ISSN 1070-3632, Russian Journal of General Chemistry, 2019, Vol. 89, No. 13, pp. 1–5. © Pleiades Publishing, Ltd., 2019.
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Estimation of the Soil Toxicity Level in the Areas of Anthropogenic Mineral Deposits by Means of Quantitative Parameters and Biotesting

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Received October 22, 2018; revised January 7, 2019; accepted January 11, 2019

Abstract—The level of soil pollution in the areas of manganese slug dumps from ferroalloy production has been estimated on the basis of heavy metal content of soils and response of test plants. The concentrations of heavy metals in soils have been determined, the corresponding hazard factors have been calculated, and the toxicity level of soils has been assessed. Such studies make it possible to simultaneously judge the amount of toxicants (namely heavy metals) in soils and evaluate the level of soil toxicity by the response of biological species used in biotesting.

Keywords: environment, soil, slag, heavy metals, biotesting, pollution

DOI: 10.1134/S1070363219130012

All processes related to the management of industrial waste pose a serious hazard to the environment [1–3]. Significant land areas are allocated for waste storage, including hundreds of thousands of hectares of land suitable for agricultural use. Transportation and storage of metallurgical waste divert significant funds from the main production and are serious sources of local pollution [4]. The gap between the progressive accumulation of waste and the level of their disposal threatens to deepen the environmental crisis and aggravate the economic situation. Accumulation of industrial waste, especially in industrialized regions, causes a significant environmental impact.

Particularly significant changes in the environment are observed in old industrial areas, where anthropogenic impact is permanent in nature [5]. Anthropogenic mineral deposits (AMD) were generally formed without preliminary engineering and geological research and installation of anti-filtration screens of their bases. Therefore, there is a significant migration of various chemical elements, in particular heavy metals. Anthropogenic mineral deposits as sources of environmental pollution are characterized by significant concentrations of heavy metals in various forms. They affect natural resources such as the atmosphere, water, and soil. This publication focuses on the effect of AMDs on soil. The impact of AMDs on land resources can be considered in terms of mechanical and chemical contamination of the soil adjacent to anthropogenically affected areas, which leads to disturbance of physical and mechanical compositions and properties of the soil cover [5]. The problem of heavy metal pollution of soils exists not only in some particular regions; every year it is aggravated on a global scale [6]. Secondary pollution due to the removal of heavy metals from dumps of mines or metallurgical enterprises by water or air flows can serve as a source of contamination of biocenoses with heavy metals [7].

It is known that the slag from ferrosilicomanganese production at the Nikopol Ferroalloy Plant (Nikopol, Ukraine) contains the following heavy metals: nickel, cobalt, zinc, and manganese [8].

Both low and high manganese content of soil cover adversely affect animals and plants [7, 9]. Manganese is an element that accumulates in soils [10]. Weathering of both rocks and AMDs releases nickel which then precipitates mainly with iron and manganese oxides. However, bivalent nickel can migrate over a long distance [1, 4]. The relatively high fraction of nickel leached from soil suggests that this element is weakly held by various soil components in comparison to cobalt [1, 11]. The crystalline structure of manganese oxides and hydroxides is important from the geochemical viewpoint. According to [9], it is responsible for the high degree of association with manganese nodules of some heavy metals, such as Co, Ni, Cu, and Zn [4]. Zinc is toxic only in very high concentrations. Acute zinc poisoning causes death of leaves and shoots of plants is observed, and respiratory organs, liver, kidneys, and skin are affected in animals [5]. Zinc entering soil with ferroalloy waste is very mobile [12–14].

A typical soil type for the Northern Steppe of Ukraine is ordinary low humus heavy loamy chernozem on loess, with a pH value of more than 6 [15]. Heavy metal oxides and hydroxides are poorly soluble in neutral soils. The mobility of zinc is strongly reduced due to formation of poorly soluble compounds in soils with pH > 6, corresponding to the Northern Steppe of Ukraine, especially in the presence of phosphates [7]. As noted in [16], a high concentration of heavy metals is generally observed in the upper layers of soil (0–5, 0–10, and 0–30 cm). The highest heavy metal mobility is typical for the 0–10-cm layer, and heavy metals migrate mainly in the vertical direction from top to bottom within a 30-cm layer.

In general terms, taking into account the solubility of various heave metal compounds, they can be ranked with respect their toxicity depending on the acidity in the following series: $\mathrm{Ni} \geq \mathrm{Zn} \geq \mathrm{Mn}$ according to [7] or $\mathrm{Co} \approx \mathrm{Ni} < \mathrm{Zn}$ according to [17]. The bioavailability of anthropogenic heavy metals such as Mn and Zn decreases as the soil particle size decreases. This shows that significant amounts of anthropogenic heavy metals exist in their stable form in small soil particles [18]. For example, Yu et al. [19] showed the possibility of stabilizing heavy metals in soils with the use of organobentonites, which could restore polluted soils.

Unlike other pollutants that decompose in soil by the action of physicochemical and biological factors, heavy metals reside therein for a long time, even after the source of pollution has been removed; therefore, soil can be regarded as a long-term indicator of environmental pollution with heavy metals [20].

In recent years, decrease in the amount of industrial waste has been observed in both Ukraine and Russia, which is associated with a drop in industry, in particular due to the economic crisis; however, the accumulated industrial waste has a significant impact on the state of the Dnipropetrovsk region as one of the industrialized regions of Ukraine. The largest manganese concentrate processing and ferroalloys production enterprise is located in Nikopol, Dnipropetrovsk region. The total heavy metal content of soils of this settlement exceeds the maximum allowable concentration (MAC). According to [15], manganese contributes most to soil pollution (5.7–8.1 MAC). The total pollution index calculated from the total content of heavy metals is 28.4 for Nikopol. The concentration of mobile forms of heavy metals in chernozems of the Northern Steppe of Ukraine under naive conditions is usually small, and it rarely reaches 1.0% of their total content [15]. Pavlichenko [21] proposed to consider manganese and zinc to be priority metals in the territory of Nikopol; on the basis of soil toxicity assessment, he ranked the state of soils in the city as “unsatisfactory.”

The available data indicate that often a general assessment of the urban environment is carried out, whereas there is no data on local soil pollution outside the sanitary protection zone of enterprises. These studies are especially relevant for the territory of the Nikopol Ferroalloy Plant, in the immediate vicinity of which agricultural land is located. It is known that bioavailable heavy metals present in soil can accumulate in agricultural crops, in particular in rice grains [22].

The goal of this study was to determine the level of soil pollution near anthropogenic mineral deposits using physicochemical research methods and biological indicators. To achieve this goal, a number of tasks were set: determination of heavy metal content of soil at the border of the sanitary protection zone of the enterprise; determination of the hazard index of heavy metals; and soil toxicity assessment using bioassay.

EXPERIMENTAL

The actual concentration of various forms of heavy metals of hazard classes I–III in the ferrosilicomanganese slag from ferroalloy production, as well as in soil samples, was determined by atomic absorption spectroscopy.

Studies were carried out in Ukraine according to the state regulatory documents. The toxicity indices for heavy metals were determined according to GSanPiN (state sanitary norms and rules) 2.2.7.029-99 “Hygienic requirements for industrial waste management and determination of their hazard class for public health” by calculating toxicity indices [23]. To assess the environmental impact of ferroalloy slags, soils were sampled at a distance of 1000 m from the ferroalloy slag dump which can be regarded as an AMD. Soil samples were prepared for analysis in accordance with GOST (state standard) 17.4.3.01-83 “Environmental protection. Soils. General sampling requirements.” For monitoring soil pollution

Table 1. Background and maximum allowable concentrations of elements in soil, mg/kg

Element	Background	MAC
Mn	600	1500.0
Zn	30	100.0
Ni	10	85.0
Co	9	50.0

Table 2. Concentrations of heavy metals (mg/kg) in ferrosilicomanganese slag

Form	Zn	Ni	Co	Mn
Total	60.8	108.5	140.7	3300.0
Mobile	13.9	9.6	26.9	649.0
Water-soluble	3.6	3.7	13.1	158.7

near industrial enterprises, sampling sites were selected with account taken of the wind rose according to GOST 17.4.4.02-84 “Environmental protection. Soils. Methods of sampling and sample preparation for chemical, bacteriological, and helminthological analysis.” The list of chemicals that are subject to control was determined by the functional purpose of the land in accordance with GOST 17.4.2.01-81 “Environmental protection. Soils. Nomenclature sanitary state parameters.” The risk of soil pollution with chemicals was assessed using a number of geochemical and sanitary–hygienic parameters, including hazard index of a substance (K_0), its background concentration, and MAC (total content) (Table 1) [24] according to the “Guidelines for assessing the degree of hazard of soil pollution with chemicals, no. 4266–87” and “Guidelines for the hygienic justification of MAC for chemicals in soils.”

To study the level of soil contamination with heavy metals near the slag dump, the main wind directions were taken into account according to GSTU-N B V.1.1-27: 2010 “Construction climatology”, since the wind regime is an important factor determining the spread of anthropogenic pollution of the atmosphere and further air pollutant deposition on the soil surface [25]. In the given region (Nikopol), these directions are the east, north-east, and north (in order of decreasing occurrence).

Soil toxicity can be determined by the level of response of a test object. Soil biotesting was carried out according to MP 2.2.12-141-2007 “Survey and zoning of a territory with respect to the degree of anthropogenic impact on the environment using cytogenetic methods. Guidelines” by the growth test. Experiments were carried out in Petri dishes. The lengths of seedlings and roots were measured [26] in the seedling phase (seven days for barley) [27]. The test culture was *Galaktik* spring barley, and soil samples taken from the territory of the Soleny Liman health-improving complex located in the Dnipropetrovsk region were used as control. The effect of a particular factor on the bioindicator was assessed according to the classification proposed by Kabirov et al. [26].

RESULTS AND DISCUSSION

Table 2 shows the total concentrations of heavy metals of hazard classes I–III in the ferrosilicomanganese slag from ferroalloy manufacture. It is seen that the manganese content is much higher than the concentrations of other heavy metals. The total toxicity index of the ferroalloy slag was calculated on the basis of the toxicity indices of cobalt, nickel and zinc (85, 100, and 150, respectively). It was estimated at 37.2, which characterizes the Fe/Si/Mn slag as a low-hazardous waste belonging to public health hazard class IV.

Table 3 contains the average total concentrations heavy metals in soil samples taken in predominant wind directions. It is seen that the total nickel content in soils sampled in the western and southern directions exceeds the background values. The concentration of this element in other soil samples is below the background value. The total cobalt concentrations do not exceed the background value and MAC. The zinc concentrations exceed the MAC

Table 3. Average total heavy metal contents of soils (mg/kg)

Direction	Mn	Zn	Ni	Co
Western	1722.37±17.13	185.43±2.97	16.28±3.53	4.39±0.44
Southwestern	1698.70±25.45	91.20±2.74	8.89±1.14	4.39±0.93
Southern	1702.87±43.39	96.14±5.69	10.87±1.57	4.71±0.47

Table 5. Корректно ли вычислять среднее значение для разных параметров7. По-видимому, эту строку следует удалить.

Table 4. Hazard indices of manganese and zinc (in total)

Metal	Western direction	Southwestern direction	Southern direction
Mn	1.15	1.13	1.14
Zn	1.85	0.91	0.96

Table 5. Biotesting of soils sampled in the western, southwestern, and southern directions

Parameter	Western direction	Southwestern direction	Southern direction	Control
Root length	9.10±0.20	10.20±0.19	8.69±0.21	11.97±0.32
Seedling length	12.40±0.20	13.90±0.21	13.03±0.25	14.96±0.36
Average	10.75	12.05	10.86	13.47
Toxicity index	0.80	0.90	0.80	

for the western direction. The concentrations of manganese in all samples are higher than MAC. The hazard index of nickel was not calculated since the concentration of all its forms is below MAC.

The calculated hazard indices are given in Table 4. According to the accepted classification, the hazard indices of substances determined from their concentrations in soil are quite high; and their values range from 0.91 to 1.85.

The toxicity indices of the assessed factors were calculated on the basis of the test function values (lengths of seedlings and roots; Table 5). The best values (maximum length of seedlings and roots) are typical for control samples grown on a "standard" soil sample; next follow those found for the southwestern direction. The shortest seedlings and roots were obtained on soils sampled in the western and southern directions.

Soil samples from the western, southwestern and southern directions were assigned toxicity class IV, i.e., the soil is low toxic. Mathematical processing of the biotesting data gave Fisher *F* test ranging from 1.06 to 1.45. The variance can be regarded as medium (11–25%).

Such studies should be continued in order to generalize information on the impact of metallurgical enterprises on the soil and obtain a more reliable assessment of the state of the soil. The obtained results are useful for the impartial environmental assessment of the level of soil pollution in the vicinity of anthropogenic mineral deposits such as slag dumps of metallurgical production.

CONCLUSIONS

(1) The concentrations of heavy metals in the ferrosilicomanganese slag from ferroalloy production have been determined; and their potential environmental hazard has been estimated by calculating the total toxicity index which is equal to 37.2; the slag can be regarded as a low-hazardous waste corresponding to public health hazard class IV.

(2) The total heavy metal contents of soil samples taken at a distance of 1000 m from the ferroalloy slags of the Nikopol Ferroalloy Plant, Ukraine, have been determined. The results indicate a high risk of pollution since the hazard indices of heavy metals range from 0.91 to 1.85.

(3) The level of soil toxicity has been assessed by the plant growth test. The soil toxicity at a distance of 1 km from the anthropogenic mineral deposit in the predominant wind directions corresponds to the fourth class, i.e., the soil is low toxic.

(5) Such studies provide simultaneous assessment of the amount of toxicants in soils, namely heavy metals, and estimation of the level of soil toxicity from the response of biological objects.

CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

REFERENCES

1. Makarov, A.B. and Talalai, A.G., *Litosfera*, 2012, no. 1, p. 172. doi ????
2. Reuter, M., Xiao, Y., and Boin, U., Abstracts of Papers, *VIIth Int. Conf. on Molten Slags Fluxes and Salts*, The South African Institute of Mining and Metallurgy, 2004, p. 349.
3. Zvereva, V.P. and Krupskaya, L.T., *Ekol. Khim.*, 2012, vol. 21, no. 4, p. 225.

4. Orlov, D.S., Sadovnikova, L.K., and Lozanovskaya, I.N., *Ekologiya i okhrana biosfery pri khimicheskom zagryaznenii: uchebnoe posobie dlya khimicheskikh, khimiko-tekhnologicheskikh i biologicheskikh spetsial'nostei Vuzov* (Ecology and Biosphere Protection under Chemical Pollution. Tutorial for Students Specializing in Chemistry, Chemical Technology, and Biology), Moscow: Vysshaya Shkola, 2002.
5. Shil'tsova, G.V., Morozova, R.M., and Litinskii, P.Yu., *Tyazhelye metally i sera v pochvakh Valaamskogo arkhipelaga* (Heavy Metals and Sulfur in Soils of Valaam Archipelago), Petrozavodsk: Karelian Scientific Center, Russian Academy of Sciences, 2008.
6. Khalid, S., Shahid, M., Niazi, N.K., Murtaza, B., Bibi, I., and Dumat, C., *J. Geochem. Explor. (Amsterdam)*, 2017, p. 247.
7. Berrow, M.L. and Mitchell, R.L., *Trans. R. Soc. Edinburgh: Earth Sci.*, 1980, vol. 71, p. 103.
8. Makarova, V.N., *Visn. Pridnipr. Derzh. Akad. Budivn. Arkhit.*, 2016, no. 4 (217), p. 35.
9. Kabata-Pendias, A. and Pendias, H., *Trace Elements in Soils and Plants*, Boca Raton: CRC, 1984.
10. Trifonov, K.I. and Devisilov, V.A., *Fiziko-khimicheskie protsessy v tekhnosfere: uchebnik* (Physicochemical Processes in the Technosphere. Textbook), Moscow: Forum Infra, 2007.
11. Isidorov, V.A., *Ekologicheskaya khimiya* (Ecological Chemistry), St. Petersburg: Khimizdat, 2001.
12. John, M.K., VanLaerhoven, C.J., and Cross, C.H., *Environ. Lett.*, 1975, vol. 10, no. 1, p. 25.
13. Raghbir, S. and Shukla, U.C., *Geoderma*, 1976, vol. 15, no 4, p. 313.
14. Cheremisinoff, N.P., *Handbook of Solid Waste Management and Waste Minimization Technologies*, Amsterdam: Butterworth-Heinemann, 2003.
15. Yakovishina, T.F., //должна быть ссылка на конференцию: название, место проведения, год //. www.rusnauka.com/27_OINXXI_2011/Ecologia/6_92589.doc.htm
16. Perel'man, A.I. and Kasimov, N.S., *Geokhimiya landshafta* (Landscape Geochemistry), Moscow: Vysshaya Shkola, 1966.
17. Seyed, A.M., Reza, S.A., and Faezeh, H., *J. Afr. Earth Sci.*, 2017, vol. 134, p. 106. doi ?????
18. Liua, G., Wang, J., Liu, X., Liu, X., Li, X., Ren, Y., Wang, J., and Dong, L., *Geoderma*, 2018, vol. 312, p. 104. doi ?????
19. Yu, K., Xu, J., Jiang, X., Liu, C., McCall, W., and Lu, J., *Chemosphere*, 2017, vol. 184, p. 884. https://doi.org/10.1016/j.chemosphere.2017.06.040
20. Grushka, V.V. and Serdyuk, S.M., *Visn. Dnipropetr. Univ., Biol. Ekol.*, 2009, vol. 1, no. 17, p. 51.
21. Pavlichenko, A.V., *Cand. Sci. (Biol.) Dissertation*, Chernovtsy, 2008.
22. Xiao, L., Guan, D., Peart, M.R., Chen, Y., Li, Q., and Dai, J., *Chemosphere*, 2017, vol. 185, p. 868. https://doi.org/10.1016/j.chemosphere.2017.07.096
23. Savin, L.S. and Makarova, V.N., *Zbirn. Nauk. Prats' NGU* //расшифровать//, 2012, no. 38, p. 217.
24. Fateeva, A.I. and Pashchenko, Ya.V., *Fonovii vmist mikroelementiv u gruntakh Ukraïni* (Background Levels of Trace Elements in Soils of Ukraine), Kharkiv: //издательство//, 2003.
25. Makarova, V.N. and Gilev, V.V., *Visn. Pridnipr. Derzh. Akad. Budivn. Arkhit.*, 2015, no. 4 (205), p. 62.
26. Kabirov, R.R., Sagitova, A.R., and Sukhanova, N.V., *Ekologiya*, 1997, no. 6, p. 408.
27. Talanova, V.V., Titov, A.F., and Boeva, N.P., *Fiziol. Rast.*, 2001, vol. 48, no. 1, p. 119.