	-	14.2	66	149	13	0.29	[77]
Africa										
Tadla plain, Morocco	19249.27	-	138.10	-	-	32.72	162.11	31.72	0.92	[78]

The results were compared to the average metal contents in soils of Poland. It is worth underlining that each soil environment is unique in terms of the geological structure, relief, climate, or socio-economic characteristics, etc. Moreover, the results are usually obtained using different research methods, then a comparison may be only estimated. However, it is worth noting that in the case of soils in the Bug River catchment, the average elemental contents were much lower than the average contents of these metals in soils of Poland [23, 56] and Europe [45, 57–61] and in other parts of the world [66–73]. The Bug River catchment is subtly affected by humans. Forested areas and the river valley are particularly valued, distinguished by a high degree of naturalness and high scenic values. About 14% of the Bug River basin area is covered by international, national, or regional law protection. The most important ones are the Polish-Ukrainian Polesie West International Biosphere Reserve and 18 areas of The General Directorate for Environmental Protection Natura 2000 created in the Polish Bug River basin.

Polluton indicators

Geoaccumulation index I_{geo}

I_{geo} values were calculated for each metal in arable soils and presented in a box plot (Fig. 2). The geoaccumulation index is a parameter used in determining the contamination of soils by toxic elements [2, 5, 17].

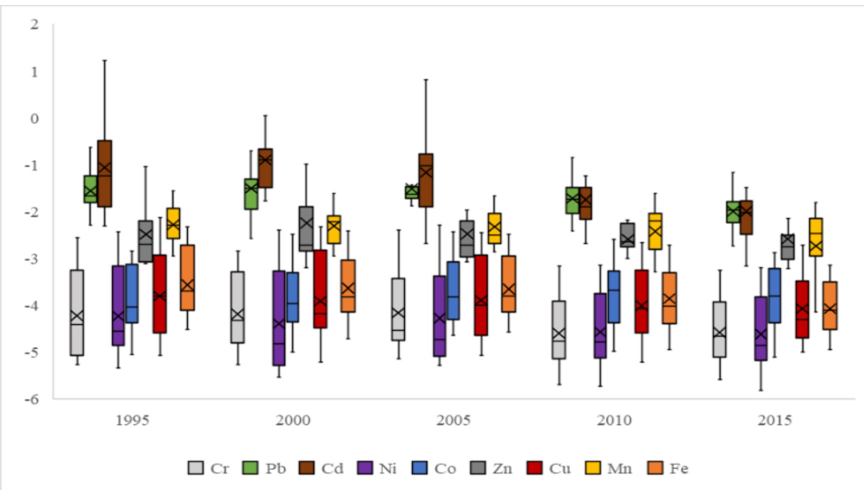

Fig. 2. I_{geo} values for the studied metals in each study period

The mean values for each I_{geo} element were ranked as follows: Cd > Pb > Zn > Mn > Co > Fe > Cu > Cr > Ni. The highest average I_{geo} values occurred for Cd and Pb. According to *G.*

Müller's [24] standard level of contamination, the average I_{geo} values indicate that arable soils in the Bug River catchment are uncontaminated. Analysis of the maximum I_{geo} values for Cd (1.2, 0.9, 0.8, and 0.6) for research point located in Józefin, indicates class 1 (not polluted too moderately polluted). At the same research point, Pb was between 0 and 1, indicating low contamination. This observation coincides with the analysis of metal content in the soil. In the village of Józefin, the soil has the highest organic matter content (average 5.55%). According to *A. Karczewska* [74], heavy metals may be bound by organic matter either by exchange sorption, complexation, or chelation. The enrichment of soil in Cd and Pb in Józefin is related to local sources of pollution also (chalk mine, cement plant, alternative fuel production plant, steel construction plant, glassworks, concrete, and building materials production plant).

Contamination factor CF

Contamination factor (CF) supply information about individual metal concentrations at a specific location relative to the geochemical background (Fig. 3). CF values ranged for: Fe (0.05-0.29), Mn (0.06-0.50), Cu (0.04-0.34), Co (0.04-0.27), Ni (0.02-0.30), Cr (0.03-0.28), Zn (0.16-1.02), Pb (0.19-1.71), Cd (0.17-3.47). Of the four CF contamination categories (low, moderate, considerable, very high), the mean values for all metals tested indicated low contamination. CF values for Cd indicated moderate contamination in 11 soil samples in villages: Polatycze (1 sample), Sławacinek Stary (3 samples), Rybie (3 samples), Józefin (4 samples), and significant contamination in 1 sample in Józefin collected in 1995. In contrast, CF values for Pb (3 samples) indicated moderate contamination in Józefin in the years: 1995, 2000, and 2005, and also the locality showed moderate Zn contamination (Rybie at 2015).

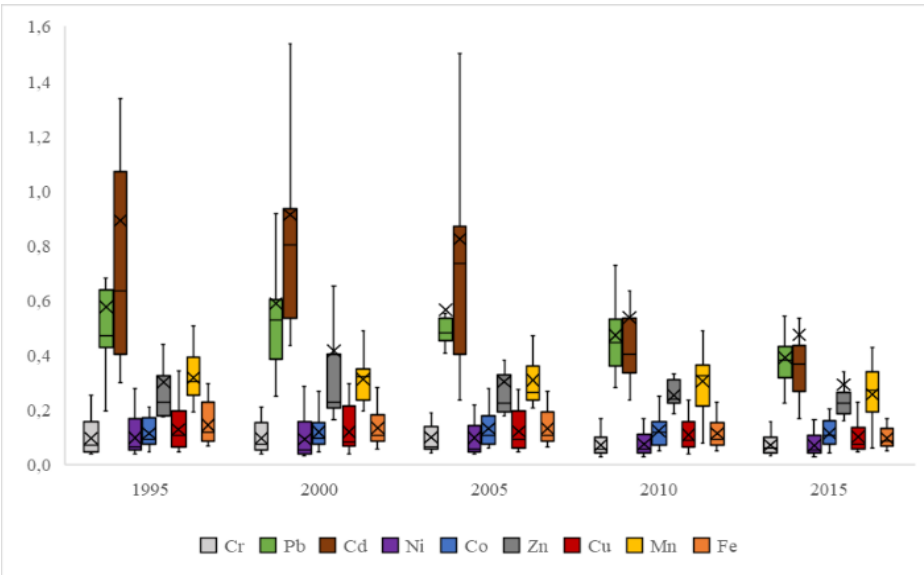

Fig. 3. CF values for the metals studied in each study period

Pollution load index PLI

The status of soil contamination by metals was evaluated using the pollution load index (PLI). The PLI ranged from 0.09 to 0.48, with an average of 0.19, which indicates that the soils analyzed are uncontaminated. PLI = 1 indicates a load of toxic elements near the background level, while PLI > 1 means contamination with toxic substances. Of the 15 locations, the PLI value indicated the highest value in Józefin, but still lower than 1 (Fig. 4).

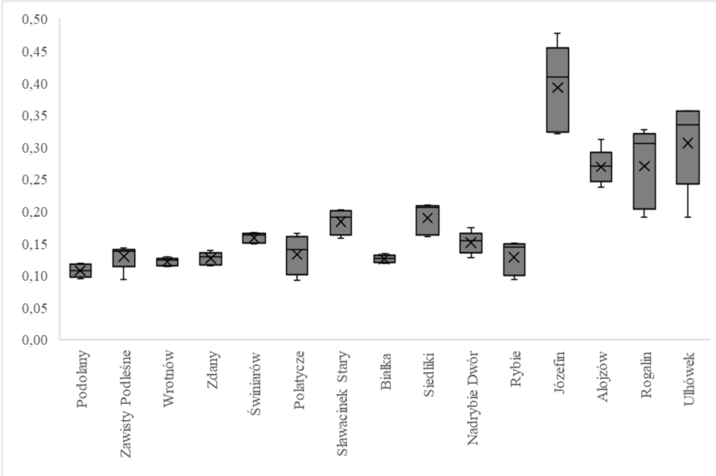

Fig. 4. PLI values for research points

Spatial distribution of metals in soils

The spatial distribution of iron and manganese in soils indicates that these elements have quite similar geochemistry and probably origin. Manganese and iron are redox-sensitive elements and tend to coexist as oxides and hydroxides [75]. The contents of both these metals are the highest in soil among all the studied elements. The spatial distribution maps of Fe, Mn, Cu, Co, Ni, Cr, Zn, Pb and Cd (Fig. 5) show similarities, and although they differ in detail, some general regularities may be observed.

The most enriched research points are Józefin, Alojzów, Ulhówek and Rogalin. It seems that similar phenomena influence the spatial distribution of metals, as does their origin, which was proven by correlation coefficients between individual metal pairs ranging from 0.68 (for Co - Cu) to 0.91 (for Cr - Ni) (Table 4).

Table 4. Spearman correlation matrix for soil metal content. Correlation is significant at the 0.05

	Cr	**Mn**	**Pb**	**Co**	**Cd**	**Zn**	**Ni**	**Fe**	**Cu**	**pH_{KCl}**	**OM**
Cr	1.00										
Mn	0.69	1.00									
Pb	0.49	0.44	1.00								
Co	0.75	0.80	0.44	1.00							
Cd	0.48	0.27	0.70	0.18	1.00						
Zn	0.52	0.38	0.62	0.45	0.49	1.00					
Ni	0.91	0.70	0.49	0.78	0.42	0.52	1.00				
Fe	0.92	0.76	0.47	0.82	0.39	0.53	0.87	1.00			
Cu	0.85	0.56	0.40	0.68	0.40	0.51	0.82	0.83	1.00		
pH_{KCl}	0.49	0.38	0.44	0.31	0.52	0.61	0.54	0.44	0.45	1.00	
OM	0.41	0.08	0.34	0.12	0.47	0.44	0.41	0.31	0.51	0.44	1.00

These phenomena also appear to be consistent with observations for Fe and Mn because spatial models of their distributions show many similarities. What distinguishes Cu, Co, Ni, Cr, and Zn from Fe and Mn is their origin, which in this instance seems to be caused by human activities. On the other hand, a comparison between studied soil and the local geochemical background values [27] showed only a slight exceedance, visible especially for Ni and Zn. It means that the soils analyzed are little enriched in these metals, but they pose a threat to the natural environment of the Bug River catchment.

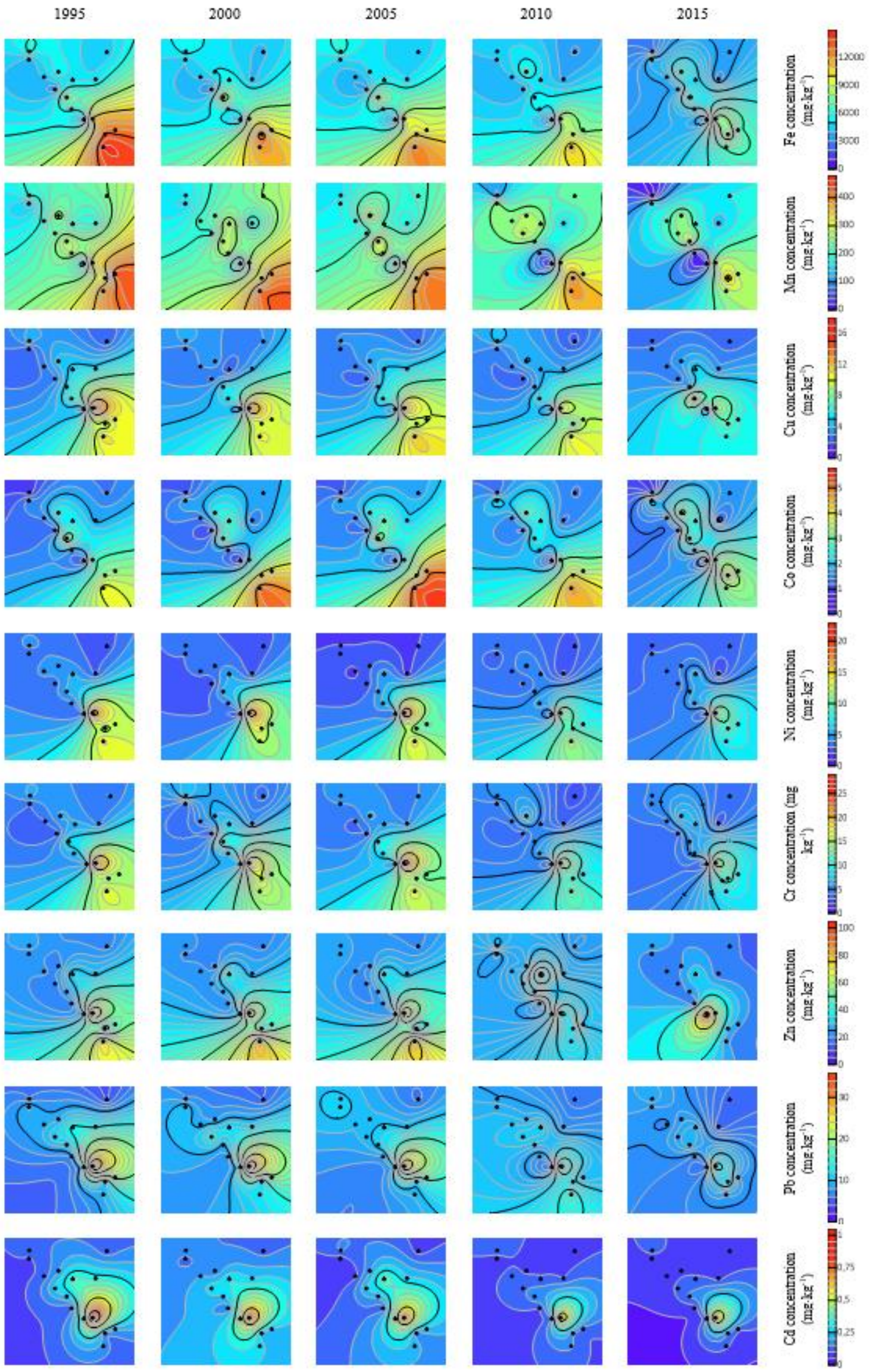

Fig. 5. Distribution of heavy metals in soils of the Bug River catchment area

Spatial distributions of Pb and Cd in 15 study points show relatively low variability, except Józefin, where the highest amounts of these elements occurred. The soils analyzed were most enriched in Cd and Pb. It is difficult to point out specific factors that influence the spatial distribution of these elements in soils - we may suggest the influence of local sources of pollution: industry, transport, mineral and organic fertilization, and precipitation. In the time interval covering 25 years, the levels of the analyzed metals did not change significantly, but an improvement in the soil environment in 2010 and 2015 is visible.

Identification of pollution sources using statistical analyses

The statistical inference process began with a basic analysis of the content of studied metals and the properties of the soils of the Bug River catchment. Coefficients of variation are used to reflect the variation of the observed values of each indicator from the mean. The greater the CV value, the greater the variability. As shown in Table 2, CV values of all metals followed the order Cd (82.86%) > Ni (68.95%) > Cu (60.41%) > Cr (58.35%) > Zn (53.22%) > Fe (46.46%) > Pb (44.94%) > Co (37.74%) > Mn (31.79%). The high CV value for Cd indicates high variability and suggests that the sources of metals may come from external consideration. The least variability was shown for Mn (31.79%) simultaneously, the level of Mn in the studied soils follows the normal distribution. No normal distribution was obtained for the other metals and parameters. The low variability of Mn may signify a natural origin of this element in the soils of the Bug catchment in contrast to Cd and Ni. Therefore, the basic analyses indicated HMs, the origin of which should be explained in the course of further statistical analyses. Based on the analysis of the normal distributions of the obtained test results, it was decided to look for relationships between parameters using Spearman's non-parametric correlation.

Table 4 presents a series of significant correlations, which are divided into groups. The first group of correlations of the analyzed parameters concerns the metal binding mechanisms in the soils of the Bug catchment (Mn-Cr $r = 0.69$), (Mn-Co $r = 0.80$), (Mn-Ni $r = 0.70$), (Mn-Fe $r = 0.76$), (Mn-Cu $r = 0.56$). The above correlations relate to the processes of metal binding by manganese oxides. Manganese present in the soil solution significantly increases the adsorption of metals in soils [40]. The second component of soils, even more strongly binding metals, are iron compounds, which play a key role in the immobilization processes of trace elements through adsorption and occlusion [76]. Calculations showed strong relationships between Fe and the following metals: Cr $r = 0.92$, Mn $r = 0.76$, Co $r = 0.82$, Ni $r = 0.87$, Cu $r = 0.83$. Another component of soils actively involved in metal fixation is organic matter (OM). *S.M. Shaheen et al*. [77] found that the total content of Cd, Cr, Cu, Fe, Mn, Ni, and Zn was higher in the MO-rich soil than in the adjacent MO-poor soil. Also, *T. Zhou et al*. [78] pointed out the key role of organic matter in soil Cd and Zn content.

The study showed moderate relationships between OM and the following metals: Cr $r = 0.41$, Cd $r = 0.47$, Zn $r = 0.44$, Ni $r = 0.41$, Cu $r = 0.51$. Soil pH is involved in reducing the mobility of metals, which is related to their immobilization [40]. The mean correlations presented in the table confirm the above thesis: pH (KCl) - Cr $r = 0.49$, Pb $r = 0.44$, Cd $r = 0.52$, Zn $r = 0.61$, Ni $r = 0.54$, Cu $r = 0.45$. The second group of correlations concerned the interdependence of metals of different binding strengths with their common sources, which will be identified and verified in the progress of further statistical analyses. Statistical multivariate analyses, which are essentially statistical models based on a large number of variables, were used to identify the processes and sources of the studied metals. The first is the multi-factor analysis - (FA), which is aimed at advanced data mining and effective reduction of the studied parameters. The second one is Ward's statistical cluster analysis, which is mainly used to identify the sources of substances in the environment. Based on factor analysis (FA), two factors were detected in the structure of commanded variables. The first factor (Factor 1), explaining as much as 68% of the variation, is correlated with Pb, Cd, Zn and organic matter (OM). Two processes can be identified here. The first one is related to the binding of soil organic matter with Pb, Cd, and Zn, which results are organometallic compounds. The second one is associated with enrichment (pollution) of soils of the Bug River basin with these elements. A try to discover the sources of metals within the catchment will be made in the further course of analysis. The second factor (Factor 2) explains only 19% of the variability of the analyzed parameters (Table 5). The distribution of factor loads indicates ongoing processes of Cr, Co, Ni, and Cu binding by Mn and Fe oxides, as well as processes of metal delivery from nearby sources, which will be identified below.

Table 5. Factor analysis (FA) results, factor loadings >0.70

	Factor 1	Factor 2
Cr	0.69	**0.70**
Mn	0.07	**0.95**
Pb	**0.91**	0.26
Co	0.08	**0.97**
Cd	**0.97**	0.01
Zn	**0.70**	0.31
Ni	0.69	**0.71**
Fe	0.32	**0.93**
Cu	0.63	**0.72**
pH_{KCl}	0.64	0.47
OM	**0.95**	0.09
% of total variance	**68**	**19**

Figure 6 shows the dynamics of changes in factor values representing the two factors described earlier. The factor values show the impact of the detected and previously described factor at each measurement and control point. The leading influence of factor 1 occurred at the points Józefin and Rybie, and factor 2 at the points Ulhówek and Alojzów.

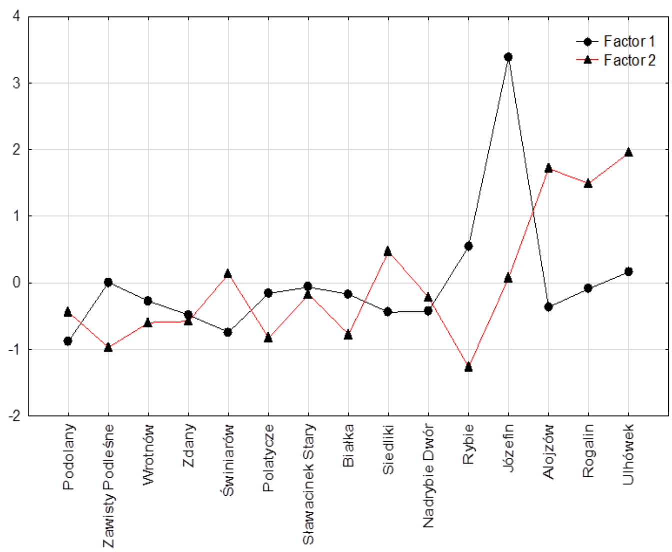

Fig. 6. Linear variability of factor values (FA) in soils in the Bug River catchment area

To verify the obtained model, reasons for the actual detected and identified processes and their location looked for. It should be noted following industrial plants are located in the Józefin:

chalk mine, cement plant, alternative fuel production plant, truck service, aggregate supplier, industrial gas production plant, steel construction plant, glassworks, concrete, and building materials production plant, and two fuel depots. The listed industrial facilities may be a source of emissions of previously detected Pb, Cd and Zn in the vicinity of the site. Transportation is also a source of these metals in soil. Since the investigated soils have features of agriculturally used soils, the sources of variability of their chemical composition can be additionally identified. It may be related mainly to the organic and mineral fertilization carried out in the studied areas. The effect here may be primarily an increase in the content of organic matter and metals added to mineral fertilizers (Cd and Cu), which was confirmed by FA analysis. Significant points for factor 2 are Alojzów and Ulhówek, where Cr, Co, Ni and Cu, as well as Mn and Fe, were detected. The sugar mills in Alojzów and the store of building materials, fuel, metallurgical products, and fertilizers in Ulhówek may be active sources of detected metals, but with lower potency, as shown in the FA analysis. The second factor explains only 19% of the variability of the studied parameters.

Ward's version of multivariate statistical cluster analysis (CA) was performed to verify previously detected metal sources. Cluster analysis base on Euclidean distances. The results of the CA analysis depended primarily on the obtained metal contents in the soils. Based on the CA analysis, two verifiable clusters (groups) were detected. The first group consisted of the following measurement and control points: Ulhówek, Alojzów, Rogalin, Józefin, and Siedliki. The second group consisted of the remaining research points. The first group of locations includes towns with the most developed industry among all surveyed. The list of localities in the first group of CA analysis mostly coincides with that obtained earlier from the FA analysis (Fig. 7).

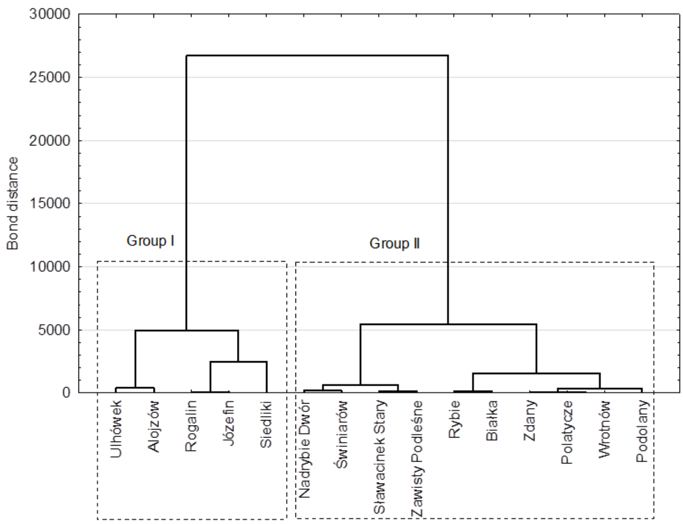

Fig. 7. Dendogram based on hierarchical clustering (CA - Ward)

Conclusions

This paper is a summary of a long-term study of arable soils in the Bug River catchment area. A large set of data and the usage of different statistical methods made it possible to highlight and draw attention again to some environmental issues. The average MH contents in the arable soils of the Bug River catchment occurred in the following descending order: Fe > Mn > Zn > Pb > Cr > Ni > Cu > Co > Cd. The analyses conducted showed that all metals are at the geochemical background level except for a slight enrichment in Cd and Pb, especially in Józefin.

The studied coefficients (I_{geo}, CF and PLI) can be considered as the best tool to evaluate HM pollution - they helped to determine the degree of anthropogenic impact on soils. The highest values of the calculated ratios, which means the sublime influence of human activity on the soil environment, were found for Cd. For the other elements (Fe, Mn, Zn, Pb, Cr, Ni, Cu and Co), the calculated ratios were low, indicating that the environment was not polluted with these metals at all or to a low extent.

Spearman's correlation analysis proved that all the studied elements came from both natural and anthropogenic sources and their contribution was variable. HMs were bound by organic matter and iron and manganese oxides. Cd, Pb, and Zn contents in soils were largely related to human activities. Statistical models (FA and CA) identified two sources of HMs. The first source of pollution is local industry, communication, and precipitation. The second source is related to organic fertilization, mineral fertilization, and application of plant protection products. The present study demonstrated the complex relationships shown by FA and CA methods between HMs sources and their contents in soils.

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