**Original Scientific Paper**
10.7251/AGRENG1701083M
UDC 504.5:546.3

# INFLUENCE OF AGROCHEMICAL REHABILITATION ON THE HEAVY METAL MIGRATION TO THE WATER

Yuri MAZHAYSKIY[1], Olga CHERNIKOVA[2], Alexey KARPOV[2], Otilija MISECKAITE[3*]

[1]Russian Scientific-Research Institute of Hydrotechnyc and Melioration, Russian Federation
[2]Federal State Budgetary Educational Institution of Higher Professional Education Ryazan State Agrotechnological University n. a. P. A. Kostichev, Russian Federation
[3]Aleksandras Stulginskis University, Lithuania
*Corresponding author: otilija. miseckaite@asu. lt

## ABSTRACT

Soil plays the main role in the sustaining life of Earth ecosystems –it is the fundamental foundation of agriculture resources, food security, economy and environmental quality. The heavy metal pollution has been increasing in agricultural soils worldwide. For example, Cu is widely used as a pesticide against fungal and bacterial diseases in crops or as a contaminant in organic amendments, or for irrigation as pig manure or sewage sludge. Soil and water pollution have the great impact on food safety and to human health: polluted soils have direct health risks, and secondary risk is connected to contamination of water supplies. The articlepresents the lysimetric experiment with the chemical composition results. This exploratory study aims to evaluate the influence of agrochemical rehabilitation on the heavy metal migration to the water. The chemical composition of intra soil water has shown that contaminated black soil has a high absorption capacity of heavy metals. The bulk of heavy metal brought about in a form of water-soluble salts wasabsorbedand converted by soil colloids of podzolized chernozeminto relatively stable compositions. Results of the analytical research showed that organic and organic-mineral systems, where phosphates were used in the average volume of 60 kg of $P_2O_5$per hectare a year, reduced intake of cadmium in the subsurface water. Mineral systems also impeded migration of zinc and copper to the ground water. On the contrary, high doses of superphosphate in the fertilizer system increased the leaching of Cd, Pb and Cu to the infiltration waters.

**Keywords**: *heavy metals, pollution, water, soil, detoxification methods.*

## INTRODUCTION

Environmental pollution and food safety are two of the most important issues of our time. Soil and water pollution, in particular, have historically impacted on food safety which represents an important threat to human health (Lu *et al*., 2015). It has been widely accepted that soil plays a key role in sustaining life of Earth ecosystems with the huge abundance of soil microbiota(Young and Crawford, 2004). Soils polluted with heavy metals have become common across the globe due to increase in geologic and anthropogenic activities (Chibuike and Obiora, 2014). Soils may become contaminated by the accumulation of heavy metals and metalloids through pesticides, wastewater irrigation, spillage of petrochemicals, leaded gasoline and paints, animal manures, sewage sludge, emissions from the rapidly expanding industrial areas, mine tailings, disposal of high metal wastes, land application of fertilizers, coal combustion residues, and atmospheric deposition (Khan et al., 2008; Zhang et al., 2010).

Heavy metal pollution is increasingly threatening to crop production in agricultural soils (Weber *et al*., 2001). In the environment, Cu is widely used as a pesticide against fungal and bacterial diseases in crops or as a contaminant in organic amendments such as pig manure or sewage sludge (Christie and Beattie, 1989). Microorganisms are generally described as more sensitive to Cu and other heavy metal stresses than other organisms in soil biocenosis (Giller *et al*.,1998). While crop production in agricultural lands has been increasingly threatened by heavy metal contamination (Weber *et al*., 2001), long term impacts of heavy metal pollution on soil microorganisms have been increasingly concerned. Metals can exist in various chemical forms (or species). These forms often exist in a complex equilibrium governed by many soil factors and properties. For any given heavy metal, only a fraction is bioavailable and thus potentially it is only this fraction that can be taken up by the plants. More of the metal could be converted to the bioavailable fraction as it is gradually removed by the plant but the extent to which this happens and the kinetics of such processes are not known and would invariably be soil specific (Khan *et al*., 2000). Microbial biomass has been shown sensitive to increased heavy metal concentrations in soils(Giller *et al*., 1998). Heavy metal Cu and Cr pollutants can be attributed to various anthropogenic activities related to the industry; nevertheless, natural weathering process may also play a role as a source of these heavy metals (Ismail et al., 2016). The concern over soil contamination stems primarily from health risks, both of direct contact and from secondary contamination of water supplies (Soil Contamination, 2008). Migration of contaminants into non-contaminated sites as dust or leachate through the soil, and the spreading of sewage sludge are examples of events that contribute towards contamination of our ecosystems (Khan et al., 2000).

Contaminated soil can be remediated by chemical, physical or biological techniques (McEldowney et al., 1993). The rehabilitation technologies of agricultural land polluted with organic substances, are based on biodegradation of pollutants "in situ" and the cultivating of tolerant plants, parallel to implementation of agro-technical measures, which aim: the soil aeration through loosening; the soil reaction correction and balancing of the ratio carbon/nitrogen C/N through the administration of organic and mineral fertilizers (Sabau and Sandor, 2014). It was possible to reduce the content of hydrocarbons markedly in oil-polluted soils, even without fertilizers and amendments, as a result of intensive loosening. This indicates a sufficiently large potential of sod-podzolic soils for self-recovery and high effectiveness of loosening in the first period after pollution (Lednev, 2007). Migratory capacity of heavy metals depends on cumulative properties of soil, chemical pollutants and landscape environment (Breus *et al*., 2001; Dybin, 2001). Pollutants coming from the atmosphere tend to concentrate in the soil horizons containing humus. However, in soil with low buffering capacity and under the influence of physic-chemical, biological and other processes heavy metals (HMs) are transferred from exchange-absorbed state into the soil solution and with downdrafts can be moved into the underlying layers. The objective of research– to evaluate the influence of agrochemical rehabilitation on the heavy metal migration to the water.

## MATERIAL AND METHODS

Long-term stationary experiments were conducted in lysimeters of experimental design of Russian Institute of Hydraulic Engineering and Land Reclamation (VNIIGiM) with pristine soil profile. The area of stationary soil lysimeters was equal to 0. 78 and 1. 17 m. Within the research program there were carried out experiments to study the following fertilizer systems: organic (cattle manure), organomineral and mineral. High doses of double superphosphate were used periodically and annually in rotational cropping. The allowance of 100 t ha$^{-}$ (table 1) was accepted for podzolic heavy loam chernozem.

Table 1. Scheme of establishment and implementation of the field lysimeter experiment

| Variants | Names of variants and the fertilizer application system in the crop rotation link |
|---|---|
| I | Control |
| II | Cattle manure 100 t ha$^{-}$ – Periodic application |
| III | Cattle manure 100 t ha$^{-}$ – Periodic application,<br>$N_{60-90}$ $P_{60}$ $K_{60-120}$ – Annually, depending on a culture |
| IV | Application of phosphorus, once in 2 years in a dose of 120 kgha$^{-}$ andannual application of $N_{60-90}$ $K_{60-120}$ |
| V | Application of phosphorus, once in 4 years 240 kg ha$^{-}$ and annual application of $N_{60-90}$ $K_{60-120}$ |
| VI | Annual application of an elevated dose of phosphorus (120 kg ha$^{-}$)and<br>$N_{60-90}$ $K_{60-120}$ |

The research was conducted in the period between 2006 and 2008. Barley of Nevskiy variety, fodder beet Eckendorf yellow, oat – Horizon.

In the experiment an elevated level of soil contamination was modelled based on the geochemical background of the region: Cu – 90, Zn – 110, Pb – 40, Cd – 0. 6 mg kg$^{-}$. For this purpose, chemically pure salts Zn $(CH_3COO)_2x2H_2O$, $CuSO_4x5H_2O$, $Pb(CH_3COO)_2$, $CdSO_4$were used, taking into account background levels of gross forms of heavy metals in the soil.

## RESULTS AND DISCUSSION

In our conditions pollution of the soil with heavy metals was conducted in autumn of the year 2004 by means of water-soluble salts. It is known that due to sorption processes when salt is applied to the soil HMs are absorbed by soil colloids, which are presented in the soil as mineral, organic and organomineral compounds. Due to polyfunctionality of soil as a sorbent, its sorption capacity is not the same for different HMs and their cations. And processes of internal diffusion of molecules and ions may limit the speed of sorption. It may be also limited by the dissolution rate of soil compounds involved in the subsidence of contaminants. Consequently, when contaminants are released into the soil it takes a long time to establish sorption equilibrium.

There are two periods in the water regime of chernozem: 1. Draining - covers all summer and the first half of autumn, when water is rapidly consumed by plants and evaporates because ascending currents prevail over descending ones; 2. Soaking - starts from the second half of autumn, is interrupted by frosts and continues in spring, because of snowmelt waters and spring rainfall. Mainly the depth of rainfall, its distribution over time and its temperature determines these factors. Summer rainfall moistures only the topsoil. Moisture in the subsurface of chernozems is created by precipitation during the cold period (Elpatyevskiy, 1993). Therefore, precipitation of the late period creates additional moisture, which contributes to pollution of intrasoil waters with heavy metals.

The studies of Meshchersky Branch of VNIIGiM (Mazhayskiy et al.,2000) carried out at the ecological testing area “Meshchera” (Russia) showed the following concentration ranges of HMs in the water infiltrated through sod-podzolic soil: Pb - from 0. 33 to 0. 80 mg $L\cdot10^{-}$; Cd from 0. 6 to 0. 11 mg $L\cdot10^{-}$; Zn from 0. 16 to 2. 37 mg $L\cdot10^{-}$; Cu from 0. 9 to 0. 21 mg $L\cdot10^{-}$.

The research conducted within a lysimetric experiment aimed at studying the chemical composition of intrasoil water has shown that contaminated black soil has a high absorption capacity for HMs (Chernikova, 2010). The bulk of HMs brought about in a form of water-soluble salts, was adsorbed and converted by soil colloids of podzolized chernozem into relatively stable compositions. Contaminated soil of the first variant during the years of research increased migration of Cu and Cd to the intrasoil waters, whereas Pb and Zn demonstrated a better resistance to washing out in comparison to natural soils (table 2, table 3). The studied fertilizer systems in varying degrees increased the release of Pb and decreased migration of Cd to the infiltration waters. Their contamination with Pb increased by 1. 6% and equalled 89%, but concentration of Cd lowered by 20% and equalled 53%, except from the variant for which increased doses of phosphate were used (variant VI) (table 2, table 3). In this variant we registered increased leaching of Cd to the infiltration waters.

Table 2. Influence of agrochemical rehabilitation on the migration of Zn and Cu to the intrasoil waters (mg L·10⁻)

| Variant | Zn | | | Cu | | |
|---|---|---|---|---|---|---|
| | 2006 | 2007 | Average | 2006 | 2007 | Average |
| I | 0. 48 | 1. 28 | 0. 89 | 0. 12 | 0. 36 | 0. 24 |
| II | 0. 51 | 2. 37 | 1. 44 | 0. 21 | 0. 19 | 0. 20 |
| III | 2. 08 | 0. 37 | 1. 23 | 0. 23 | 0. 25 | 0. 24 |
| IV | 0. 40 | 1. 32 | 0. 86 | 0. 12 | 0. 11 | 0. 12 |
| V | 0. 41 | 0. 11 | 0. 26 | 0. 17 | 0. 10 | 0. 14 |
| VI | 0. 51 | 0. 96 | 0. 78 | 1. 6 | 0. 11 | 0. 86 |

In the waters infiltrated through the profile of chernozem organic and organic-mineral fertilizers increased concentration of Zn by 62% and 38% respectively. Content of this element decreased by 3. 4% and equalled 40. 8% under the influence of mineral systems.

Table 3. Influence of agrochemical rehabilitation on the migration of Pb and Cd to the intrasoil waters (mg L·10⁻)

| Variant | Pb | | | Cd | | |
|---|---|---|---|---|---|---|
| | 2006 | 2007 | Average | 2006 | 2007 | Average |
| I | 0. 70 | 0. 58 | 0. 64 | 0. 15 | 0. 14 | 0. 15 |
| II | 0. 62 | 0. 99 | 0. 85 | 0. 06 | 0. 08 | 0. 07 |
| III | 1. 62 | 0. 80 | 1. 21 | 0. 07 | 0. 13 | 0. 10 |
| IV | 0. 88 | 0. 80 | 0. 84 | 0. 05 | 0. 19 | 0. 12 |
| V | 0. 74 | 0. 56 | 0. 65 | 0. 03 | 0. 20 | 0. 12 |
| VI | 0. 82 | 1. 19 | 1. 01 | 0. 08 | 0. 29 | 0. 18 |

Under the influence of annual dose of phosphorus (P120) copper like lead and cadmium substantially migrated to infiltration waters. Other mineral fertilizer system (variants IV and V) approximately halved concentration of copper in intrasoil waters. With the organic system a decrease of copper in the waters was less (17%), and with the organic-mineral system concentration has not changed compared to Variant I (control).

Microcosm experiments detected the microbial community modifications with greater precision in the short-term, while field experiments showed that the biological effects of Cu contamination may be overcome or hidden by pedo-climatic variations (Ranjard et al., 2006).

(Rusu et al., 2004) the experimental data confirm the positive significance of the treatments effects of reaction correction in interaction with organic or complex mineral fertilization as well as the interaction of the zeolitic tuffs and bentonite with fertilizers. These agrochemical measures aim to acidity neutralization, decrease of the heavy metals mobility activity, calcium and primary macro elements contribution and in the last but least, restoration of the soil buffering capacity (Mohammad, 2015). The results showed the effect of water temperature on the explosive extraction/degradation and redistribution of the HMs in the soil.

## CONCLUSION

Results of the analytical research showed that organic and organic-mineral systems where phosphates were used in the average volume of 60 kg of $P_2O_5$per hectare a year, reduced intake of cadmium in the subsurface water. Mineral systems also impeded migration of zinc and copper to the ground water. On the contrary, high doses of superphosphate in the fertilizer system increased the leaching of Cd, Pband Cu to the infiltration waters. The bulk of HMs brought about in a form of water-soluble salts, wasadsorbedand converted by soil colloids of podzolized chernozem into relatively stable compositions. The studied fertilizer systems in varying degrees increased the release of Pb and decreased migration of Cd to the infiltration waters: contamination with Pb incre-ased by 1. 6% and equalled 89%, but theconcentration of Cd lowered by 20% and equalled 53%, except fromthe variant for which increased doses of phosphate were used. In the waters infiltrated through the profile of chernozem organic and organic-mineral fertilizers increased aconcentration of Zn by 62% and 38% respectively. The content of this element decreased by 3. 4% and equalled 40. 8% under the influence of mineral systems. Under the influence of the annual dose of phosphorus (P120) copper like lead and cadmium substantially migrated to infiltration waters. Other mineral fertilizer system approximately halved concentra-tion of copper inintrasoilwaters. With the organic system a decrease of copper in the waters was less (17%), and with the organic-mineral system concentration has not changed compared to control.

## REFERENCES

Breus, I. P., Sadriev, G. R., Ignatyev, Yu. A. (2001). Lysimetric research of toxicants infiltration in typical soils of the Volga-Kama forest-steppe. Bulletin of the All-Russian Research Institute of Agrochemistry, No. 114, pp. 66 – 67.

Chernikova, O. V. (2010). Ecological study of complex techniques of rehabilitation of chernozem polluted with heavy metals (the case of the Ryazan region). Doctoral thesis (Biology), Ryazan, 172 p.

Chibuike, G. U., Obiora, S. C. (2014). Heavy Metal Polluted Soils: Effect on Plants and Bioremediation Methods. Applied and Environmental Soil Science. Vol. 2014, Article ID 752708, 12 pages, http://dx. doi. org/10. 1155/2014/752708 Accessed on 16/06/2016.

Christie, P., Beattie, J. A. M. (1989). Grassland soil microbial biomass and accumu-lation of potentially toxic metals from long term slurry application. Journal Soil Ecology, Vol. 26, pp. 597–612.

Dybin, V. V. (2001). Influence of heavy metals on composition of lysimetric waters. Bulletin of the All-Russian Research Institute of Agrochemistry, No. 115, pp. 127 – 128.

Elpatyevskiy, P. V. (1993). Geochemistry of migration flows in natural and natural-technical environments. – Moscow, Science. – 253 p.

Giller, K. E, Witler, E., McGrath, S. P. (1998). Toxicity of heavy metals to micro-organisms and microbial processes in agricultural soils: a review. *Soil Biology&Biochemistry*, Vol. 30, pp. 1389–1414.

Ismail, A., Toriman, M. E., Juahir H., Md Zain, S., Habir, N. L. A., Retnam, A., Amri M. K. Kamaruddin, Roslan Umar, R.,Azid A. (2016). Spatial assessment and source identification of heavy metals pollution in surface water using several chemometric techniques. Marine Pollution Bulletin, Vol. 106, pp. 292–300.

Khan, A. G., Kuek, C., Chaudhry, T. M., Khoo, C. S., Hayes, W. J. (2000). Role of plants, mycorrhizae and phytochelators in heavy metal contaminated land remediation Chemosphere, Vol. 41, pp. 197-207.

Khan, S., Cao, Q., Zheng, Y. M., Huang, Y. Z., Zhu, Y. G. (2008). Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, China. Environmental Pollution, Vol. 152, no. 3, pp. 686–692.

Lednev, A. V. (2007). Effect of a Set of Agrochemical Practices on Rate of Decomposition of Oil in Polluted Sod-Podzolic Soils. Russian Agricultural Sciences, Vol. 33 (2), pp. 107–108.

Lu, Y., Song, S., Wang, R., Liu, Z., Meng, J., Sweetman, A.J., Jenkins, A., Ferrier, R.C.,, Li, H., Luo, W., Wang, T. (2015). Impacts of soil and water pollution on food safety and health risks in China. Environment International. Vol. 77, pp. 5–15.

Mazhayskiy, Yu. A., Bochkarev Ya. V., Zheliazko V. I. (2000). Regulation of water regime under technogenic pollution of soil. Modern energy and resource saving environmentally sustainable technologies and agricultural production systems: Collection of scientific works. Ryazan State Agricultural Academy, pp. 8-12.

McEldowney S., Hardman D. J., Waite S. (1993). Treatment Technologies. Pollution Ecology and Biotreatment Technologies, p. 341.

Mohammad N. I., Ho-Young J. Jeong-Hun P. (2015). Subcritical water treatment of explosive and heavy metals cocontaminated soil: Removal of the explosive, and immobilization and risk assessment of heavy metals. Journal of Environmental Management, Vol. 163, pp. 262-269.

Ranjard L., Echairi A., Nowak V., Lejon D. P. H., Nouaim R., Chaussod R. (2006). Field and microcosm experiments to evaluate the effects of agricultural Cu treatment on the density and genetic structure of microbial communities in two different soils. Federation of European Microbiological Societies, Vol. 58, pp. 303-315.

Rusu, M., Marghitas, M., Mihaiescu, T., Todoran, A. (2004). Agrochemical measures for soil reclamation in connection with heavy metals pollution. 53-58p.,XXXIV Annual Meeting of ESNA / jointly organised with IUR working group soil-to-Plant transfer University of Novi Sad, Serbia and Montenegro, August 29-September 2, 2004. Working Group 3, Soil-Plant-Relationships Proceedings December 2004.

Sabau, N. C., Sandor, M. (2014). The influence of fertilization on wheat yield losses achieved during the agrochemical melioration of a soil, under control polluted with crude oil, from Oradea. Analele Universităţii din Oradea, Fascicula: Protecţia Mediului, Vol. 23, pp. 763-768.

Soil Contamination: New Research (2008). (Edt. Anton N. Dubois), Nova Science Pub Inc, ISBN: 978-1-60456-144-92008, 215p.

Weber, O., Scholz, R. W, Bühlmann, R., Grasmuck, D. (2001). Risk Perception of Heavy Metal Soil Contamination and Attitudes toward Decontamination Strategies. Risk Analysis, Vol. 21, pp. 967–977.

Young, M., Crawford, J. W. (2004). Interactions and self-organization in the soil-microbe complex. Science, Vol. 304, pp. 1634–1637.

Zhang, M. K., Liu, Z. Y., Wang, H. (2010). Use of single extraction methods to predict bioavailability of heavy metals in polluted soils to rice. Communications in Soil Science and Plant Analysis, Vol. 41 (7), pp. 820–831.