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DOI: 10.2478/cdem-2021-0004 CHEM DIDACT ECOL METROL. 2021;26(1-2):55-64

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THE ASSESSMENT OF HEAVY METAL CONTAMINATION OF THE CULTIVATED SOILS IN THE ODRA RIVER FLOODPLAIN

Abstract: The aim of the study was to assess the contamination of selected heavy metals in cultivated soils of the Odra river floodplain. The heavy metals Mn, Fe, Cu, Zn, Ni, Cd and Pb were determined in soil samples collected in the autumn of 2020 - after the vegetation period of plants from designated measurement points. Concentrations of the analytes were measured using an atomic absorption spectrometer (F-ASA). A comparison was made between concentrations of heavy metals in soil samples collected from areas flooded in 1997 and from areas flooded as a result of rainfall, snowmelt and winter floods. The results of the studies were compared with the data for soils taken from non-flooded areas. The studies confirmed enrichment of soils subjected to precipitation, snowmelt and winter floods in heavy metals. Also samples taken from two measurement points located on floodplains of the Odra river were characterised by high concentrations of Zn, Cd and Pb.

Keywords: soil, floodplain, Odra river, heavy metals, atomic absorption spectrometry

Introduction

With increasing industrialisation, the content of, among others, heavy metals in various components of the environment is successively increasing, posing a great threat to flora and fauna [1-3]. Heavy metals, which belong to the group of basic environmental pollutants, pose a particular threat to human health and many of them are carcinogens [4-7]. The target organs and clinical manifestations of chronic exposures to the metal are given in Table 1 [8]. The distribution of heavy metals in soils is differentiated and their concentrations depend on the composition of the parent rock and on natural and anthropogenic pollution sources, e.g. traffic roads, industrial plants, agricultural activities or on floodplains/watercourse analyte pollution [9, 10]. The chief toxic metals in industrial effluents are shown in Table 2 [8].

From a physiographic point of view, Opole voivodship is a part of the upper Odra river basin with a relatively high frequency of flood events. In the upper Oder basin the occurrence of major floods is favoured by meteorological and topographic conditions, the shape of the drainage basin and the layout of the river network. The semi-circular shape of the river basin causes simultaneous inflow of flood waters from all directions of the basin. The Popielow and Lubsza Communes are especially endangered by rainfall, snowmelt and winter floods [11]. These areas were also flooded in July 1997.

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Table 1

Clinical aspects of chronic toxicities [8]

Metal	Target organs	Primary sources	Clinical effects
Arsenic	Pulmonary, nervous system, skin	Industrial dusts, medicinal uses of polluted water	Perforation of nasal septum, respiratory cancer, peripheral neuropathy: dermatomes, skin, cancer
Cadmium	Renal, skeletal pulmonary	Industrial dusts and fumes and polluted water and food	proteinuria, glucosuria, osteomalacia, aminoaciduria, emphysemia
Chromium	Pulmonary	Industrial dusts and fumes and polluted food	Ulcer, perforation of nasal septum, respiratory cancer
Manganese	Nervous system	Industrial dusts and fumes	Central and peripheral neuropathies
Lead	Nervous system, hematopoietic system, renal	Industrial dusts and fumes and polluted food	Encephalopathy, peripheral neuropathy, central nervous disorders, anemia
Nickel	Pulmonary, skin	Industrial dusts, aerosols	Cancer, dramatis
Tin	Pulmonary system, nervous	Medicinal uses, industrial dusts	Central nervous system disorders, visual defects and EEG changes, pneumoconiosis
Mercury	Renal, nervous system	Industrial dusts and fumes and polluted water and food	Proteinuria

Table 2

Toxic metals in industrial effluents [8]

Metal	Manufacturing industries
Arsenic	phosphate fertiliser, metal hardening, paints and textile
Cadmium	phosphate fertiliser, electronics, pigments and paints
Chromium	metal plating, tanning, rubber and photography
Copper	plating, rayon and electrical
Lead	paints, battery
Nickel	electroplating, iron steel
Zinc	galvanising, plating iron and steel
Mercury	chlor-alkali, scientific instruments, chemicals

The problem of soil pollution is very important due to the possibility of direct or indirect negative impact on human health [12]. The Regulation of the Minister of the Environment of 1 September 2016 on the manner of conducting the assessment of contamination of the earth's surface defines the limit values of concentrations of heavy metals and other pollutants in soil or land. This Regulation takes into account the current and planned functions of soils and land, and qualifies them for appropriate management, taking into account the limit values of analyte concentrations given in this Regulation [13].

Contaminants from soils can enter the human body indirectly through the consumption of plants that have taken up harmful components from contaminated soils, or have been contaminated by atmospheric deposition of particles emitted by industrial plants, or have been subject to wind erosion or rain ablation [14, 15]. The physicochemical properties of soils influence the uptake of elements by plants and their incorporation into the food chain. Of these, soil pH is the most important for heavy metal accumulation in plants. In an acidic environment, plants can take up large amounts of these elements, especially Cd, Zn and Ni, even from poorly polluted soils [14, 15].

The aim of the study was to assess the contamination with selected heavy metals of cultivated soils of floodplains in the Opole voivodeship located in the Odra river basin.

Research methodology

Soil samples for the study were collected in the autumn season of 2020 after the vegetation period of the plants. The material was collected from four areas, each with 6 samples of topsoil (Fig. 1). Study area no. I (Czepielowice village, Lubsza commune) is the area which was flooded in the so-called flood of the millennium in Poland in 1997. Soil collected from area no. II (Nowe Kolnie, Lubsza commune) was regularly flooded during rainfall, snowmelt and winter floods. Study site III (Kurznie, Popielow commune) was not affected by floods. Area IV (Koscierzyce, commune of Lubsza) is located in the direct vicinity of the Odra river.

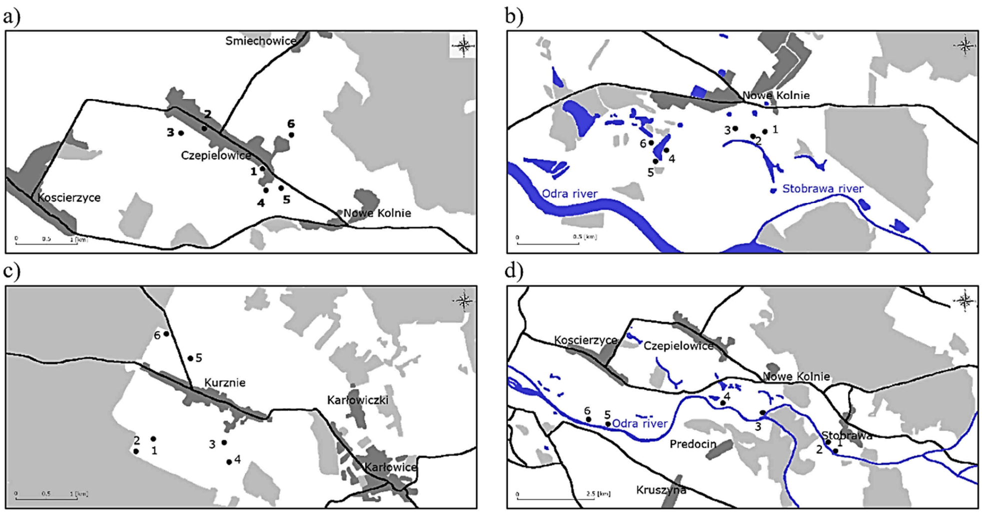


Fig. 1. Areas from which soil samples were taken: a) Czepielowice, b) Nowe Kolnie, c) Kurznie, d) Koscierzyce

The GPS location of the measurement sites is shown in Table 3.

Apparatus and reagents

Representative (averaged) soil samples of 0.500 ±0.001 g d.m. (d.m. - dry mass) were mineralised in a mixture of nitric acid(V) and perhydrol (HNO_3 65 % : H_2O_2 30 % = 3:1) in a Speedwave Four microwave mineraliser from Berghof, DE. The mineralisation process was carried out at 180 °C. Solutions were prepared using MERCK reagents. Heavy metals (Mn, Fe, Ni, Cu, Zn, Cd and Pb) in mineralised samples were determined by atomic absorption spectrometry (AAS) using an iCE 3500 instrument from Thermo Electron Corporation (USA). The calibration of the apparatus was performed using standards from ANALYTIKA Ltd. (CZ).

Table 3

GPS location of measurement points

Number of measuring site	GPS location
I Czepielowice, commune of Lubsza, Opole voivodeship	
1	50°52'21.8"N, 17°34'20.9"E
2	50°52'42.7"N, 17°33'29.8"E
3	50°52'41.9"N, 17°33'16.7"E
4	50°52'11.6"N, 17°34'19.9"E
5	50°52'10.7"N, 17°34'36.7"E
6	50°52'36.4"N, 17°34'42.9"E
II Nowe Kolnie, commune of Lubsza, Opole voivodeship	
7 (1)	50°51'44.3"N, 17°35'37.3"E
8 (2)	50°51'41.6"N, 17°35'32.4"E
9 (3)	50°51'43.9"N, 17°35'23.8"E
10 (4)	50°51'38.3"N, 17°34'56.7"E
11 (5)	50°51'37.2"N, 17°34'53.8"E
12 (6)	50°51'40.0"N, 17°34'52.7"E
III Kurznie, Popielow Commune, Opole voivodeship	
13 (1)	50°52'51.0"N, 17°39'25.1"E
14 (2)	50°52'47.1"N, 17°39'07.1"E
15 (3)	50°52'50.7"N, 17°40'23.5"E
16 (4)	50°52'41.3"N, 17°40'23.6"E
17 (5)	50°53'36.5"N, 17°39'55.8"E
18 (6)	50°53'48.2"N, 17°39'38.2"E
IV Koscierzyce, commune of Lubsza, Opole voivodeship	
19 (1)	50°50'40.3"N, 17°37'32.0"E
20 (2)	50°50'44.9"N, 17°37'21.8"E
21 (3)	50°51'14.7"N, 17°35'32.2"E
22 (4)	50°51'24.1"N, 17°34'14.2"E
23 (5)	50°51'06.3"N, 17°31'08.2"E
24 (6)	50°51'09.7"N, 17°30'35.0"E

Quality control

Table 4 shows the detection and quantification limits for heavy metals characterising the iCE 3500 spectrometer [16].

Table 4

The instrumental detection limits (*IDL*) and instrumental quantification limits (*IQL*) for the spectrometer iCE 3500 [mg/dm^3] [16]

Metal	*IDL*	*IQL*
Mn	0.0016	0.020
Fe	0.0043	0.050
Ni	0.0043	0.050
Cu	0.0045	0.033
Zn	0.0033	0.010
Cd	0.0028	0.013
Pb	0.0130	0.070

The values of the highest concentrations of the standards used for calibration (2.0 mg/dm^3 for Cd, 5.0 mg/dm^3 for Cu, Zn, Ni and Pb, 7.5 mg/dm^3 for Mn and 10 mg/dm^3 for Fe) were taken as the limit of the linear dependence of signal on concentration.

Table 5 shows the heavy metal concentrations determined in the certified reference material BCR-482 lichen, produced by the Institute for Reference Materials and Measurements, Belgium.

Table 5

Comparison of measured and certified concentrations in BCR-482 lichen [17]

Metal	BCR-482 *lichen*		AAS		*Dev.* **
	Concentration	**± Measurement uncertainty**	**Average**	**±*SD* ***	
	[mg/kg d.m.]				**[%]**
Mn	33.0	0.5	31.70	0.68	–3.9
Fe	804	160	771	154	–4.1
Ni	2.47	0.07	2.16	0.32	–13
Cu	7.03	0.19	6.63	0.17	–5.7
Zn	100.6	2.2	95.1	2.3	–5.5
Cd	0.56	0.02	0.53	0.03	–5.3
Pb	40.9	1.4	38.2	1.0	–6.6

* Standard deviation

** Relative difference between the measured (c_z) and certified (c_c) concentration $100\% \cdot (c_z - c_c)/c_c$

Results and analysis

Table 6 shows the concentrations of heavy metals determined in the analysed soil samples.

Table 6

Concentrations of selected analytes determined in soil samples [mg/kg d.m.]

Number of measuring site	Mn	Fe	Ni	Cu	Zn	Cd	Pb
1	565	10688	5.51	17.0	111	1.15	28.1
2	964	12600	10.2	20.2	167	0.98	40.6
3	472	13506	5.04	9.85	48.0	0.87	25.3
4	649	13931	5.46	11.2	58.3	0.92	24.2
5	442	9657	3.52	8.91	38.9	< 0.65	25.1
6	213	10282	2.62	7.67	55.6	0.97	20.3
7	1552	50170	45.9	104	1575	6.66	229
8	1754	50809	46.6	107	1486	6.80	217
9	1849	49564	44.6	90.7	1199	5.64	219
10	1861	51417	47.3	83.4	1104	5.06	213
11	1391	41409	37.4	68.0	861	4.25	200
12	1540	43840	43.5	78.4	1071	4.88	221
13	485	7055	3.96	7.43	49.8	0.67	30.0
14	478	7945	3.21	6.13	42.8	0.78	27.6
15	406	6889	3.49	7.23	64.9	1.02	31.8
16	505	9431	< 2.50	11.8	74.0	0.71	24.7
17	757	12318	7.05	10.0	53.9	1.15	29.1
18	376	6661	2.55	5.20	37.4	< 0.65	21.1
19	413	18784	17.7	29.8	482	2.02	91.9
20	983	32287	31.9	63.0	1004	4.34	172

Number of measuring site	Mn	Fe	Ni	Cu	Zn	Cd	Pb
21	659	22177	21.2	41.6	604	3.00	114
22	1270	43513	46.4	92.5	1534	6.88	151
23	621	20097	17.9	19.1	211	1.66	43.9
24	782	19294	18.1	23.8	329	1.91	61.6

Table 7 presents minimum and maximum values of concentrations of analysed elements determined in soil samples collected from selected areas differing in degree of exposure to flooding by the Odra river. The coefficient of variation *CV* and standard deviation for the measured concentrations of the analytes were also calculated.

Table 7

Values of min., max., standard deviation of concentrations of selected analytes determined in soil samples and value of coefficient of variation *CV*

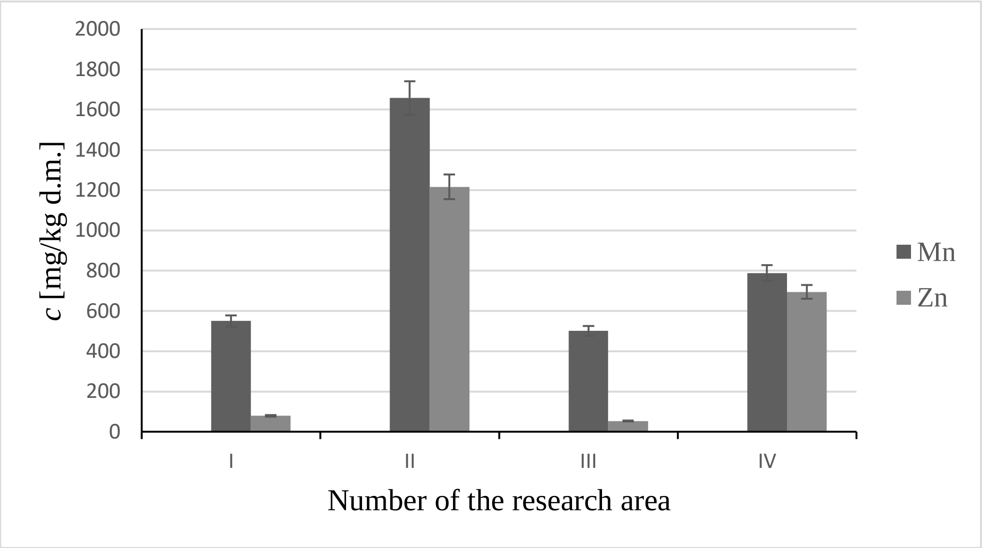
Parameter	Mn	Fe	Ni	Cu	Zn	Cd	Pb
I Czepielowice, commune of Lubsza, Opole voivodeship							
Min. [mg/kg d.m.]	213	9657	2.62	7.67	38.9	< 0.65	20.3
Median [mg/kg d.m.]	518	11644	5.25	10.51	56.9	0.94	25.2
Max. [mg/kg d.m.]	964	13931	10.2	20.2	167	1.15	40.6
±*SD*	250	1801	2.63	5.00	49.7	-	7.00
CV [%]	45.4	15.3	48.7	40.1	62.3	-	25.7
II Nowe Kolnie, commune of Lubsza, Opole voivodeship							
Min. [mg/kg d.m.]	1391	41409	37.4	68.0	861	4.25	200
Median [mg/kg d.m.]	1653	49867	45.2	87.1	1151	5.35	218
Max. [mg/kg d.m.]	1861	51417	47.3	107	1575	6.80	229
±*SD*	191	4180	3.60	15.2	269	1.02	10.0
CV [%]	11.5	8.73	8.17	17.1	22.1	18.4	4.55
III Kurznie, Popielow Commune, Opole voivodeship							
Min. [mg/kg d.m.]	376	6661	<2.50	5.20	37.4	< 0.65	21.1
Median [mg/kg d.m.]	482	7500	<3.35	7.33	51.8	<0.75	28.4
Max. [mg/kg d.m.]	757	12318	7.05	11.8	74.0	1.15	31.8
±*SD*	135	2179	-	2.48	13.7	-	3.90
CV [%]	26.9	26.0	-	31.2	25.4	-	14.3
IV Koscierzyce, commune of Lubsza, Opole voivodship							
Min. [mg/kg d.m.]	413	18784	17.7	19.1	211	1.66	43.9
Median [mg/kg d.m.]	720	21137	19.7	35.7	543	2.51	103
Max. [mg/kg d.m.]	1270	43513	46.4	92.5	1534	6.88	172
±*SD*	302	9927	11.6	28.1	494	2.01	50.0
CV [%]	38.3	38.1	45.2	62.5	71.2	61.1	47.2

- not calculated

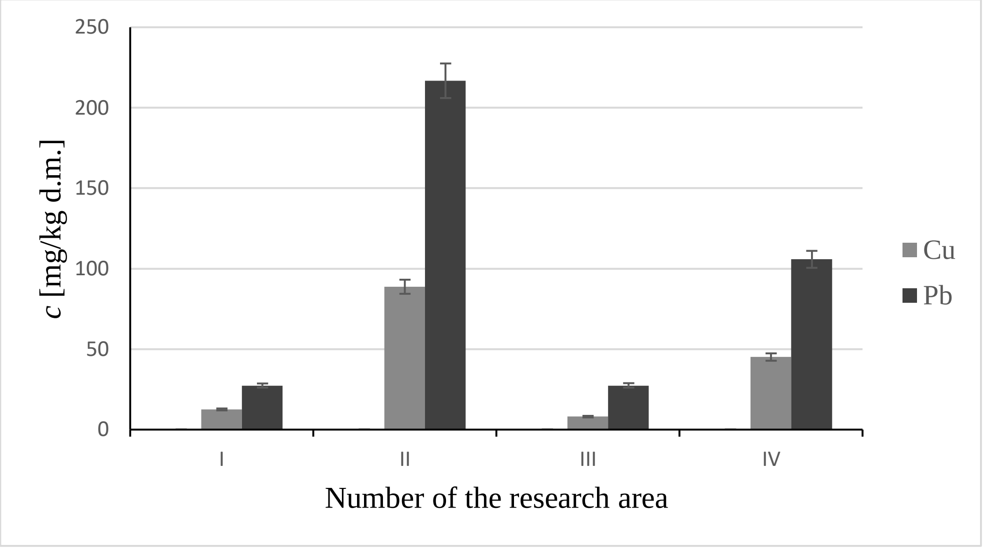
The highest concentrations of the analysed elements were determined in soil samples collected from the second study site (Nowe Kolno, Lubsza commune). This area is systematically flooded during rainfall, snowmelt and winter floods. The soil taken from the area flooded in 1997 (Czepielowice, commune of Lubsza) was characterised by much lower concentrations of analytes.

The graphs in Figure 2 show the mean values of heavy metal concentrations determined in soil samples taken from the four study sites.

a)



b)



c)

d)

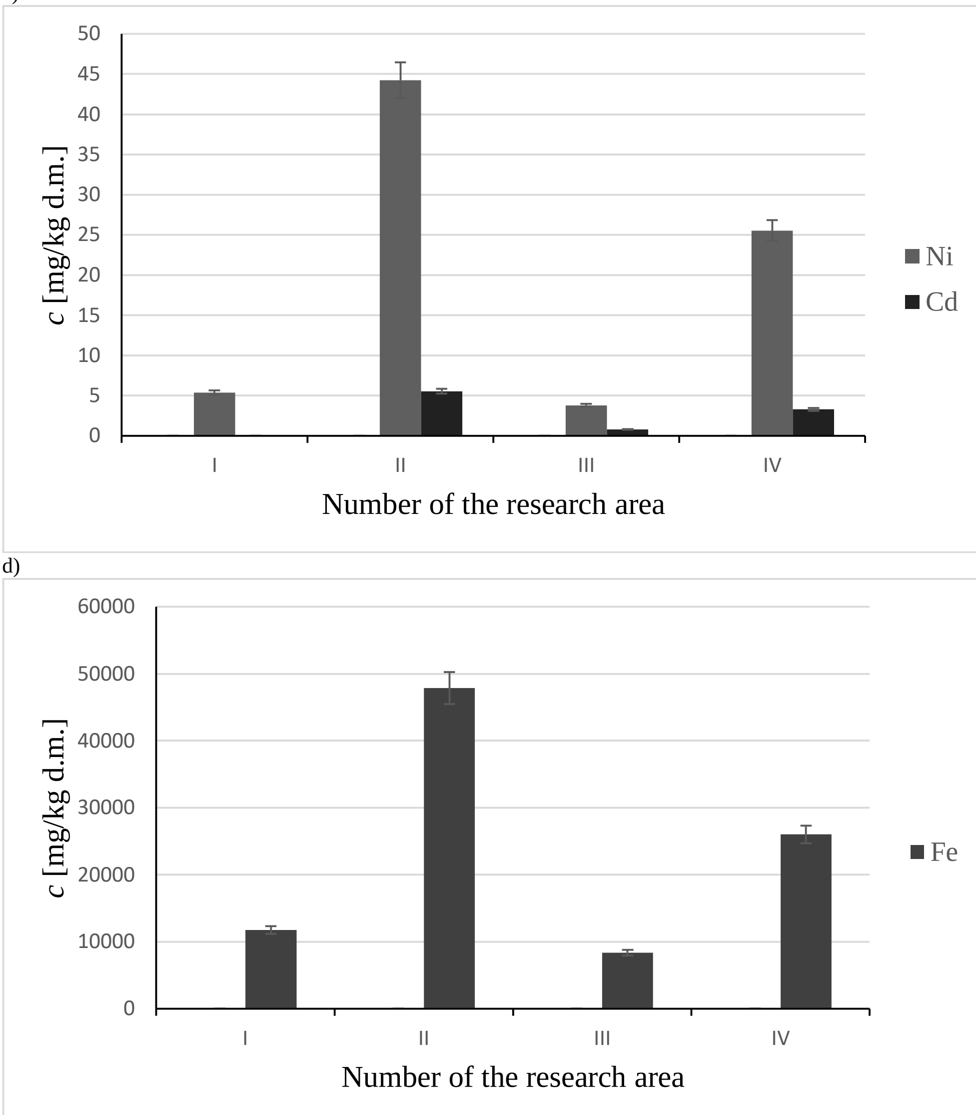


Fig. 2. Mean values of heavy metal concentrations determined in soil samples taken from the four study sites

Analysing the results of the conducted studies, it can be clearly stated that the study site No. II was characterised by the highest average concentrations of all analysed elements in the topsoil: Mn, Fe, Ni, Cu, Zn, Cd and Pb. The lowest concentrations of Cd and Pb were determined in soil sampled from study site I (Czepielowice, Lubsza commune) and of the remaining analytes in topsoil samples from study site III (Kurznie, Popielow commune).

For all soil samples taken from Site II, the permissible values for Zn, Cd and Pb, as specified in the Regulation of the Minister of Environment on soil and land quality standards, amounting for soil group B: for Zn - 300 mg/kg, for Cd - 4 mg/kg and for Pb - 100 mg/kg were exceeded [18]. Exceeding of permissible concentration of Zn, Cd and Pb was also found in soil collected from measurement points No. 20 and 22 located in the study area IV. No exceedances of Ni, Cu concentrations were found in all analysed soil samples [18].

The study confirmed enrichment of soils subjected to precipitation, snowmelt and winter floods in heavy metals. Also, samples taken from two measurement points located in floodplains of the Odra river (study area IV) were characterised by high concentrations of Zn, Cd and Pb, and the influence of the river itself on the level of contamination of agricultural soils is also confirmed by literature data [19]. Soil sampled from study site III, not subjected to flooding, was characterised by the lowest concentrations of Mn, Fe, Ni, Cu and Zn. On the other hand, the lowest concentrations of Cd and Pb were determined in soil taken from study area I, flooded in 1997.

Conclusion

Heavy metals include both elements essential for living organisms and elements with as yet unknown physiological roles. Their common feature is that even those which are essential in trace amounts have a toxic effect on plants and animals when the permissible dose is exceeded. The most toxic metals are cadmium, mercury and lead.

Soil sampled from all sampling points located in the village of Nowe Kolnie, commune of Lubsza and from two sampling points located in the village of Koscierzyce, commune of Lubsza, was characterised by exceeding permissible, according to [18] concentrations of Zn, Cd and Pb. According to our research, their sources in soils used for agricultural purposes are among others the processes of frequent flooding as a result of periodic floods as well as enrichment by river flood waters.

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