Journal of Ecological Engineering
Volume 15, No. 2, April 2014, pp. 53–59
DOI: 10.12911/22998993.1094978

Research Article

CONTENT OF COPPER AND NICKEL IN SOILS OF VISTULA RIVER CATCHMENT

Elżbieta Skorbiłowicz[1], Anna Samborska[1]

[1] Department of Technology in Engineering and Environmental Protection, Technical University in Bialystok, Wiejska 45A, 15-351 Bialystok, Poland, e-mail: e.skorbilowicz@pb.edu.pl; anulkasamborska@gmail.com

Received: 2014.01.05
Accepted: 2014.03.10
Published: 2014.04.04

ABSTRACT
Metal pollution attracts growing interest mainly due to their toxic effects on the entire natural environment. It is therefore necessary to monitor, not to exceed acceptable standards of elements in ecosystems. Heavy metals in soils are derived from natural and anthropogenic sources. The purpose of this article is to present the contents of copper and nickel in agricultural soils within the Vistula river catchment based on research carried out by the Institute of Soil Science and Plant Cultivation in the period since 1995 to 2010. The assessment of a degree of soil contamination by these elements according to standards has been also performed. It has been proven that about 91% of agricultural soils in Vistula river catchment shows natural (0°), while approximately 9% higher (I°) copper concentrations. It was found that in the total agricultural area of the Vistula river catchment, soils not contaminated with nickel (0°), with elevated (I°), and weakly contaminated soils (II°) are respectively 85%, 11%, 4% of the analyzed soils area. There was a significant relationship between the content of copper and nickel in soils and such features as organic matter and pH. Analysis of results confirmed that the highly developed industrial activity affects the increased amount of pollutants in soils; the greatest accumulation occurred in soils of the upper Vistula river catchment, which is caused primarily by interaction of the Upper Silesian Industrial District.

Keywords: soil, copper, nickel, Vistula river catchment.

INTRODUCTION

Metal pollution attracts growing interest mainly due to their toxic effects on the entire natural environment [Hsio et al, 2007, Skorbiłowicz E., 2012]. It is therefore necessary to monitor, not to exceed acceptable standards of elements in ecosystems. Heavy metals in soils are derived from natural and anthropogenic sources. The most important natural source of heavy metals in the soil, which is the bedrock, provides diverse amounts of metals, depending on its type, mineralogical composition and origin [Karczewska, 2002]. Anthropogenic sources of metals are primarily associated with steel industry and metallurgy [Kabata-Pendias and Pendias 1999]. Gruca-Krulikowska and Wacławek [2006] claim that rapidly developing industry and transport, or improper use of pesticides in agriculture, contributes to the acidification of soils and hence the accumulation of heavy metals in the environment. Gray and McLaren [2005]have shown that the activity of metals in the soil solution is dependent on the soil pH, metal concentration, and the total content of potential sorption centers within the soil. Ottosen et al. (2001) in their study showed that metals have a tendency to transfer onto larger areas in contaminated soil, mainly in the finest fractions.

The purpose of this article is to present the contents of copper and nickel in agricultural soils within the Vistula river catchment based on research carried out by the Institute of Soil Science and Plant Cultivation in the period from 1995 to 2010. The assessment of a degree of soil contamination by these elements according to standards has been also performed [Kabata-Pendias et al. 1993].

METHODS

Vistula is the longest and largest Polish river, which flows into the Baltic Sea, and its length is 1047 km. Source of the Vistula river is located in the southern part of Polish part of Silesian Beskid. Tributaries of the Vistula represent almost 54% of the Polish area. Vistula river consists of 3 sections: Upper Vistula, Central Vistula, and Lower Vistula. Table 1 shows dominant soil types in the Vistula river catchment divided into provinces.

Table 1. Types of soils in Vistula river catchment

Province	Predominating soil type
Lesser Poland	Lithosols, Cambisols, Haplic Phaeozems
Subcarpathian	Lithosols, Arenosols, Podzols
Holy Cross	Cambisols, Podzols, Arenosols
Lublin	Cambisols, Podzols, Arenosols, Haplic Phaeozems
Łódź	Podzols, Arenosols, Luvisols, Phaeozems
Masovian	Podzols, Arenosols, Luvisols
Warmian-Masurian	Cambisols, Podzols, Arenosols
Kuyavian-Pomeranian	Eutric Fluvisols, Cambisols, Podzols, Luvisols, Arenosols
Pomeranian	Arenosols, Luvisols, Eutric Phaeozems, Eutric Cambisols

Climate in Poland should be counted to transitional between oceanic in western part of the country and continental temperate in the eastern part. The climate is characterized by frequent variability and different states of the weather. The growing season amounts to about 200 days, the shortest it continues in the southern part of the country, while the longest in western Poland. Average annual rainfall is about 600 mm, while mean annual air temperature is 8 °C. Winds are characterized by high changeability, although western winds predominate. In winter, winds blow mainly from east [Kożuchowski, 2011].

The research presented in this work have been carried out by the Institute of Soil Science and Plant Cultivation, Puławy, on agricultural soils. The study contains the analysis of copper and nickel contents in years: 1995, 2000, 2005, and 2010, in nine provinces (Lesser Poland, Subcarpathian, Holy Cross, Lublin, Łódź, Masovian, Warmian-Masurian, Kuyavian-Pomeranian, and Pomeranian) located in the catchment of the Vistula river. The studied object is shown in Figure 1. The total number of soil samples was 129. Sampling was done at a depth of 0–20 cm and from

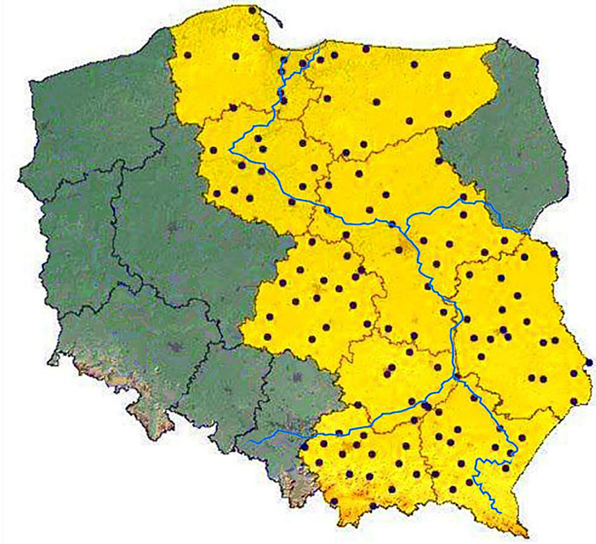

Figure 1. Soil sampling points in Vistula river catchment

the surface of approximately 100 m^2 area [http://www.gios.gov.pl/chemizm_gleb/].

Copper and nickel were determined using a spectrophotometer by means of ASA technique. Digestion was performed applying closed CEM Mars-5 system in teflon vials using hydrochloric and nitric acids. The pH of H_2O and KCl suspensions was determined by potentiometry. The organic matter in the soil samples was determined by volumetric modified Tiurin method that involves the wet combustion of organic substances.

RESULTS AND DISCUSSION

The data in Table 2 indicate that copper content varies slightly, and the average level is in the range from 4.7 ± 2.3 mg·kg^{-1} to 15.6 ± 7.6 mg·kg^{-1}. The minimum amount of copper was recorded for 1.2 mg·kg^{-1} in Lublin province, while the highest 32.3 mg·kg^{-1} in Subcarpathian province. Differentiation of copper content in agricultural soils of Vistula river catchment is associated with many factors, such as mineralogical composition and grain size of the soil, bedrock origin, and human activities. Kabata-Pendias and Pendias [1999] reports concentration of copper in Polish soils within the range: 50–140 mg·kg^{-1}. According to the Decree of the Minister of Environment from 9 September 2002 on standards for soil quality and land quality standards, the limiting copper concentration, which is 150 mg·kg^{-1} DM, is not exceeded in soils of Vistula river catchment.

Data in Table 2 indicate that the largest areas of soils with natural (0 °) copper content are present in the lower Vistula river catchment. Soils of the upper Vistula river catchment are characterized by increased copper content in provinces: Lesser Poland, Subcarpathian, and Holy Cross, which exceed 10%. Also increased copper content occurred in Warmian-Masurian region: (0 °) – 84%, (I °) – 16% (Table 2).

Referring to lowlands, the average copper content in soils is 3 mg·kg^{-1}, while in the bedrock, this amount is slightly higher than 7.1 mg·kg^{-1} [Pasieczna, 2003]. According to research by Zawadzki (2002), copper content in soils of central part of the country occurred at the level of 10 mg·kg^{-1}. Studies conducted in the area of Lublin revealed that copper content was 3.1–11.4 mg·kg^{-1} [Zgłobicki and Rodzk 2007].

Spatial distribution of copper in Vistula river catchment (Figure 2) in the period under research shows that the highest accumulation of this element occurred in the upper catchment of the river.

Table 2. Copper content and soil proportions according to the level of contamination with this element

Area	Arithmetic mean and standard deviation [mg·kg^{-1}]				Share of soils in contamination levels (%)					
	1995	2000	2005	2010	0°	I°	II°	III°	IV°	V°
Lesser Poland N = 68	14.0±6.3	14.7±6.5	15.6±7.6	14.3±6.1	90.0	10.0	0.0	0.0	0.0	0
Subcarpathian N = 56	10.7±7.1	11.4±7.1	10.7±6.2	11.9±7.5	86.0	14.0	0.0	0.0	0.0	0.0
Holy Cross N = 36	9.0±7.9	9.0±8.3	8.8±9.0	6.6±5.3	89.0	11.0	0.0	0.0	0.0	0.0
Lublin N = 80	6.7±3.4	6.2±3.0	6.0±2.9	6.2±3.5	90.0	10.0	0.0	0.0	0.0	0.0
Łódź N = 64	4.7±2.3	5.1±2.6	5.1±3.3	6.2±5.9	100.0	0	0.0	0.0	0.0	0.0
Masovian N = 80	5.0±4.3	4.9±3.8	5.3±4.5	5.5±4.6	87.5	12.5	0.0	0.0	0.0	0.0
Warmian-Masurian N = 44	9.1±7.2	8.8±6.8	8.0±6.0	8.0±4.9	84.0	16.0	0.0	0.0	0.0	0.0
Kuyavian-Pomeranian N = 52	5.4±2.7	5.0±2.2	5.6±2.6	5.0±2.5	100.0	0.0	0.0	0.0	0.0	0.0
Pomeranian N = 36	11.5±6.9	12.1±7.7	11.5±7.1	9.7±6.4	100.0	0.0	0.0	0.0	0.0	0.0
Vistula river catchment	8.4±2.2	8.6±2.4	8.5±2.3	8.2±1,5	91.0	9.0	0.0	0.0	0.0	0.0

N – total number of samples in 1995–2010.

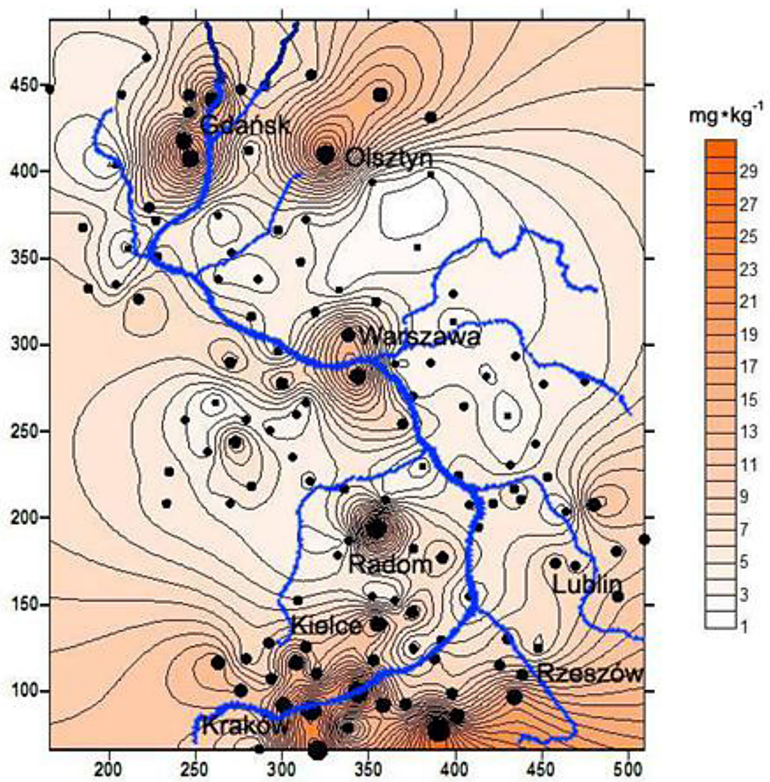

Figure 2. Spatial distribution of copper content in soils of Vistula river catchment

This is due to the impact of the Legnica-Głogów Copper District (LGOM). Annual emissions of dust containing heavy metals, especially Cu and Pb, into the atmosphere from steel works of LGOM progressively increased since the launch of plants (Legnica 1954 as well as Głogów I and II in 1971 and 1977) till the mid-eighties, when each year these plants emitted more than 2600 t of metallurgical dusts, including more than 200 t Cu and 150 t Pb. Controlling the emission in the next few years did not solve the problem of existing soil contamination with heavy metals, mainly Cu and Pb, as well as Zn, Cd, As and others. He contents of Cu and Pb in soils decreases with increasing the distance from steel works. The highest contents of these metals were recorded in the immediate vicinity of these plants (at distances <200 m), which amounted to 9800 mg·kg^{-1} Cu and 45 080 mg·kg^{-1} Pb in the area of Legnica smelter as well as 5000 mg·kg^{-1} Cu and 18 400 mg·kg^{-1} Pb in the region of Głogów steel work [Karczewska, 2002]. Quantity of analyzed element in the south-western part of the country was, according to Kaszubkiewicz and Kawałko [2009], from 6.5 to 1016 mg·kg^{-1}. A much smaller proportion of Cu recorded in the heavily industrialized village. Studies performed by Lu, Bai [2006] indicate that the average copper content in the soils of China amounted to 44.1 mg·kg^{-1} Cu in the eastern part. According to a study conducted in Botswana, South Africa, concentration of this metal ranges from 20 mg·kg^{-1} to 372 mg·kg^{-1} (Cngole and Ekosse 2012). The copper content of soils in New Zealand averaged from 2 to 2116 μg·g^{-1} [Gray and McLaren, 2005]. Excessive copper concentrations in the soil involve a negative impact on the whole environment.

Analysis of middle and lower parts of Vistula river catchment reveals the highest copper concentrations were found near Warsaw, Olsztyn, and Tricity Gdynia-Sopot-Gdańsk (Figure 2).

The arithmetic mean of nickel in soils of Vistula river catchment was recorded at 10.5 ± 2.4 mg·kg^{-1} (Table 3). Nickel content analysis showed that the maximum quantities of the element, like in the case of copper, occurred in the lower and upper catchments of the river. In Lesser Poland province, the average nickel content in 1995 was 21.3 ± 17.3 mg·kg^{-1}. In subsequent years, mean nickel content increased to 23.6 ± 17.3 mg·kg^{-1} (2010). High amounts of nickel were also reported in Subcarpathian province, which ranged from 15.4 ± 6.2 to 17.0 ± 7.1 mg·kg^{-1}. Amounts of nickel in soils of the lower river basin in Pomeranian province appeared to be on a similar level (15.9 ± 11.2 mg·kg^{-1}) in 1995, whereas the concentration of nickel slightly decreased in 2010 (15.4 ± 10.9 mg·kg^{-1}). The city of Gdańsk exerts significant impact on an elevated state of soil contamination in the lower Vistula river catchment; there are major pollution emitters including: "Lotos" refinery, shipbuilding industry, as well as landfill GZHF "Phosphates". Large accumulation of nickel in soils of the southern Poland is associated with continued development of industrial activities. According to Telerak [2005], Polish soils contain small amounts of heavy metals; their higher accumulation occurred in the industrialized parts of the country, such as the southern and the south-west regions. The largest soil surface area of natural nickel content (0°) (Table 3, Figure 3) is located in Lodz and Kuyavian-Pomeranian provinces

Table 3. Nickel content and soil proportions according to the level of contamination with this element

Area	Arithmetic mean and standard deviation [mg·kg^{-1}]				Share of soils in contamination levels [%]					
	1995	2000	2005	2010	0	I	II	III	IV	V
Lesser Poland N=68	21.3±17.3	22.6±6.5	23.3±7.6	23.6±17.3	75.0	18.0	7.0	0.0	0.0	0.0
Subcarpathian N=56	16.1±11.1	17.0±7.1	15.4±6.2	16.3±11.6	61.0	32.0	7.0	0.0	0.0	0.0
Holy Cross N=36	6.4±3.6	5.6±8.3	6.3±9.0	7.2±6.5	97.0	3.0	0.0	0.0	0.0	0.0
Lublin N=80	8.2±4.8	7.4±3.0	8.4±2.9	6.5±3.1	96.0	4.0	0.0	0.0	0.0	0.0
Lodz N=64	5.0±1.9	4.5±2.6	5.5±3.3	4.4±1.5	100.0	0.0	0.0	0.0	0.0	0.0
Masovian N=80	5.0±4.4	5.1±3.8	5.0±4.5	4.9±4.4	95.0	5.0	0.0	0.0	0.0	0.0
Warmian-Masurian N=44	12.1±10.5	10.9±6.8	10.2±6.0	11.2±8.7	81.0	5.0	14.0	0.0	0.0	0.0
Kuyavian-Pomeranian N=52	5.6±3.2	4.8±2.3	5.8±2.6	6.1±3.8	100.0	0.0	0.0	0.0	0.0	0.0
Pomeranian N=36	15.9±11.2	16.2±7.7	14.5±7.1	15.4±10.9	56.0	33.0	11.0	0.0	0.0	0.0
Vistula river catchment	10.6±5.2	10.5±2.4	10.5±2,3	10.6±5.1	85.0	11.0	4.0	0.0	0.0	0.0

N – total number of samples in 1995–2010.

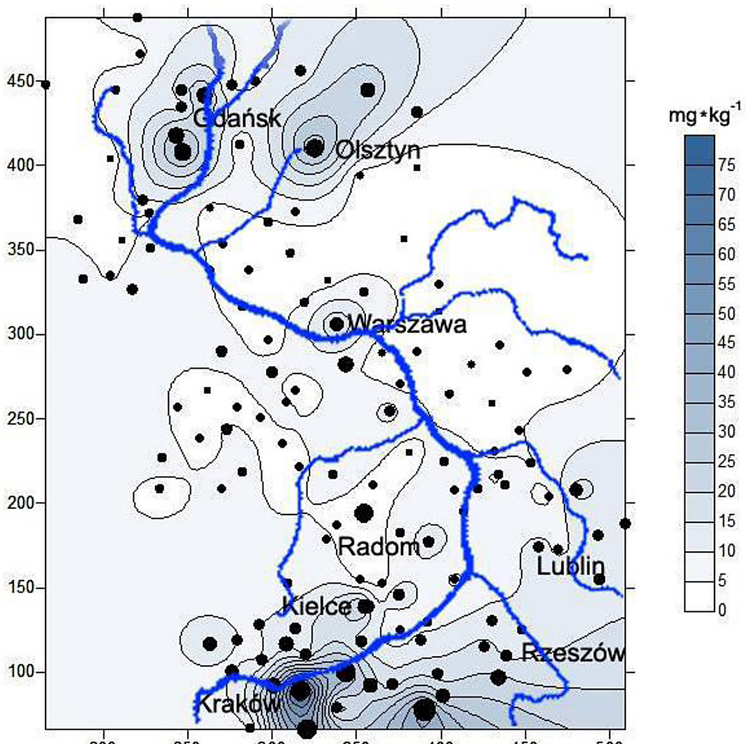

Figure 3. Spatial distribution of nickel content in soils of Vistula river catchment

and it is caused by the lack of anthropogenic contamination by this element.

Zawadzki [2002] showed the amount of nickel in soils of central Vistula river catchment at the level of 1–31 mg·kg^{-1}. The central part of Poland is characterized by a small amount of nickel in soils, which ranges from 4.02 to 31.3 mg·kg^{-1} [Jaremko and Kalembasa, 2011]. Soils of the south-western part of Poland contain average proportions of analyzed element that ranges from 6.2 to 68.3 mg·kg^{-1} [Kaszubkiewicz and Kawałko, 2009]. Areas of mining areas are more contaminated with nickel, which was proved by Cngole and Ekosse [2012], who determined the amount of this element between 22.3 mg·kg^{-1} to 266 mg·kg^{-1}. In Serbian soils, the average nickel content was high amounting up to 114,2 ppm [Jakovlejevic, 1996].

The main factor determining the solubility of heavy metals in soils is pH, which is the well-known relationship and confirmed by numerous authors. Cadmium is considered the most mobile (and most readily soluble) heavy metal, which is subject to mobilization already at pH of about 6.5, while other metals are mobilized at much stronger soil acidification: Zn (pH about 6.0) as well as Cu and Ni [Karczewska, 2002]. The soil organic matter, in particular humus, is also very impor-

Table 4. General soil properties (0–20 cm)

Area	Percentage of samples with pH in H_2O			Percentage of samples with pH in 1N KCl			Percentage of samples with humus content		
	<6.6	6.6–7.2	>7.2	<6.6	6.6–7.2	>7.2	≤1.0	1.0–2.0	>2.0
Lesser Poland	9	4	4	13	3	0	1	3	14
Subcarpathian	7	4	3	13	1	0	0	8	6
Holy Cross	5	4	0	9	0	0	1	7	1
Lublin	8	4	8	12	5	3	1	16	3
Lodz	12	3	1	14	3	0	0	13	4
Masovian	16	2	2	18	2	0	0	15	5
Warmian-Masurian	6	2	3	8	2	1	1	5	5
Kuyavian-Pomeranian	9	1	3	10	0	3	1	9	1
Pomeranian	2	4	3	7	2	0	0	3	6

Table 5. Correlation coefficient

Dependencies	Pearson coefficient	Significance level (p)
Cu – pH $_{H2O}$	0.347	0.000
Cu – pH $_{KCl}$	0.321	0.000
Cu – S.O	0.515	0.001
Ni – pH $_{H2O}$	0.386	0.000
Ni – pH $_{KCl}$	0.357	0.000
Ni – S.O	0.555	0.000

pH $_{H2O}$ – acidity in water.
pH $_{KCl}$ – acidity in 1N KCl.
S.O – organic matter.

tant in binding heavy metals from the soil solution. Table 4 presents general soil properties: pH and organic matter. The study proved that copper and nickel contents depend on soil characteristics such as pH and organic matter. The correlation coefficient values for the contents of copper and nickel in soils vs. their properties (Table 5) indicate the existence of significant dependence between: Cu content in the soil and the organic substance (R = 0.515) and pH value (R = 0.341, R = 0.321). Similar correlations were observed in case of nickel (Table 5).

CONCLUSIONS

1. The agricultural soils in the Vistula river catchment are characterized by low content of copper, the average value of which was 8.2 ± 1.5 mg·kg^{-1}, while the average nickel content was 10.6 ± 5.1 mg·kg^{-1}.
2. It has been proved that about 91% of agricultural soils in the Vistula river catchment shows natural (0°), while approximately 9% higher (I^{o}) copper concentrations.
3. It was found that in the total agricultural area of the Vistula river catchment, soils are not contaminated with nickel (0°), with elevated (I^{o}), and weakly contaminated soils (II^{o}) are respectively 85%, 11%, 4% of the analyzed soils area.
4. There was a significant relationship between the content of copper and nickel in soils and such features as organic matter and pH. This indicates that the levels of analyzed metals in soils are also determined by other factors.
5. Analysis of results confirmed that the highly developed industrial activity affects the increased amount of pollutants in soils; the greatest accumulation occurred in soils of the upper Vistula river catchment, which is caused primarily by interaction with the Upper Silesian Industrial District.

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