DOI: 10.2428/ecea.2019.26(1-2)15 ECOL CHEM ENG A. 2019;26(1–2):137–149

Małgorzata WIDŁAK[1*], Magdalena DAŃCZUK[1]
and Wojciech NOWAK[1]

CONTENT OF SELECTED HEAVY METALS IN CAMPUS OF THE KIELCE UNIVERSITY OF TECHNOLOGY

ZAWARTOŚĆ WYBRANYCH METALI CIĘŻKICH NA TERENIE KAMPUSU POLITECHNIKI ŚWIĘTOKRZYSKIEJ

Abstract: The content of heavy metals in soils is a serious problem, especially in the case of agricultural soils. Metals are entering human body not only with animal and plant products but also through the skin and by inhalation. They can cause poisoning or chronic disease of the body. The aim of the study was to assess the contamination of green areas of the Kielce University of Technology by following metals Cd, Cu, Pb, Ni, Zn and Al, due to the location of the university and its campus. The range of tests performed including pH, iodine value, organic carbon, granulometry and metal content indicate the varied and significant pollution and varying degree of soil degradation. The results of the study also show that the analysed soils are formations of equally and varigrained, sand fractions. The lead concentration has been exceeded, in relation to the standards, in the sampling areas impacted by high traffic (point No. 6 located in area of Kielce University of Technology at Millennium PP7 avenue and playgrounds for volleyball).

Keywords: heavy metals, urban soils, toxic effects of metals, pH, organic matter

Introduction

Together with development of civilization is increasing environmental pollution. The environmental status is influenced by the processes occurring in the atmosphere, hydrosphere and lithosphere, which are characterized by inter-linkages. The development of industry and communications contributed very negatively to the cleanliness of the water, air, soil. Atmospheric air is very variable and undergoing continual movement. The degree of its contamination depends not only on emissions of harmful substances in a given territory, but it is also conditioned by the emissions on neighbouring areas. A serious problem is the massive pollution of rivers, the source of

[1] Department of Water and Wastewater Engineering, Faculty of Environmental Engineering, Geomatics and Power Engineering, Kielce University of Technology, al. Tysiąclecia PP 7, 25-314 Kielce, Poland, phone: +48 41 342 48 07, email: mwidlak@tu.kielce.pl, magdar@tu.kielce.pl, primo17@interia.pl

* Corresponding author: mwidlak@tu.kielce.pl

which is mainly industrial [1]. Depending on effects of degrading factors, soils are degraded in varying degrees. Such factors include: agricultural crops leading to soil depletion, causing excessive fertilizer with nitrates, acidification by acid rain, industrial wastewater; waste and heavy metals.

The content of heavy metals is one of the fundamental parameters determining the status of pollution and the degree of soil degradation. Heavy metals are present in each soil. Their natural level is not dangerous, but in case of exceeding the permissible standards they are very harmful [2]. Accumulation of metals in soil is very dangerous, because it is a link in the trophic chain: soil – plant – animal – human. Physical and chemical properties of soils affect the uptake of elements by plant and incorporating them into the food chain. These include soil pH, organic matter and soil sorptivity which are of utmost importance for the accumulation of heavy metals [3]. It should be noted that soil particles belonging to different granulometric fractions have varied physical and physicochemical properties, which has an impact on soil richness in minerals, sorption and thermal properties [4, 5]. Under acidic conditions the plants may uptake large amounts of these elements, especially of Cd, Zn and Ni, even from slightly contaminated soil.

Cadmium is an unnecessary element, harmful heavy metal, but easily assimilated. It enters the body mainly through food and to a lesser extent by inhalation. Nickel is a trace element that is required for normal human development. Too small amount of nickel in the body leads to growth inhibition. Excess of nickel collects in the lymph nodes.

Zinc is also a trace element essential to life. Zinc deficiency leads to stunting, lack of appetite, endocrine disorders [1]. Copper and lead enter the human body by oral route, as well as dermal and inhalation. Lead enters the human body almost entirely to the blood, combining with the red blood cells and through the blood circulation reaches the organs and tissues. Copper, as a trace element is essential to the functioning of the organism, if the amount of copper is too low, the consumption of iron is not possible which is involved in hemoglobin synthesis.

The harmfulness of metals is manifested by damage of the human nervous system, leading to imbalances, respiratory disorders, gastrointestinal problems, dizziness, thus general poisoning of the body. Heavy metals can also accumulate in the body leading to cancer formation, and damaging internal organs, as well as get from the food the mother to the fetus, damaging or impairing it [6, 7].

Aluminum is not a heavy metal, but due to the negative environmental impact is classified as one of the toxic metals. It can enter the human body by the oral route, inhalation, blood and skin. Long-term impact of aluminum on the human body in low doses, that are accumulated causes disturbances in its proper functioning [8]. Cationic forms of aluminum at $pH < 4.7$, and anionic at $pH > 8$ exhibit good solubility (Figure 1).

In assessing the quality of the soil important role is to determine its sorption properties and the content of humus compounds (organic carbon), because they determine the buffering capacity of soils, regulate the pH of the soil solution, are responsible for water retention in the soil, storage of nutrients, immobilization of

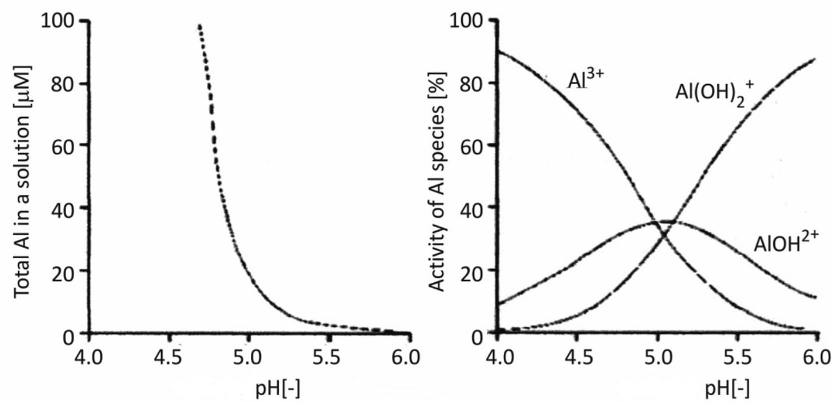

Fig. 1. The influence of pH on aluminium solubility [11]

potentially toxic components and bioavailability of trace elements [9]. To assess the sorption capacity of the soil may be used parameter of the iodine number (*IV*) [10], the values of iodine number decrease with reduction in the content of organic matter.

Materials and methods

For study purposes 8 sampling points were selected. They are located in Kielce, on the campus or in areas directly adjacent to Kielce University of Technology (PSK). Location of sampling points of urban soils in relation to PSK (Fig. 2) – 4 points (No. 1, 2, 3, 4) located on the west side, 3 points (No. 5, 6, 7) from the southern side, 1 point (No. 8) on the east side. Characteristic of sampling points (Table 1, 2). Points 1, 2 and 3 [area 1] are the areas used by the residents of neighbouring buildings, decorative and recreational.

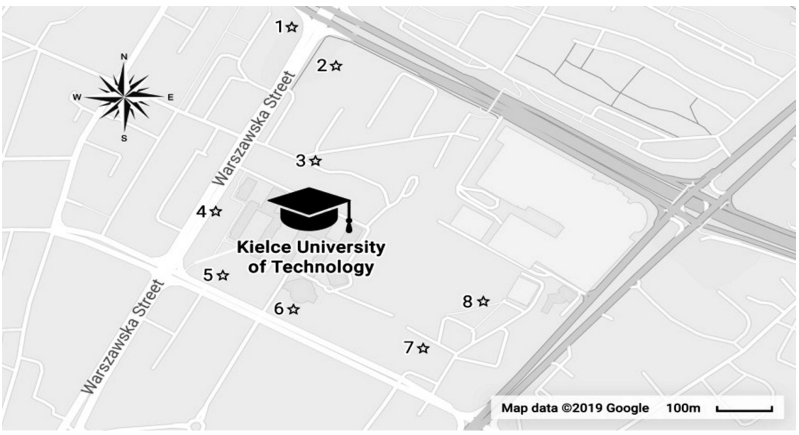

Fig. 2. Location of sampling points on the Kielce map [12]

Next, the soil of points 4, 6 and 7 [area 2], a recreation area with a sports court and a small solid waste disposal facility. Points 5 and 8 [area 3] are located in the vicinity of the car park for employees, the intersection of the road with heavy traffic and parking in the mall.

The study was conducted in Kielce in green areas of the Kielce University of Technology. Kielce University of Technology is located on a 22-hectare campus (approx. 1 km from the city center) and educates approx. 10 thousands students.

Table 1

The location and place number, including the forms of land use and the amount of soil samples

Sampling point	1	2	3	4	6	7	5	8
The location in relation to the PSK Campus	W (West)				S (South)			E (East)
Form of land use	Recreational and decorative [area 1]				Recreation and sports [area 2]			Car parks [area 3]
The number of samples in the series	From each point 80 samples were taken							

Table 2

Location of sampling soil with regard to forms of land use and the mean values of the examined parameters: pH, organic carbon and an iodine value *(IV)*

Sampling point	1	2	3	4	6	7	5	8
Form of land use	Recreational and decorative [area 1]			Recreational and sports [area 2]			Car parks [area 3]	
The average pH value	8.49			8.30			7.61	
The average content of C_{org} [%]	1.99			1.54			1.18	
The average value of *IV* [mg/g]	90.5			61.8			47.9	

The analysed soil samples were mixed. By each point the soil layer up to 30 cm were sampled, in the period March 2016 – May 2016, in varying weather conditions. From the chemical properties, the pH in 1 M KCl was determined potentiometrically, according to [13]. The content of total forms of the metals Cd, Cu, Pb, Ni, Zn and Al were determined spectrophotometrically by using the camera Spectroquant Nova 60 MERCK, after digestion with aqua regia [14]. The organic substance was determined by Tiurin method, the sorption abilities – by determining the iodine number *(IV)* [15]. The granulometric analysis was performed by laser diffraction using a Mastersizer 3000 apparatus [16]. Granulometer Mastersizer 3000 was purchased under the Project Energies – Placed in the teaching – laboratory building of Environmental Engineering, Kielce University of Technology, Kielce (No: POIS.13.01.00-00-047/08).

Results and discussion

In the analysed period March–May 2016, within 56 days, soil samples were taken up 8 times, in different weather conditions (09.03; 15.03; 22.03; 30.03; 09.04; 12.04; 26.04; 03.05.16). In the analysed period soil pH ranged from 6.87 to 8.79 in the whole research area. The highest pH value was observed for the sampling point number 3, and the lowest for sampling point 8. Soil in points 1–7 showed a pH in the range of neutral and slightly alkaline (Fig. 3 and 4), in point 8 a slightly acidic (Fig. 4).

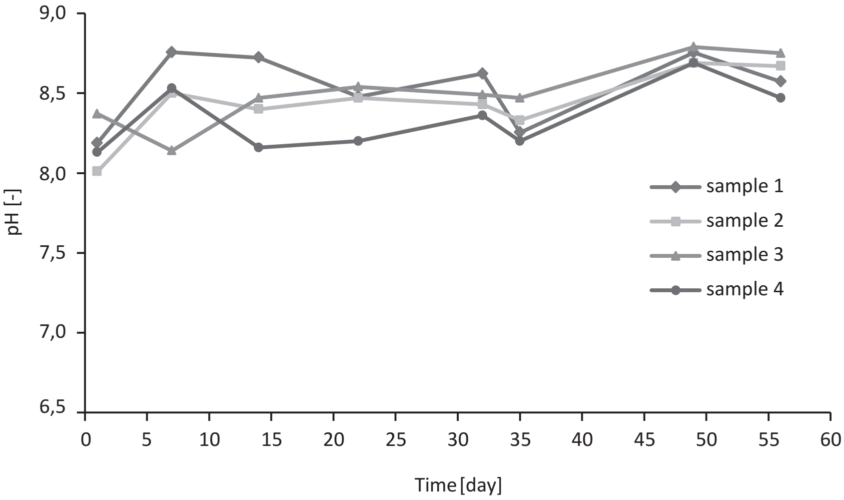

Fig. 3. The pH of tested soil for points 1–4 during sampling period

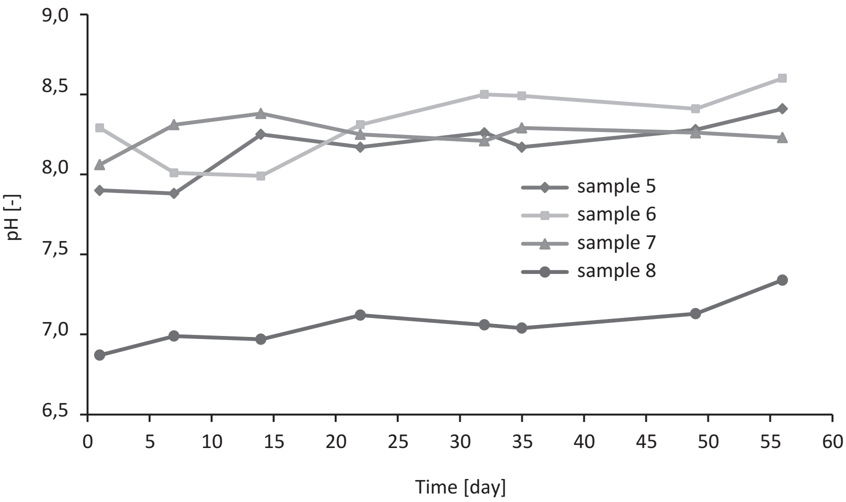

Fig. 4. The pH of tested soil for points 5–8 during sampling period

The pH of the studied soils is related to the variable weather conditions and the location of their sampling.

Average pH values of the tested soils depended on soils usage are shown in Table 2.

For the obtained results have been calculated the measures of location (arithmetic mean, median), measures of variation (standard deviation, coefficient of Pearson)

Curves of the composition and particle size distribution, trend curve and the value of R^2 were plotted on the graph for the selected dependencies.

There is a high diversity of iodine value (*IV*) and organic carbon (C_{org}) for the studied soils. High sorption was observed in soil samples No. 2 [area 1] (108 mg/g), and very low in soil samples No. 5 [area 3] (32 mg/g).

Organic carbon content of the test samples is in the range of 1.11 % to 2.36 %. The highest % C_{org} content occurs in the sampling point No. 2 [area 1], the lowest in sampling point no. 8 [area 3]. Differentiation of iodine value that is sorptivity of tested soil is influenced by the way of tested area use and the organic carbon content (Figure 5). Mean values for iodine value (*IV*) and organic carbon (C_{org}) are shown in Table 2.

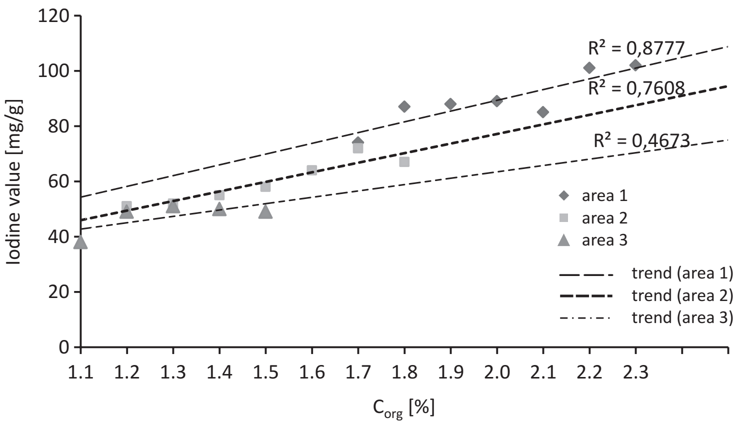

Fig. 5. Correlation of organic carbon (C_{org}) and iodine value (*IV*) in the whole studied area

At C_{org} content of 1.1–1.5 %, iodine values (*IV*) are in the medium range of 47.9 mg/g for the points 5 and 8; abundance of studied soils in organic carbon to the content of 2.3 % results in increase of iodine causes in an average of 90.5 mg/g (Table 2 and Figure 5). With the increase of organic carbon content increases sorptivity of lands used (Fig. 5) [17].

The results of granulometric analysis of the studied soils are presented in the form of a cumulative curves and particle size distribution curve in Figs. 6–9.

The highest percentage was recorded for particles with a diameter in the range of (250–500) microns. They accounted for 27 to 36 %. Particles having a diameter from 50μm to 100μm accounted for 8.8 %, and the grains in the range of (2–50) μm for 10.4 %. Most smallest particles of less than 50 μm were observed in the sample No. 4. This share stood at 10%. Samples 2 and 3 were also characterized by significant number of grains less than 50 μm of 8%.

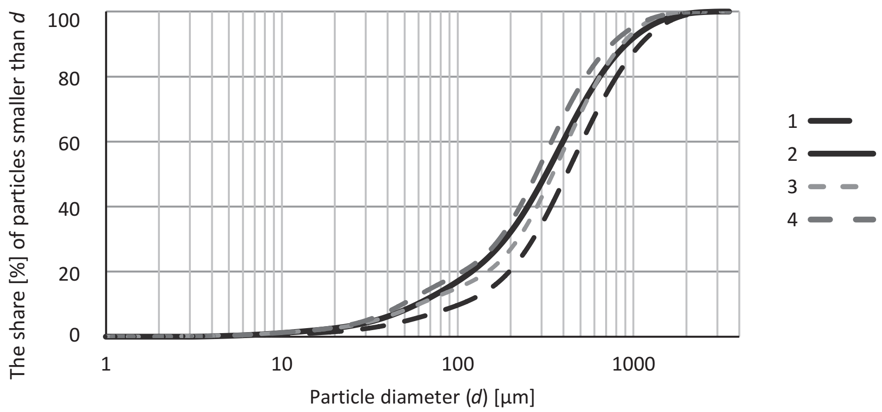

Fig. 6. The curve of grain composition for the soil samples 1–4 during the sampling period

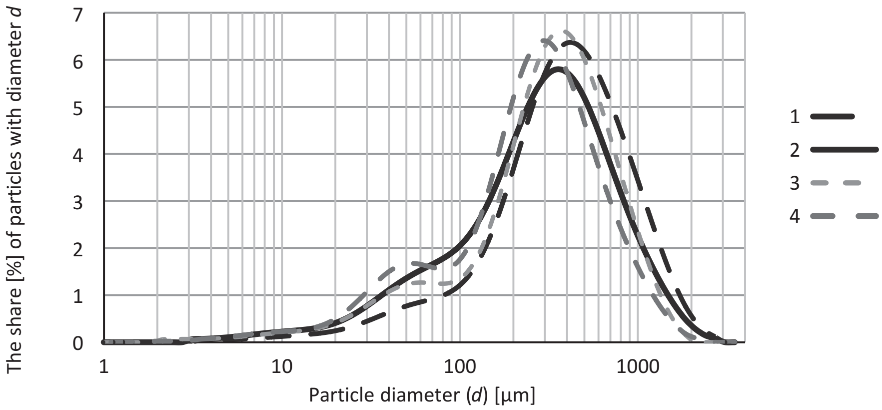

Fig. 7. The curve of particle size distribution for the soil samples 1–4 during the sampling period

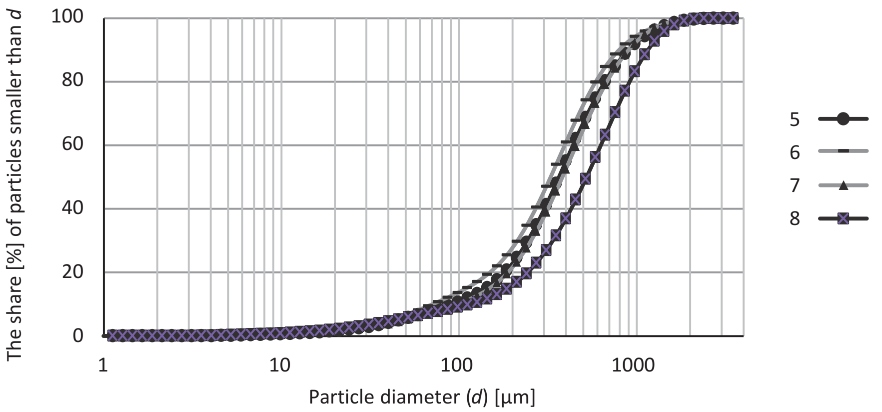

Fig. 8. The curve of grain composition for the soil samples 5–8 during the sampling period

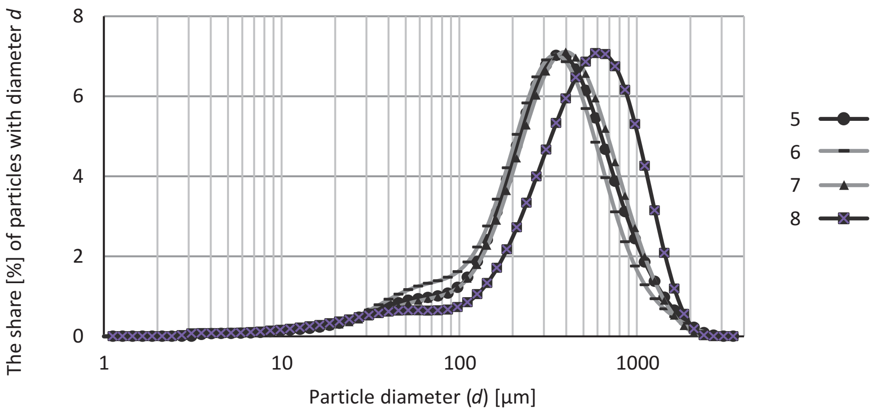

Fig. 9. The curve of particle size distribution for the soil samples 5–8 during the sampling period

Table 3

Statistical parameters for the overall content of selected metals in soils, March–May 2016

Parameters	Cd	Cu	Pb	Zn	Ni	Al
	[mg · kg^{-1} d.m.]					
Minimum	3.9	17.0	32.0	5.0	7.0	11.0
Maximum	3.9	85.0	137.0	26.0	44.0	72.0
Average	2.5	37.8	74.6	15.3	22.2	28.3
Median	5.1	36.0	71.0	16.0	22.0	22.0
Standard deviation	0.5	12.9	21.9	4.6	7.1	15.8

The analysed soils are equally and varigrained forms. The soils No. 1, 5, 6, 7, 8 are equally grained. Their uniformity coefficient (D_C) is smaller than or equal to 5. In contrast, the soil samples No. 2, 3, 4 characterized by the D_C in range of 5–15 and belong to varigrained forms (Table 4).

Table 4

Diversity of investigated soils

No soil sample	The diameter of the particles which weight together with the weight of all the smaller particles is 10 % d_{10} or 60 % d_{60} of the soil mass [µm]		Uniformity coefficient D_C [-]
	d_{10}	d_{60}	
1	103	510	5
2	59	397	7
3	60	421	7
4	49	280	6
5	91	437	5
6	71	327	5
7	97	456	5
8	114	627	5

By assessing the content of organic carbon (C_{org}), sorption and dust fraction 2–50 μm of soil tested, it is not possible to clearly define the occurring correlations.

The highest content of C_{org} and sorptivity show soils from sampling points no 1, 2, 3; while the highest % of fraction 2–50 μm, in the range of 8.2 % – 10.4 % occurs for samples No. 2, 3, 4. Pearson coefficient for C_{org} and dust fraction $r = 0.1446$, and for the iodine number (*IV*) and the dust fraction $r = 0.1145$ (Figure 10).

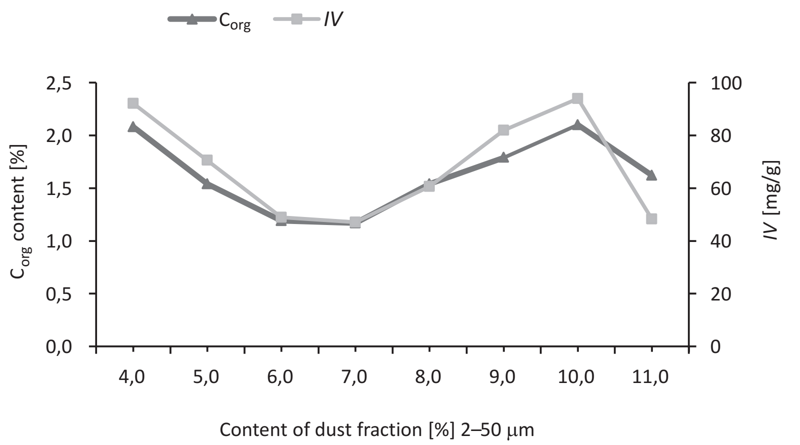

Fig. 10. Correlation of content of organic carbon (C_{org}), soil dust fraction and soil sorption expressed in iodine value (*IV*)

The metal contents – copper and nickel in the soils of the campus does not exceed 50 %, and the concentration of zinc is in the range of 10 % in relation to the standard (Table 3) [18].

Lead in the tested soil ranges from 32 mg/kg to 137 mg/kg. Low concentrations of Pb was found in soil with a high content of humus – 1, 2, 3 points; high average concentration from studied period amount – around 80 %, but not exceeding the standards is in points 4, 5. These areas are located close to busy streets and car park (Tables 1, 5).

Table 5

Average concentrations of lead, cadmium and aluminum in soil sampling points, March–May 2016

No. of soil sampling point / Average content [mg /kg]	1	2	3	4	5	6	7	8
Lead	70.6	64.8	62.8	80.4	79.8	96.5	74.5	67.5
Cadmium	3.6	4.5	4.9	4.9	4.3	3.4	4.3	3.0
Aluminum	27.4	40.0	20.5	14.5	15.5	41.3	27.8	49.0

With the increase of % organic carbon content it is observed the decrease of lead concentration, average correlation $R^2 = 0.1139$ (Figure 11). Correlation of nickel and lead concentration is characterized by the average Pearson linear correlation coefficient $R^2 = 0.1562$ (Figure 12).

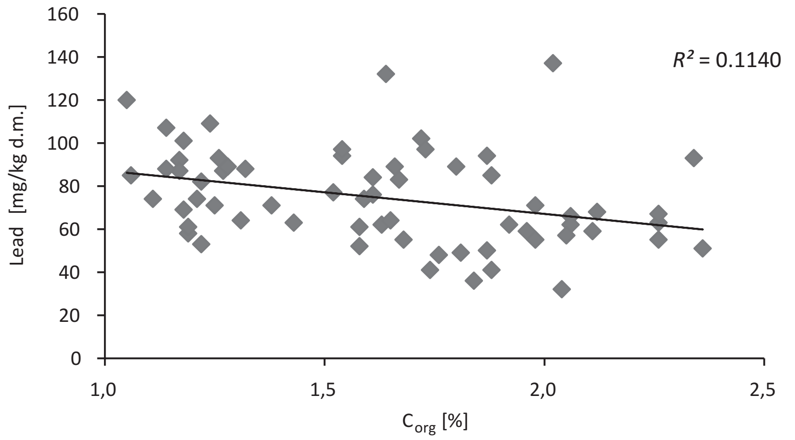

Fig. 11. Dependency between lead content and organic carbon (C_{org}) in tested soil

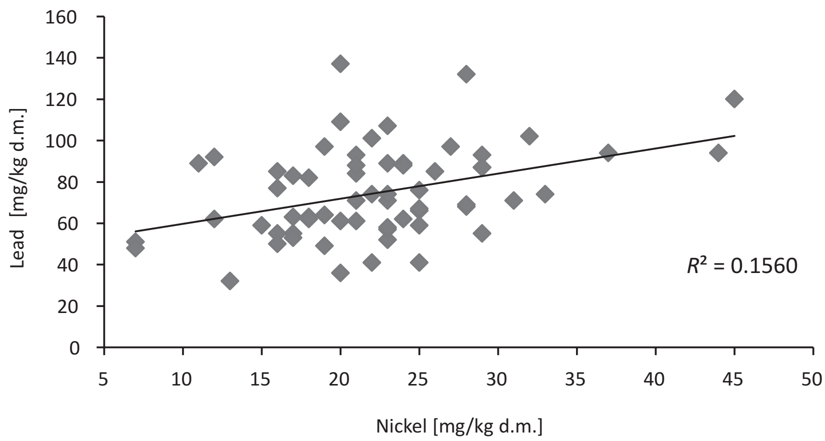

Fig. 12. Dependency between nickel and lead contents in tested soil

The aluminum content in the whole study period was at an average level of 28.3 mg/kg dry matter. Most aluminum was found in the test points 2, 6 and 8 located in areas affected by streets with increased traffic. In tested point No. 6 (only in one) where additionally is located entrance to the Staff parking and driveway to the administrative buildings of the university, there is a higher concentration of all analysed metals: Al, Pb, Ni, Cu, Zn in relation to the arithmetic mean and median (Table 3) [19].

The lowest aluminum concentration was recorded in point 4, isolated from the busy street by the line of shrubs (twice lower compared to the arithmetic mean), but the concentrations of other metals showed values exceeding the arithmetic mean (Table 3) [20].

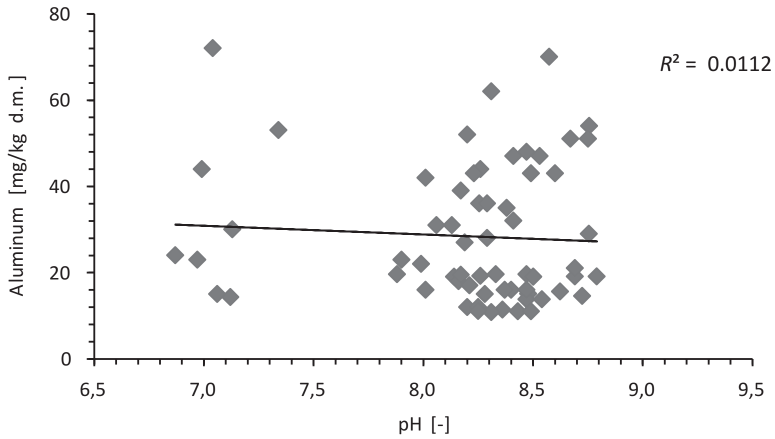

Fig. 13. Dependency between aluminum and pH of tested soil

The dependence of the aluminum content of the soil pH is statistically not significant as indicates the correlation coefficient R^2 = 0.0112 (Figure 13). Average pH of soil tested in points 1, 2, 3 – recreational and decorative areas pH = 8.49 and 4, 5, 6 – recreational and sports areas pH = 8.30 are characterized by the formation of anionic forms of aluminum with good solubility (Fig. 1 and Fig. 13). They can be complexed by the organic matter of the soil.

Conclusion

1. Location of sampling are green areas used as recreation, decoration and sports. They are located around and in areas of the Kielce University of Technology

2. The range of tests performed including pH, iodine value, organic carbon, granulometry and metal content indicate the varied and significant pollution and varying degree of soil degradation.

3. The results of the study also show that the analysed soils are formations of equally and varigrained, sand fractions.

4. The content of organic carbon and the iodine value used to assess the sorption capacities is reflected in contamination changes by metals.

5. The granulometric analysis indicates no significant correlation between the granulometric composition and sorption properties, it is related with anthropogenic nature of the soil tested and the manner of its use.

6. The lead concentration has been exceeded, in relation to the standards, in the sampling areas impacted by high traffic – point 6 located in area of Kielce University of Technology at Millennium PP7 avenue and playgrounds for volleyball.

7. Examination of the cadmium content was performed 3 times over the study period. The results of the cadmium content were on the borderline of admissibility or slightly exceeded in average up to approx. 10 % in the sampling points located in areas with increased traffic.

8. Soils tested are not developed for agriculture, so do not pose a direct threat to life and health, but because of the way they are used the appropriate monitoring studies and activities protecting health of the inhabitants of that area are indicated.

References

[1] Perczak A, Waśkiewicz A, Goliński P. Metal pollution of surface water from Wielkopolska region. Ecol Chem Eng A. 2015;22(3):285-96. DOI: 10.2428/ecea.2015.22(3)23.

[2] Łukowski A, Wiater J, Dymko A. Bioaccumulation of heavy metals in forage grasses. Ecol Eng. 2017;18(1):149–58. DOI: 10.12912/23920629/66999.

[3] Pivic R, Stanojkovic Sebic A, Josic D. Evaluation of the heavy metals content in soil and plant material at different distances from the motorway E75 in the section Belgrade-PreSevo (SERBIA). Bulgarian J Agricult Sci. 2014; 20(2):330-336, https://www.agrojournal.org/20/02-15.pdf

[4] Sankhla M.S, Kumari M, Nandan M, Kumar R, Agrawal P. Heavy Metal Contamination in Soil and their Toxic Effect on Human Health: A Review Study. Int J All Res Educ Sci Methods (IJARESM). 2016; 4(10):13-19, https://www.researchgate.net/publication/309340676

[5] Świsłowski P, Rajfur M. Mushrooms as biomonitors of heavy metals contamination in forest areas. Ecol Chem Eng S. 2018;25(4):557-568. DOI: 10.1515/eces-2018-0037.

[6] Chrzan A, Formicki G. Content of heavy metals in soils in different seasons. Proc ECOpole. 2012; 6(2):701-706. DOI/10.2429/proc.2012.6(2) 095.

[7] Jaradat QM, Massadeh AM, Momani KA, Al Saleem MA. The spatial distribution of Pb, Cd, Zn, and Cu in agricultural roadside soils. Soil Sediment Contam. 2009;19(1):58-71. DOI: 10.1080/ 15320380903390554.

[8] Widłak M. Evaluation of exchangeable aluminium content and selected soil parameters of Swietokrzyskie province. Ecol Chem Eng A. 2013;20(7-8):867-874. DOI/10.2428/ecea.2013.20(07) 081.

[9] Meers E, Samson R, Tack FMG, Ruttens A, Vandegehuchte M, Vangronsveld J, et al. Phytoavailability assessment of heavy metals in soils by single extractions and accumulation by Phaseolus vulgaris. Environ Experim Bot. 2007;60(3):385-96; DOI: 10.1016/j.envexpbot.2006.12.010

[10] Bezak-Mazur E, Dańczuk M. Sorption capacity of conditioned sewage sludge in environmental conditions. Archives Waste Manage Environ Protect. 2013;15(1):87-92, https://pbn.nauka.gov.pl/sedno-webapp/works/480216/

[11] Exley C. The toxicity of aluminium in humans. Morphologie. 2016;100(329):51-5. DOI: 10.1016/j.morpho.2015.12.003.

[12] Kielce University of Technology on the map of Kielce, https://www.google.pl/maps/@50.866061,20.6424588,14z

[13] PN-ISO 10390:1997 - Jakość gleby. Oznaczenie pH dotyczy oznaczania pH z użyciem szklanej roztworze chlorku potasu (Soil quality. pH determination, relates to the determination of pH using a glass solution of potassium chloride), http://sklep.pkn.pl/pn-iso-10390-1997p.html

[14] EN-13346: 2000 Characterization of sludges. Determination of trace elements and phosphorous. Aqua regia extraction methods, https://shop.bsigroup.com/ProductDetail?pid=000000000030025252

[15] PN-83C-97555.04 –- Węgle aktywne. Metodyka badań. Oznaczanie liczby adsorpcji jodu. (Activated carbons. Research methodology. Determination of Adsorption Value of iodine), http://sklep.pkn.pl/ pn-c-97555-04-1983p.html

[16] Mastersizer 3000. Laser diffraction particle size analyzer, https://www.malvernpanalytical. com/en/products/product-range/mastersizer-range

[17] Danila V, Vasarevičius S. Theoretical Evaluation of Heavy Metals Migration and Sorption in Soil. “Environmental Engineering” 10th Int Conf. 2017; Available from: https://doi.org/10.3846/enviro.2017.015.

[18] Rozporządzenia Ministra Środowiska z dnia 9 września 2002 r. w sprawie standardów jakości gleby oraz standardów jakości ziemi, Dz.U.02.165.1359 (Decree of the Minister of the Environment of 9 September 2002 on soil quality standards and ground quality standards, Dz.U.02.165.1359), http://www.abc.com.pl/du-akt/-/akt/dz-u-02-165-1359
[19] Werkenthin M, Kluge B, Wessolek G. Metals in European roadside soils and soil solution – a review. Environ Pollut. 2014;189:98-110. DOI: 10.1016/j.envpol.2014.02.025.
[20] Kim R-Y, Yoon J-K, Kim T-S, Yang JE, Owens G, Kim K-R. Bioavailability of heavy metals insoils: definitions and practical implementation – a critical review. Environ Geochem Health. 2015;37:1041-1061. DOI: 10.1007/s10653-015-9695-y.

ZAWARTOŚĆ WYBRANYCH METALI CIĘŻKICH NA TERENIE KAMPUSU POLITECHNIKI ŚWIĘTOKRZYSKIEJ

Katedra Technologii Wody i Ścieków, Wydział Inżynierii Środowiska, Geomatyki i Energetyki
Politechnika Świętokrzyska w Kielcach, Kielce

Abstrakt: Zawartość metali ciężkich w glebach jest poważnym problemem, szczególnie w przypadku gleb użytkowanych rolniczo. Metale, do organizmu człowieka przedostają się nie tylko z produktami roślinnymi i zwierzęcymi, ale również przez skórę i wdychanie. Mogą wywoływać zatrucia lub przewlekłe stany chorobowe organizmu. Celem pracy była ocena zanieczyszczenia terenów zielonych Politechniki Świętokrzyskiej metalami Cd, Cu, Pb, Ni, Zn i Al ze względu na lokalizację uczelni i jej kampusu. Wykonany zakres badań uwzględniający pH, liczbę jodową, węgiel organiczny, granulometrię i zawartość metali wskazuje na zróżnicowane i znaczące zanieczyszczenie oraz różny stopień degradacji gleby. Wyniki pokazują również, że analizowane gleby to utwory równo- i różnoziarniste, frakcje piaskowe. Stężenie ołowiu zostało przekroczone, w stosunku do standardów, w miejscach o dużym oddziaływaniu ruchu samochodowego (punkt nr 6 zlokalizowany na terenach Politechniki Świętokrzyskiej oraz boiska do piłki siatkowej).

Słowa kluczowe: metale ciężkie**,** gleby miejskie, toksyczne oddziaływanie metali, pH, materia organiczna