DE GRUYTER OPEN

CIVIL AND ENVIRONMENTAL ENGINEERING REPORTS

ISSN 2080-5187 CEER 2015; 17 (2): 61-71
DOI: 10.1515/ceer-2015-0022

CHEMICAL SOIL DEGRADATION IN THE AREA OF THE GŁOGÓW COPPER SMELTER PROTECTIVE FOREST

Jakub KOSTECKI[1], Andrzej GREINERT, Michał DRAB,
Róża WASYLEWICZ, Barbara WALCZAK
University of Zielona Gora, Institute of Environmental Engineering, Poland

Abstract

Earth surface is under the continous influence of the environmental factors – both natural and anthropogenic. The significant impact on the environment can be noted in areas adjacent to the metal industry plants, in a consequence of pollutants emission, especially dusts containing the heavy metals, into the atmosphere,. In the surroundings of Głogów Copper Smelter (GCS) elevated amounts of copper and lead has been noted. In the soils of the test sites were found up to 5250 mg·kg^{-1} Cu and 1290 mg·kg^{-1} Pb. The forest litter contained 3.3-5.1 more Cu and 3.9-8.6 Pb than the humic horizon of the soil. Analyse of the different soils covering the GCS protective forest area let specify the stabilising role of particle size distribution, TOC content and the soil reaction to Cu and Pb migration in the environment.

Keywords: heavy metal, copper, lead, industrial areas, soil pollution

1. INTRODUCTION

Contamination of surface layer of areas around the industrial facilities is common in many places of the world [6, 13, 20, 21]. t should be noted that industrial activity involves long periods of time and can lead to considerable accumulation of harmful substances in the topsoil [9].

[1] Corresponding author: University of Zielona Gora, Institute of Environmental Engineering, Szafrana st 15, 65-516 Zielona Gora, Poland, e-mail: J.Kostecki@iis.uz.zgora.pl, tel.+48 683282407

Soil degradation is evaluated on the basis of physical, chemical and biological properties. The most common effects of soil degradation found in soil of industrial areas are physical and chemical. They include, among others: geomechanical and hydrological transformation and contamination [11, 25, 28]. The hardest damages can be seen on soils without biological cover [4, 11, 33].

Pollution emitted by industrial facilities can migrate widely in the atmosphere. This phenomenon depends on many factors e.g. source of the emission and meteorological conditions. Wind speed and its direction as well as sum of precipitation are the main force modificated the deposition of heavy metals in topsoil and on the plant surface (from where they can be washed out to the soil). From the surface trace elements can migrate both vertical and horizontal in the soil profile [11]. Nevertheless, the main part of the heavy metals is binded in the organic and humic soil horizons [9].

Additional factors creating a potential threat to the soil environment is the impact of abiotic environmental elements such as water and wind. These factors can cause erosion, which is due to the different forms of existence, poses a serious threat to the soil around the world. Soil surface affected by the water erosion is being washed instantly. This may lead not only to decreasing of soil fertility by the macro and microelements lowering but also let for xenobiotics migration [4].

The aim of this work is o characterise the environmetal impact of the Glogow Copper Smelter on the soils covering the protection forest. The second aim of the study is to establish the influence of the physic-chemical properties of soil to the Cu and Pb content.

2. MATERIALS AND METHODS

2.1. Site description

GCS is a part of KGHM Polska Miedź S.A. The company is divided into a two divisions using the different technology of ore melting. First one is working on shaft furnace technology. It works since 1971. The second one is working since 1978 and its technology is based on one-stage flash furnace copper smelting [15, 29]. Summary of production in the GCS in 2008 has been shown in the table 1.

The main pollution of the copper smelter are gases (SO_2, CO, NO_x, CS_2, F) and dusts containing heavy metals, mainly Cu, Pb, Zn, Cd, As [15, 29]. The total emission of pollutants in 1985-2008 has been sumarized in table 2.

Table 1. Product asortyment of Głogów copper smelter in 2008 [17]

Product asortment	Mass, Mg
Shaft slag	551 000
Sulphuric acid	518 000
Electrolytic Cu - cathodes	425 000
Granulated slag	341 000
Crude lead	24 000
Nickel sulphate	1 689
Silver	1 193
Selenium	82
Gold	0.902
Pt-Pd concentrate	0.093

Table 2. Summarized pollution emission from the KGHM Polska Miedź S.A. in 1985-2008, $Mg \cdot y^{-1}$ [18]

Pollution	1985	1990	2000	2005	2008	Reduction comparing to 1985, %
Dust	9 596	9 211	915	601	443.1	95.4
Cu	315.6	204.0	23.2	23.6	12.6	96.0
Pb	356.2	124.3	13.8	5.3	3.8	98.9
SO_2	79 006	48 719	6 202	5 084	4 833	93.9
CO	192 636	121 499	2 683	2 552	2 803	98.5

Study sites are located in protective forest of the Głogów copper smelter, in the south-western part of Poland, in Lower Silesia region, about 3 km from the borders of the city of Głogów. The study was conducted at the test-sites located approximately 1 km to the north-east (B), 100, 200 and 300 m to the south (Z1, Z2, Z3) from the smelter (Figure 1).
The control site (S) was located abour 15 km to the west from the GCS (N 51 0 46’23.00”, E 15 0 47’23.00”).

Table 3. Dominant tree species in the protective zone of Głogów copper smelter [18]

Tree species	Foresteted area, ha	Foresteted area, %
Pine	5.17	0.65
Oak	213	26.9
Maple	35.0	4.41
Ash tree	1.33	0.17
Birch	94.1	11.9
Aspen	2.53	0.32
Poplar	425	53.6
Alder	2.53	0.32

Willow	11.7	1.47
Linden	1.89	0.24
Total	793	100

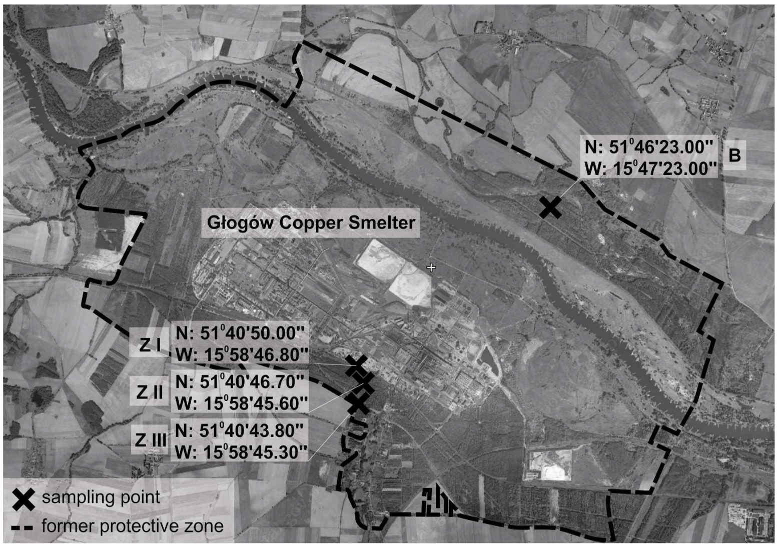

Fig. 1. Location of sampling sites in the protective forest of GCS [12]

Protective zone of the GCS was established in 1987. The purpose of this zone was to compensate the negative impact of the copper smelter on the environment. The surface of the protective zone was ca. 2.8 ha. Early works during the zone construction were started from 1973 [20]. The whole area has been afforested, using the selected tree species (table 3).

The study was conducted in the area of protective forest where the dominant species were *Populus robusta* L. and *Betula pendula* Rorth. The sanitary zone outlook has been shown in Fig. 2.

Fig. 2. Protective forest shaping at site B and Z1 [phot. by Kostecki, 2008]

The dominant species in the test-site B is poplar. Occasionally there are also birch and sessile oak. The undergrowth is rich in *Achillea millefolium* L., T*araxacum officinale* L., *Artemisia vulgaris* L., *Equisetum arvense* L., *Dryopteris filix-mas* L. and various species of grasses.
The dominant species in the test-site Z1 is birch. Undergrowth is rich in species such as *Caragana arborescen*s L., *Pinus nigra* L. and *Robinia pseudoacacia* L. Groundcover is poor – the most common species is *Rumex acetosella* L. In point Z2 main species is *Populus robusta*. No Undergrowth was found. The groundcover beside *Rumex acetosella* L. is full in *Taraxacum officinale* L., *Achillea millefolium* L., *Artemisia vulgaris* L., *Vicia* sp. and *Galium aparine* L. *Populus robusta* L. is a dominant species also in point Z3. Undergrowth at this point is full in *Pinus nigra* L., *Rosa rugosa* L., H*umulus sp*., *Sorbus aucuparia* L. and *Berberis sp*. Groundcover is planted *Achillea millefolium* L., *Taraxacum officinale* L., *Artemisia vulgaris* L., *Equisetum arvense* L., *Urtica dioica* L., *Dryopteris filix-mas* L., *Cirsium arvense* L., *Polygonum persicaria* L. and various species of grasses.
The whole described area is situated in moderate climate, climatic region nr 23 (Lower Silesia West). Mean annual sum of rainfall is about 500 mm, mean annual temperature 8.4^0C. The domination of western and south-western winds, with the average speed lower than 5 $m \cdot s^{-1}$ is characteristic for this climatic region [30]. According to data from the Głogów-Bielawy meteorological station [31], the annual rainfall can vary from year to year. For example in 2010 the mean annual rainfall was 606.7 mm, and in 2011 – only 353.3 mm.
The area is covered by the soils of different origin – alluvial, connected with the Odra river activity and terrestrial. To the south of the smelter the Cambisols, Luvisols, Arenosols, Podzols and occasionally Phaeozems are noted, in turn north from the smelter the Fluvisols are typical soils.

2.2. Material sampling

Monitoring of the environment affected by the Głogów copper smelter was conducted in 2007-2011. In the year 2008, four test-sites were selected as representative for the land exposed to the negative impact of the Głogów copper smelter. Main reasons were: location of the smelter facilities, distance from the smelter, meteorological conditions and the plant cover. Samples were taken from the litter and topsoil (up to 20 cm). Mass of the mean sample was about 1 kg and was composed from the 30 individual samples. Samples in each test-site were taken in 3 replications.

2.3. Analytical methods

Air-dried samples were examined for: particle size distribution - determined by the Casagrande-Prószynski hydrometer method; pH in H_2O and 1M KCl suspension (potentiometrically), in the 1:2.5 soil/supernatant suspension. Textural classes were established according to FAO procedure [12]; organic carbon – using Tiurin method; the Cu and Pb content in aqua regia (HCl + HNO_3 in a 3:1 ratio) using atomic absorption FAAS according to ISO 11466.

3. RESULTS AND DISCUSSION

The particle size distribution of the soils covering the sanitary zone is mostly sandy loam and loamy sand. The particle size distribution has been summarized in table 4. The area of GCS protective forest is covered by different soils, genesis of which has been connected with the activity of the Odra river (floodplain terrace) and glacier activity of the Middle-Poland glaciation period (Dalkowskie Heights). In Zukowice (Z 1, 2, 3) locality, Cambisols and Luvisols are mainly presented, in Bogomice (B) locality – Fluvisols, Cambisols and Histosols [2, 29, 30]. The formation of soils in Stypulow (S) locality is connected both with glacier and Odra river activity, which formed Haplic Luvisols from loamy sands and boulder clays [14].
The reaction of tested soils is slightly acidic to neutral (B, Z1, Z2, S). In the soils samples taken in Żukowice II the alkaline reaction was noted (table 1). Similar pH values was found by other researchers [13]. The difference of pH between the test-sites Żukowice I and II should be connected with the different lime input in the eraly stage of the protective zone formation.

Table 4. Grain-size composition of tested soils

Study site	Depth, cm	Sand, %	Silt, %	Clay, %	Soil texture
Z1	4÷0	-	-	-	-
	0÷20	74	25	1	Loamy sand
Z2	2÷0	-	-	-	-
	0÷18	57	43	0	Sandy loam
Z3	2÷0	-	-	-	-
	0÷18	65	33	2	Sandy loam
B	3÷0	-	-	-	-
	0÷23	54	41	5	Sandy loam
S	0÷30	82	18	0	Loamy sand

The ability of contaminants migration depends not only on the plant cover, but also on organic matter content and grain size composition of the soil. These parameters determine the capacity of the sorption complex of the soil [32].

The average content of total organic carbon ranged from 7.95 to 17.0 mg·kg^{-1}. The lowest content was found in the Z1 site. Othere aforestated sites (Z2, Z3, B) cointaine comparable higher amounts of TOC (Table 5).

Total content of copper and lead vary with depth of the soil profiles. Concentration of copper in the litter horizon was 3320 mg·kg^{-1} (Z2) up to 5250 mg·kg^{-1} (Z1). The concentration of lead was smaller than copper and vary from 960 mg·kg^{-1} (Z2) to 1480 mg·kg^{-1} (B). The content of selected heavy metals in the humic horizon vary from 860 mg·kg^{-1} (Z3) to 1350 mg·kg^{-1} (point B) for copper and 145 mg·kg^{-1} (Z3) to 275 mg·kg^{-1} (B) for lead, what has been shown in table 5.

Plant cover plays the essential role in protecting soil from the erosion and other form of degradation, which draws attention of many authors [3, 4, 7, 8, 11, 27]. Protective forest around Głogów copper smelter, despite of a significant proportion of poplar, is a real multispecies habitat (Table 3). Zhan et al. [35] proved that the introduction of pioneer plants and some agrotechnical treatments can prevent significant blurring of the surface layers. Plant cover affects the retention of minerals. It is also preventing them from leaching from the area likely to be affected by erosion. Poplars and birches effectively stop the pollution of heavy metals, preventing their further horizontal and vertical migration.

Table 5. Total content of Cu and Pb in tested soils

Study site	Depth, cm	pH_{H2O}	pH_{KCl}	Cu, mg·kg^{-1}	Pb, mg·kg^{-1}	TOC, mg·kg^{-1}
Z1	4÷0	6.6	5.9	5250	1290	9.30
	0÷20	5.1	4.4	1210	330	6.60
$\bar{x}$	-	-	-	3230	810	7.95
Z2	2÷0	6.9	6.6	3320	960	21.0
	0÷18	8.0	7.4	1000	200	12.9
$\bar{x}$	-	-	-	2160	580	17.0
Z3	2÷0	7,.4	7.0	4390	1250	15.5
	0÷18	7,4	7.2	860	145	9.5
$\bar{x}$	-	-	-	2630	695	12.5
B	3÷0	7.0	6.5	3970	1480	14.3
	0÷23	5.1	4.1	1350	275	7.90
$\bar{x}$	-	-	-	2660	875	11.1
S	0÷30	7.5	74	6.60	24.3	13.8

Table 6. The correlation matrix

	Soil fraction, %			TOC, mg·kg^{-1}	pH	
	Sand	Silt	Clay		H_2O	KCl
Cu, mg·kg^{-1}	-0.156	0.013	0.596	-0.874	-0.931	-0.593
Pb, mg·kg^{-1}	0.329	-0.405	0.180	-0.865	-0.886	-0.685

Cu and Pb are present in the soil naturally (parental rock) and as a result of anthropogenic activities. The copper content of the Polish soil is 1-110 mg·kg^{-1}, and lead 5-85 mg·kg^{-1} [16]. Cu plays significant role as the fertilizer, but in an amount of 20-100 mg·kg^{-1} may be harmful to plants. There was no data of lead importance to the biochemical cycles of plants. In an amount of 30-300 mg·kg^{-1}, like the copper, lead can be toxic to plants [16]. These toxicity depend on the species, variety and environmental factors.

Numerous studies [16, 23] indicate that both copper and lead is easily sorb by the soil organic matter. Immobilisation of these elements is natural in alkaline reaction. The acidic reaction contributes to incrising of their mobility.

As the main source of the anthropogenic pollution around the Głogów Copper Smelter mentioned activities such as: mining, ore treatment and copper ore smelting [19, 22].

The highest concentration of heavy metals was found in the organic matter horizon (for Cu 3320–5250 mg·kg^{-1} d.m., for Pb 960–1480 mg·kg^{-1} d.m.), a bit smaller concentrations were found below organic horizon. According to Polish Law [7], the limit of copper and lead content in industrial areas have been establishd at the level of 600 mg·kg^{-1} d.m. The content of Cu and Pb in its total form in the tested soil exceed these values. Statistical analysis showed no significant correlation between the content of any Cu and Pb and soil properties in the sites located in the former sanitary zone.

Research carried out by othere researchers [26, 29, 30] in the area of Glogow Copper Smelter confirm the relationship on connections of copper and lead, with organic matter and reaction. The previous studies have shown a significant enrichment of soil affected by the copper smelting in copper and lead [19, 22]. Lower content of heavy metals was found in cultivated soils. This may indicate a second step of contamination which is typical to forested industrial site - the initial deposition of contaminants on the leaves at the end of growing season enrich the litter horizon. In agricultural areas, biomass is removed periodically.

4. CONCLUSIONS

1. The area of Glogow Copper Smelter protective forest is covered with soils showing clear symptoms of the chemical degradation. The content of Cu

and Pb in the liter horizon and the topsoil exceed Polish threshold values for industrial areas, which is established up to 600 mg kg^{-1} d.m.

2. There is a significant difference between the Cu and Pb content in the litter horizon and the humic topsoil. The forest litter contains 3.3-5.1 more Cu and 3.9-8.6 Pb than the humic horizon of the soil.
3. The main factors influencing the content of heavy metals in soils covering the research site are the particle size distribution of the soil, soil reaction and the soil organic matter content.

REFERENCES

1. Ashman M.R., Puri G.: *Essential soil science: a clear and concise introduction to soil science*, Wiley-Blackwell 2008 pp. 208.
2. Bieroński J., Pawlak W., Tomaszewski J., 2000, Commentary on hydrographic map, scale 1:50000, Arkusz M-33-21-A Głogów, (in Polish).
3. Blume H.P., (Hrsg.): Handbuch des Bodenschutzes Bodenökologie und – belastung Vorbeugende und abwehrende Schutzmaβnahmen, Ecomed 2010 p.782.
4. Dunjó G., Pardini G., Gispert M., 2003: Land use change effects on abandoned terraced soils in a Mediterranean catchment, NE Spain, Catena, **52**, 23–37.
5. Dz. U. 2002 nr 165 poz. 1359 – Order of the Minister of Environment of 9. September 2002 on soil quality and earth quality standards, (in Polish).
6. European Environment Agency, 2000: Down to earth: soil degradation and sustainable development in Europe. A challenge for the 21st century, Environmental issues series no. 16, Copenhagen, Denmark.
7. Fen-Li Z., 2006: Effect of Vegetation Changes on Soil Erosion on the Loess Plateau, Pedosphere, **16**, 4, 420-427.
8. Fu B., Liu Y., Lu Y., He C., Zeng Y., Wu B., 2011: Assessing the soil erosion control service of ecosystems change in the Loess Plateau of China, Ecological Complexity, **8**, 284–293.
9. Fullen M.A., Brandsma R.T., 1994: Property changes by erosion of loamy sand soils in east Shropshire, UK, Soil technology, **8**, 1-15.
10. Geoportal, 2014. Access by http://maps.geoportal.gov.pl/.
11. Greinert H., Greinert A.: Protection and remediation of soil environment (in Polish), Wydawnictwo Politechniki Zielonogórskiej, Zielona Góra 1999, 51-75.
12. Guidelines for soil description. 2006. 4rd Edition, FAO, Rome. 98 pp. 109.
13. Gzyl J., 1999: Soil protection in Central and Eastern Europe, Journal of Geochemical Exploration **66**, 333–337.

14. Kaniecki A., Baczyńska A., Gogołek A., 2005: Komentarz do mapy hydrograficznej w skali 1:50000, Arkusz M-33-8-C Nowa Sól.
15. Karczewska A., Spiak Z., Kabała C., Gałka B., Szopka K., Jezierski P., Kocan K., 2008: Possibility of using methods of assisted phytoextraction for remediation of soils contaminated by copper smelting emissions (in Polish), Wydawnictwo Zante, Wrocław.
16. Kabata-Pendias A., Pendias H., 1999: Biogeochemistry of trace elements, PWN, Warszawa, p. 400.
17. KGHM, 2014. Internet site of KGHM Polska Miedź S.A. Available at http://www.kghm.com/.
18. Leśniczak A., 2005: Forest management plan for the protective zone of Głogów copper smelter from 01.01.2005 to 31.12.2014 r. Volume 1. The general part of the plan - elaboration of nature protection program (in Polish), Brzeg pp. 44.
19. Lis J., Pasieczna A., 2005: Anthropogenic soils pollution within the Legnica–Głogów copper district, Polish Geological Institute Special Papers, 17 (2005), p. 42–48.
20. Luo X., Yu S., Zhu Y., Li X., 2012: Trace metal contamination in urban soils of China, Science of the Total Environment, **421/422**, 17–30.
21. Marques J.J., Schulze D.G., Curi N., Mertzman S.A., 2003: Trace element geochemistry in Brazilian Cerrado soils, Geoderma, **121**, 31–43.
22. Medyńska-Juraszek A., Kabała C. 2012: Heavy metal pollution of forest soils affected by the copper industry, J. Elem. **17** (3), 441-451, DOI 10.5601/jelem.2012.17.3.07.
23. Mengel K., Kirkby E.A., Kosegarten H., Appel T., 2001: Princeples of plant nutrition, Kluwer, Netherlands, p. 864.
24. Ming H., Hea W.X., Lamb D.T. ,b, Megharaj M., Naidu R., 2012: Bioavailability of lead in contaminated soil depends on the nature of bioreceptor, Ecotoxicology and Environmental Safety **78**, 344–350.
25. Montanarella L., 2007: Trends in land degradation in Europe, in: SivaKumar M.V.K., Ndiang'Ui N. (red.): Climate and Land Degradation, Springer, 84-86.
26. Rosada J., Grzesiak J., 2009: Distribution of copper, lead and zinc forms in solid phase of soil influenced by emission of copper smelter "Głogów", Progress in Plant Protection/Postępy w Ochronie Roślin, **49** (3), 1155 – 1158.
27. Shrestha R.P., Schmidt-Vogt D., Gnanavelrajah N., 2010: Relating plant diversity to biomass and soil erosion in a cultivated landscape of the eastern seaboard region of Thailand, Applied Geography, **30**, 606–617.

28. Singer M.J., Munns D.N.: Soils an introduction, New York, Macmillan Publishing Company 1987 pp. 492.
29. Szerszeń L., Karczewska A., Roszyk E., Chodak T., 1991: Distribution of Cu, Pb and Zn in soil profiles adjacent to the copper smelters (in Polish), Roczniki Gleboznawcze, **42**, 3/4, 199–206.
30. Szerszeń E., Chodak T., Kabała C., 2004: Zmiany zawartości miedzi, ołowiu i cynku w glebach w rejonie hut miedzi Głogów i Legnica w latach 1972-2002, Roczniki Gleboznawcze, **55**, 3, 195-205.
31. Traxelektronik, 2012, Access by http://www.traxelektronik.pl (in Polish).
32. Vega F.A., Covelo E.F., Andrade M.L., Marcet P., 2004: Relationships between heavy metals content and soil properties in minesoils, Analytica Chimica Acta, **524**, 141–150.
33. Vrščaj B., Poggio L., Marsan F.A., 2008: A method for soil environmental quality evaluation for management and planning in urban areas, Landscape and Urban Planning, **88**, 81–94.
34. Wilkinson A.G., 1999: Poplars and willows for soil erosion control in New Zealand, Biomass and Bioenergy, **16**, 263–274.
35. Zhan B., Yang Y.S., Zepp H., 2004: Effect of vegetation restoration on soil and watererosion and nutrient losses of a severely eroded clayey Plinthudult in southeastern China, Catena, **57**, 1, 77–90.

DEGRADACJA ZIEMI NA TERENACH BYŁEJ STREFY OCHRONNEJ HUTY MIEDZI GŁOGÓW

Streszczenie

Powierzchnia ziemi jest nieustannnie narażona na oddziaływania o charakterze naturalnym i antropogenicznym. Znaczące oddziaływanie jest łatwo zauważalne na terenach przemysłowych. Szczególnie na obszarach objętych wydobyciem i przeróbką metali. Na terenach przyległych do Huty Miedzi Głogów stwierdzono wysoką koncentrację miedzi i ołowiu sięgającą 5250 $mg \cdot kg^{-1}$ Cu i 1290 $mg \cdot kg^{-1}$ Pb. Poziom ściółki leśnej zawierał 3,3-5,1 raza więcej Cu i 3,9-8,6 Pb niż poziom próchniczny analizowanych gleb. Analiza różnych gleb pokrywających las ochronny HMG pozwoliła wskazać na znaczącą rolę składu granulometrycznego, zawartości węgla organicznego oraz odczynu na stabilizację migracji Cu i Pb w środowisku.

Słowa kluczowe: metale ciężkie, miedź, ołów, tereny przemysłowe, zanieczyszczenie gleby

Editor received the manuscript: 03.12.2014