POLISH JOURNAL OF SOIL SCIENCE
VOL. XLIX/2 2016 PL ISSN 0079-2985

DOI: 10.17951/pjss/2016.49.2.101

MIROSŁAW WYSZKOWSKI*, BEATA MODRZEWSKA

DEVELOPMENT OF THE SELECTED PROPERTIES OF ZINC-CONTAMINATED SOIL FOLLOWING AN ADDITION OF NEUTRALISING SUBSTANCES

Received: 2016.03.25
Accepted: 2016.08.01

Abstract. Studies have been undertaken which assess the possibility of neutralising the effect of zinc on the contents of: organic carbon, total nitrogen, available forms of: phosphorus, potassium and magnesium in soil by applying neutralising substances – compost, bentonite and zeolite. In the series without an addition of neutralising substances, increasing zinc soil contamination resulted in an increase in the contents of total nitrogen, available forms of phosphorus, magnesium and potassium (especially), and a decrease in the organic carbon content, compared to the control object (without Zn). Application of bentonite and zeolite had an advantageous effect on the contents of carbon and available phosphorus and on the C:N ratio in soil, compared to the series without additions. Bentonite had a similar effect on the available potassium content in soil. It had a much greater effect on the organic carbon content in soil than zeolite. Not all of the neutralising substances added to soil had a significant effect on the contents of nitrogen and available magnesium in soil, compared to the series without neutralising substances.

Keywords: zinc contamination, compost, bentonite, zeolite, soil properties

Soil is an integral element of the land ecosystem (Haslmayr *et al*. 2016) and is a non-renewable natural resource (Lal *et al*. 2015). It also plays a very important role in the cycling of elements, including heavy metals, in the terrestrial environment (Gorlach, Gambuś 1991). Due to the constant contact with air and water (Zhang *et al*. 2015) soil is susceptible to excessive enrichment with

* Department of Environmental Chemistry, University of Warmia and Mazury in Olsztyn, Łódzki 4 Square, 10-727 Olsztyn, e-mail: miroslaw.wyszkowski@uwm.edu.pl. Corresponding author: Prof. M. Wyszkowski, DSc.

trace elements as a consequence of human activity (Cabral-Oliveira *et al*. 2015; Puga *et al*. 2015; Rovira *et al*. 2015). It causes slow and practically irreversible soil destruction (Cabral-Oliveira *et al*. 2015, Lal *et al*. 2015). Another source of trace elements may be bedrock weathering (Temmerman *et al*. 2003). Some trace elements are essential for living organisms to function properly (often the necessary amounts are very small, trace amounts actually), but after exceeding a certain level they become toxic (Wyszkowski, Wyszkowska 2009; Borowik *et al*. 2014; Puga *et al*. 2015; Zhang *et al*. 2015).

Soil is able to bind heavy metals and to limit their solubility (Gorlach, Gambuś 1991). The elements availability then decreases, they can even become unavailable. Thus, they become less toxic to soil living organisms (Feng *et al*. 2007). Their availability to plants depends on their content and form and on the soil properties: pH, organic matter content, granulometric composition, sorption capacity, fertilisation, the species of the plant grown and on the soil microorganism activity (Gorlach, Gambuś 1991; Wołoszyk *et al*. 2009; Ociepa 2011; Skwaryło-Bednarz *et al*. 2011; Kargar *et al*. 2015). Soil sorption can be improved by introducing unconventional fertilisers, such as compost or brown coal, since it is an effective way of limiting heavy metal availability to plants (Ociepa 2011; Fijałkowski *et al*. 2012). The following minerals also have similar properties: loams, bentonite or zeolite and iron oxides (Feng *et al*. 2007). With increasing pH and organic matter and clay mineral contents, soil sorbs more heavy metals (Gorlach, Gambuś 1991; Ociepa 2011; Fijałkowski *et al*. 2012).

For this reason, studies have been undertaken which assess the possibility of neutralising the zinc effect on the contents of: organic carbon, total nitrogen, available forms of: phosphorus, potassium and magnesium in soil by applying neutralising substances – compost, bentonite and zeolite.

MATERIALS AND METHOD

Pot culture experiments were carried out in the vegetation hall of the University of Warmia and Mazury in Olsztyn. Acid soil formed from sand was used. The soil had the following properties: pH in a 1 mol KCl dm^{-3} solution – 5.32; hydrolytic acidity (HAC) – 33.6 mmol(+) kg^{-1}; total exchange bases: Ca^{2+}, Mg^{2+}, K^{+} and Na^{+} (TEB) – 42.1 mmol(+) kg^{-1}; cation exchange capacity (CEC) – 75.7 mmol(+) kg^{-1}; the degree of base saturation (BS) – 55.6%, the organic C content – 13.8 g kg^{-1}; the contents of available forms of: phosphorus – 40.3 mg kg^{-1}; potassium – 11.9 mg kg^{-1} and magnesium – 33.6 mg kg^{-1} of soil. The first order factor was zinc soil contamination in doses of: 0, 150, 300, 600 and 1,200 mg of Zn kg^{-1}, and the second order factor was adding the following substances to the soil: compost (3%), bentonite (2%) and zeolite (2% by weight of the soil). To the soil in all the pots macro- and microelements were introduced, in the same amounts: 30 mg of N; 30 mg of P; 100 mg of K; 50 mg of Mg; 0.33 mg of B; 5 mg of Mn and 5 mg of Mo per kg of soil. In the experiment yellow lupine (*Lupinus luteus* L.) of the Mistral variety was sown.

Soil samples for laboratory analysis were taken during the annual yellow lupine harvest, at the flowering stage. The samples were then dried and sieved through a sieve. In the prepared soil, the following properties were determined: the content of total nitrogen with the Kjeldahl method (Lityński *et al*. 1976), the content of organic carbon ($C_{org.}$) – with the Tiurin method (Lityński *et al*. 1976), the content of available phosphorus and potassium – with the Egner-Riehm method (Lityński *et al*. 1976) and the content of available magnesium – with the Schachtschabel method (Lityński *et al*. 1976). The results were statistically analysed with the Statistica software package using a two-way ANOVA analysis of variance. To assess the effect of zinc and neutralising substances on soil properties, a principal component analysis (PCA) was used. The ratio of variance components was also calculated, with the eta-squared method, using a two-way ANOVA analysis of variance.

RESULTS AND DISCUSSION

The contents of organic carbon, total nitrogen, available phosphorus, potassium and magnesium in soil depended on zinc soil contamination and on the application of neutralising substances (Tables 1–2, Fig. 1). In the series without an addition of neutralising substances, increasing zinc soil contamination resulted in an increase in the contents of available potassium and magnesium by 112% and 47%, respectively, of nitrogen and available phosphorus by 36%, and a decrease in the organic carbon content by 22% compared to the control object (without Zn). There was also a trend of narrowing the C:N ratio in soil.

The results presented in Tables 1 and 2 indicate the positive effect of the bentonite and zeolite use on the contents of organic carbon and available phosphorus in soil, compared to the series without an addition of a zinc neutralising substance. The effect of bentonite on the organic carbon content in soil was much greater than the effect of zeolite. Bentonite caused an increase in the organic carbon content in soil by 34% on average, compared to a 17% increase for the series with zeolite. The greatest average contents of available phosphorus in soil were reported for the series with the additions of bentonite and zeolite. The contents were respectively – by 35% and by 33% – higher than for the series without the additions. Bentonite and zeolite promoted broadening the C:N ratio in soil. A positive effect of bentonite on the available potassium content in soil was also reported, but an increase in the available potassium content was only 9%, compared to the series without additions. Not all of the neutralising substances added to soil had a significant effect on the contents of total nitrogen and of available magnesium in soil, compared to the series without neutralising substances. Introducing compost into soil also had no significant effect on the contents of organic carbon and of available phosphorus and potassium.

TABLE 1. CONTENT OF ORGANIC CARBON, TOTAL NITROGEN AND C:N RATIO IN SOIL

Dose of zinc [mg kg^{-1} of soil]	Kind of substance neutralizing effect of zinc				
	Without additions	Compost	Bentonite	Zeolite	Average
	Organic carbon [g kg^{-1} d.m.]				
0	10.80	9.75	13.80	10.20	11.14
150	9.30	10.35	13.95	10.50	11.03
300	9.68	9.90	13.20	11.55	11.08
600	9.53	9.60	12.00	11.40	10.63
1,200	8.48	8.40	11.10	12.45	10.11
Average	9.56	9.60	12.81	11.22	10.80
r	–0.83**	–0.90**	–0.97**	0.93**	–0.98**
LSD	a – 1.43**, b – 1.28**, a · b – 2.86**				
	Total nitrogen [g kg^{-1} d.m.]				
0	0.84	0.81	0.99	0.98	0.90
150	0.99	1.08	0.96	0.93	0.99
300	0.99	1.11	0.99	0.99	1.02
600	0.92	0.98	0.91	1.06	0.97
1,200	1.13	1.15	0.99	0.97	1.06
Average	0.97	1.02	0.97	0.99	0.99
r	0.80**	0.60*	–0.05	0.20	0.75**
LSD	a – 0.51**, b – 0.46**, a · b – 1.02**				
	C:N ratio				
0	12.93	12.06	13.98	10.39	12.34
150	9.39	9.58	14.59	11.29	11.21
300	9.77	8.92	13.35	11.69	10.93
600	10.31	9.82	13.12	10.74	11.00
1,200	7.48	7.32	11.17	12.87	9.71
Average	9.98	9.54	13.24	11.40	11.04
r	–0.79**	–0.82**	–0.95**	0.79**	–0.92**
LSD	a – 1.18*, b – 1.05**, a · b – 2.35*				

LSD (least squares deviation) for: a – zinc dose, b – kind of neutralizing substance, a · b – interaction; significant for: ** – *P*=0.01, * – *P*=0.05, n.s. non-significant; *r* – correlation coefficient.

From the Fig. 1 it follows that in the studied soil, the first two principal components represent 78.24% of the primary variable variance. The first principal component accounts for 43.36% of the total variance and the second principal component accounts for 34.88%. The vectors representing the contents of organic carbon, available phosphorus, potassium and magnesium and the C:N ratio in soil are very well represented by the first two principal components which form a coordinate system. The total nitrogen content was more weakly represented. The total nitrogen vector is most strongly slanted towards the nearest first principal component, which proves its reaction to zinc soil contamination was similar and negative. Similar, but weaker relations were observed for available magnesium and potassium. The opposite relations were reported for the organic carbon content and for the C:N ratio in soil. The vectors representing the primary variables for available potassium and magnesium, organic carbon and the C:N ratio in soil are close to each other, which indicates the relations between them were positive. The vectors between available potassium and magnesium and the C:N ratio and organic carbon, and, particularly, between total nitrogen and the C:N ratio and organic carbon were, in turn, very far apart from each other, which represents the negative correlations between these elements.

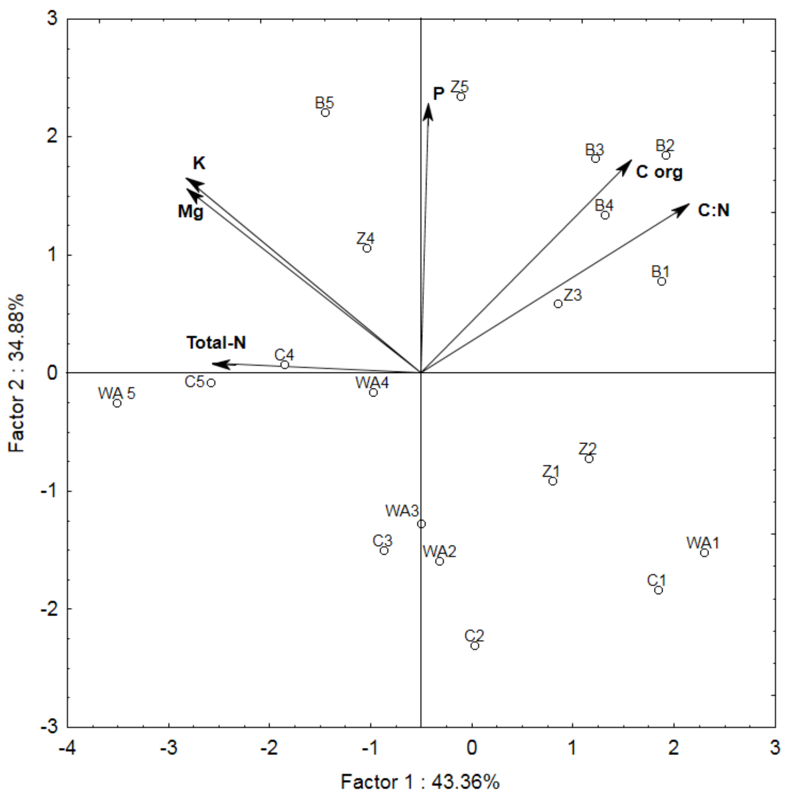

Fig.1. Content of elements in the soil illustrated with the pca method.

key: vectors represent analyzed variable (C_{org} – organic carbon, Total-N, C:N – C:N ratio, P – available phosphorus, K – available potassium, Mg – available magnesium), points show soil samples with elements (WA – without additions, C – compost, B – betonite, Z – zeolite; 1 – 0, 2 – 150 mg, 3 – 300 mg, 4 – 600 mg, 5 – 1,200 mg of Zn kg^{-1} of soil).

TABLE 2. CONTENT OF AVAILABLE FORM OF PHOSPHORUS, POTASSIUM AND MAGNESIUM IN SOIL

Dose of zinc [mg kg^{-1} of soil]	Kind of substance neutralizing effect of zinc				
	Without additions	Compost	Bentonite	Zeolite	Average
	Phosphorus [mg kg^{-1} d.m.]				
0	92.17	93.84	116.79	143.94	111.69
150	111.41	86.66	144.85	134.54	119.37
300	104.63	111.37	160.13	158.76	133.72
600	114.34	108.53	160.23	140.68	130.95
1,200	125.18	130.69	158.76	151.89	141.63
Average	109.55	106.22	148.15	145.96	127.47
r	0.88**	0.91**	0.65**	0.34**	0.87**
LSD	a – 9.27**, b – 8.29**, a · b – 18.54**				
	Potassium [mg kg^{-1} d.m.]				
0	31.52	31.52	44.33	31.15	34.63
150	34.81	32.25	43.60	32.98	35.91
300	45.06	41.40	47.99	36.64	42.77
600	56.05	62.64	47.99	56.41	55.77
1,200	66.67	65.93	71.79	63.37	66.94
Average	46.82	46.75	51.14	44.11	47.20
r	0.97**	0.92**	0.94**	0.95**	0.98**
LSD	a – 3.25**, b – 2.91**, a · b – 6.51**				
	Magnesium [mg kg^{-1} d.m.]				
0	121.43	127.26	135.13	120.81	126.16
150	144.49	121.34	152.00	128.06	136.47
300	143.96	131.24	146.17	141.58	140.74
600	173.04	186.20	141.93	170.12	167.82
1,200	178.16	175.95	185.23	177.98	179.33
Average	152.22	148.40	152.09	147.71	150.10
r	0.90**	0.81**	0.86**	0.94**	0.96**
LSD	a – 2.28**, b – 2.04**, a · b – 4.55**				

LSD (least squares deviation) for: a – zinc dose, b – kind of neutralizing substance, a · b – interaction; significant for: ** – *P*=0.01, * – *P*=0.05, n.s. non-significant; r – correlation coefficient.

TABLE 3. PER CENT CONTRIBUTION OF VARIABLE FACTORS ACCORDING TO THE CONTENT OF ELEMENTS IN SOILS

Variables	Content in soil					
	C	Total-N	C:N	P	K	Mg
Zn dose	4.99	29.37	13.46	19.43	86.52	80.24
Substance	59.63	1.81	45.30	66.12	3.58	0.85
Zn dose · substance	18.41	58.92	26.26	10.76	8.40	18.65
Error	16.97	9.90	14.99	3.70	1.50	0.26

When the percentage of observed variance was assessed with the coefficient η2, using the ANOVA method, it was demonstrated that the total nitrogen content, and particularly the contents of available magnesium and potassium, were to the greatest extent determined by zinc soil contamination; 29.37%, 80.24% and 86.52%, of the variance could be explained by this variable, respectively (Table 3). Relatively low values were reported for the contents of: available phosphorus (19.43%), organic carbon (4.99%) and for the C:N ratio (13.46%) in soil. Application of neutralising substances to soil had the greatest effect on the contents of available phosphorus (66.12%) and organic carbon (59.63%). Its effect on the C:N ratio (45.30%) was weaker. The proportion of variance in the contents of total nitrogen and available potassium and magnesium which can be explained by this variable was very small, and it did not exceed 4%.

The results of the authors' own research have been partly confirmed by other authors' studies. The studies carried out by Feng et al. (2007) confirmed that heavy metals are bound as a result of introducing loams, bentonite, zeolite, iron oxides or phosphates to soil minerals. It is also reflected in the study by Sahraoui *et al*. (2015), where clay minerals and iron and manganese oxides added to soil caused an increase in the sorption of soil trace elements. In the studies by Wyszkowski and Sivitskaya (2012), bentonite caused an increase in the contents of available forms of phosphorus, potassium and magnesium in soil. Wyszkowski and Ziółkowska (2009) confirmed that bentonite had an effect on the contents of available potassium and magnesium in soil. Zeolite can cause an increase in the contents of organic carbon and magnesium and caused a decrease in the phosphorus content in soil (Wyszkowski, Radziemska 2012).

According to Delgado and Follett (2002) and Wright *et al*. (2007), organic matter is an excellent source of nutrients for plants, particularly of organic carbon. Many authors reported an increase in the organic carbon content (Wyszkowski, Ziółkowska 2009, Wyszkowski, Radziemska 2012) and in the contents of available phosphorus (Wyszkowski, Ziółkowska 2008), potassium (Wyszkowski, Ziółkowska 2009) and magnesium (Wyszkowski, Radziemska 2012) in soil following the application of compost. Temmerman *et al*. (2003) indicated that prolonged application of organic fertilisers (manure) and mineral fertilisers to soil resulted in an increase in the total nitrogen content in soil. Delgado and Follett (2002) found that organic substance applied to soil enriches the soil in nitrogen, phosphorus and potassium. In the studies by Wright *et al*. (2007), adding compost resulted in an increase in the contents of phosphorus, potassium and magnesium in soil. However, it should be noted that compost, like other organic fertilisers, decomposes relatively slowly and the above elements become available to plants at a later time (Wright et al. 2007). Moreover, Temmerman *et al*. (2003) indicated that an application of manure to soil may result in additional heavy metal soil contamination. According to Fijałkowski *et al*. (2012), adding organic substance to soil may result in retention or release of heavy metals and other elements.

CONCLUSIONS

In the series without an addition of neutralising substances, increasing zinc soil contamination resulted in an increase in the contents of total nitrogen, available forms of phosphorus, magnesium and potassium (especially), and a decrease in the organic carbon content, compared to the control object (without Zn).

Application of bentonite and zeolite had an advantageous effect on the contents of carbon and available phosphorus and on the C:N ratio in soil, compared to the series without additions. Bentonite had a similar effect on the available potassium content in soil. Bentonite had a much greater effect on the organic carbon content in soil than zeolite.

Not all of the neutralising substances added to soil had a significant effect on the contents of nitrogen and available magnesium in soil, compared to the series without neutralising substances.

REFERENCES

[1] Borowik, A., Wyszkowska, J., Kucharski, J., Baćmaga, M., Boros-Lajszner, E., Tomkiel, M., 2014. Sensitivity of soil enzymes to excessive zinc concentrations. Journal of Elementology, 19, 3: 637–648. **http://dx.doi.org/10.5601/jelem.2014.19.2.456**

[2] Cabral-Oliveira, J., Pratas, J., Mende,s S., Pardal, M.A., 2015. *Trace elements in edible rocky shore species: Effect of sewage discharges and human health risk implications*. Human and Ecological Risk Assessment, 21, 1: 135–145. **http://dx.doi.org/10.1080/10807039.2014.890480**

[3] Delgado, J.A., Follett, R.F., 2002. *Carbon and nutrient cycles*. Journal of Soil and Water Conservation, 57, 6: 455–464.

[4] Feng, N., Dagan, R., Bitton, G., 2007. *Toxicological approach for assessing the heavy metal binding capacity of soils*. Soil and Sediment Contamination, 16: 451–458. **http://dx.doi.org/10.1080/15320380701490226**

[5] Fijałkowski, K., Kacprzak, M., Grobelak, A., Placek, A., 2012. *The influence of selected soil parameters on the mobility of heavy metals in soils*. Environment Protection Engineering, 15, 1: 81–92.

[6] Gorlach, E., Gambuś, F., 1991. *Desorption and phytotoxicity of heavy metals depending on soil properties*. Rocz. Gleboz. – Soil Science Annual, XLII, 3/4: 207–214.

[7] Haslmayr, H.P., Geitner, C., Sutor, G., Knoll, A., Baumgarten, A., 2016. *Soil function evaluation in Austria – Development, concepts and examples*. Geoderma, 264, B: 379–387. **http://dx.doi.org/10.1016/j.geoderma.2015.09.023**

[8] Kargar, M.A., Clark, O.G., Hendershot, W.H., Jutras, P., Prasher, S.O., 2015. *Immobilization of trace metals in contaminated urban soil amended with compost and biochar.* Water Air Soil Pollution, 226, 191: 1–12. **http://dx.doi.org/10.1007/s11270-015-2450-2**

[9] Lal R., 2015. *Restoring soil quality to mitigate soil degradation*. Sustainability, 7, 5: 5875–5895. **http://dx.doi.org/10.3390/su7055875**

[10] Lityński T., Jurkowska H., Gorlach E., 1976. *Chemical and agriculture analysis* (in Polish). PWN, Warszawa: 129–132.

[11] Ociepa, E., 2011. *The effect of fertilization for changing of solubility of zinc and nickel in the soil and assimilating this metals for maize and Virginia fanpetals (Sida hermaphrodita).* Environment Protection Engineering, 14, 1: 41–48.

[12] Puga, A.P., Abreu, C.A., Melo, L.C.A., Beesley, L., 2015. *Biochar application to a contaminated soil reduces the availability and plant uptake of zinc, lead and cadmium*. Journal of Environment Management, 159: 86–93. **http://dx.doi.org/10.1016/j.jenvman.2015.05.036**

[13] Rovira. J., Nadal, M., Schuhmacher, M., Domingo, J.L., 2015. *Human exposure to trace elements through the skin by direct contact with clothing: Risk assessment*. Environmental Research, 140: 308–316. **http://dx.doi.org/10.1016/j.envres.2015.03.032**

[14] Sahraoui, H., Andrade, M.L., Hachicha, M., Vega, F.A., 2015. *Competitive sorption and desorption of trace elements by Tunisian Aridisols Calcorthids*. Environmental Science and Pollution Research, 22, 14: 10861–10872. **http://dx.doi.org/10.1007/s11356-015-4288-y**

[15] Skwaryło-Bednarz, B., Brodowska, M.S., Brodowski, R., 2011. *Evaluating the influence of varied NPK fertilization on yielding and microelements contents at amaranth (Amaranthus cruentus L.) depending on its cultivar and plant spacing*. Acta Sci. Pol.-Hortoru., 10, 4: 245–261. **http://dx.doi.org/10.1016/j.chemosphere.2008.06.046**

[16] Temmerman, L., Vanongeval, L., Boon, W., Hoenig, M., Geypens, M., 2003. *Heavy metal content of arable soils in northern Belgium*. Water Air & Soil Pollution, 148: 61–76. **http://dx.doi.org/10.1023/A:1025498629671**

[17] Wołoszyk, Cz., Iżewska, A., Krzywy-Gawrońska, E., 2009. *Content, uptake and utilization by plants of copper, manganese and zinc from municipal sewage sludge and wheat straw*. Journal of Elementology 14, 3: 593–604. **http://dx.doi.org/10.5601/jelem.2009.14.3.18**

[18] Wright, A.L., Provin, T.L., Hons, F.M., Zuberer, D.A., White, R.H., 2007. *Compost source and rate effects on soil macronutrient availability under Saint Augustine Grass and Bermuda Grass Turf*. Compost Science and Utilization, 15, 1: 22–28. **http://dx.doi.org/10.1080/1065657X.2007.10702306**

[19] Wyszkowski, M., Radziemska, M., 2012. *Effect of some substances on the content of organic carbon and mineral components in soils contaminated with chromium.* Ecological Chemistry and Engineering, A, 19, 4–5: 361–368.

[20] Wyszkowski, M., Sivitskaya, V., 2012. *Changes in the content of organic carbon and available forms of macronutrients in soil under the influence of soil contamination with fuel oil and application of different substances.* Journal of Elementology, 17, 1: 139–148. **http://dx.doi.org/10.5601/jelem.2012.17.1.12**

[21] Wyszkowski, M., Wyszkowska, J., 2009. *The effect of contamination with cadmium on spring barley (Hordeum vulgare L.) and its relationship with the enzymatic activity of soil.* Fresenius Environmental Bulletin, 18, 7: 1046–1053.

[22] Wyszkowski, M., Ziółkowska, A., 2009. *The content of organic carbon and some macroelements in the soil contaminated with petrol and diesel oil*. Ochrona Środowiska i Zasobów Naturalnych, 40: 112–122.

[23] Wyszkowski, M., Ziółkowska, A., 2008. *Effect of petrol and diesel oil on content of organic carbon and mineral components in soil.* American-Eurasian Journal of Sustainable Agriculture, 2, 1: 54–60.

[24] Zhang, X., Zhong, T., Liu, L., Ouyang, X., 2015. *Impact of soil heavy metal pollution on food safety in China*. PLoS ONE 10, 8: 1–14. **http://dx.doi.org/10.1371/journal.pone.0135182**