Determination of the actual zone of influence of an industrial enterprise on the basis of the quality assessment of the environmental components

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Abstract. In this work, we determined the actual concentrations of heavy metals in the soil cover within the assumed zone of influence of a specific local source of anthropogenic impact. The joint-stock company Volgograd Metallurgical Plant (VMP) “Red October”, located in close proximity to the residential zone, was selected as an object of environmental impact. Sampling was carried out at control points at a distance of 0-4.5 km from the enterprise. The study was conducted using the precision method of atomic absorption spectrometry with preliminary preparation of samples for analysis by the method of acid decomposition of solid soil samples in open vessels. The presented measurement results, for example, concentration of labile forms of Cu, Mn, Zn in the soil cover indicate the possibility of assessing the actual zone of influence of the industrial object under study, which is relevant in determining the quality of the urban environment.

1. Introduction

Currently, the problem of reliable assessment of the current state and quality of the urban environment, taking into account local man-made pollution of terrestrial ecosystems located in close proximity to industrial enterprises in the city, has become particularly relevant [9]. One of the criteria reflecting the quality of the environment and the level of ecological well-being of residents in the area is assessment of the actual state of the soil cover of the territory and, in particular, determination of degree of contamination of various kinds of toxic elements (including heavy metals).

The real connection between the systems of chemical elements of each component of the biosphere is provided by various groups of chemical compounds specific for each of the natural environments. Chemical pollution complicates this interaction, and this fact determines the increasing attention to the chemical composition of the soil.

Urban soils, in contrast to the soils of background areas, function, among other things, in altered water and temperature conditions inherent in urban ecosystems, as well as with an increased flow of dust, the composition of which is determined by the flow of vehicles, fuel and industrial production developed in the city. Pollutant fluxes that fall into the soils of urban areas along with precipitated atmospheric emissions accumulate, some of them can be kept in the soil for tens and hundreds of years, resulting in a significant impact on soil formation processes and the evolution of urban soils [15].

So, in the soils of cities, where enterprises of the metallurgical industry are located, there is an increased concentration and activity of heavy metals. Hg, Pb, Cd, Zn, As are among the priority pollutants, since the accumulation of these elements in the environment goes at the highest rates, which, in turn, causes an increase in their concentration in plants and a further transition through trophic chains [10, 13].
With long-term intake from stationary sources, concentration of heavy metals in soils is comparable to their number in natural geochemical anomalies or even exceeds it and, thus, so-called “zones of influence” with a high concentration of metals in soil are formed around large enterprises.

Pollution can be traced at a distance of up to 10-12 km from the source of metal-containing emissions. At the same time, the degree of contamination of individual areas of the zone of influence varies considerably: the soils in the immediate vicinity of the plant contain more metals than the soils removed, and the areas that are under the emission plume are the most polluted. As the distance to the source of pollution increases, the migration capacity of metals also increases due to the dominance of vapor-gas and finely dispersed forms and greater solubility of compounds [3].

Heavy metals, entering the atmosphere with emissions from a metallurgical plant, are deposited and fall on the soil cover, where they are firmly retained due to biogeochemical barriers. In this case, soil is the main reservoir which receives and fixes microelements, and their source for other components of the natural environment, biota, for soil and plant microorganisms in particular.

Migrating through food chains, trace elements can accumulate in toxic concentrations in the organs and tissues of plant and animal organisms. Taking into account the circulation of substances and energy, it should be noted that, entering the plant component of biocenosis, heavy metals are redistributed along other rows - consumer goods (animals and humans) and decomposers, and are characterized by their durability and practical non-withdrawal from the system: soil - plants - animals - human [5, 16].

This must be taken into account, since the final link of the food chain in this case is a man. Accordingly, soil contamination with metals, in addition to the negative effects on ecosystems, can also affect the health of the local population indirectly through plants, worsening the quality of the urban environment [11, 12, 17]. This is due to the fact that, agricultural products for personal consumption are grown in households and in summer cottages both within the city and in the zones of influence of industrial enterprises [14].

2. Materials and research methods

For the northern part of Volgograd, one of the main sources of heavy metals in the environment are emissions from enterprises of the northern industrial hub, which take a significant part in formation of the quality of the environment, its individual components (soil in particular) and the general ecological well-being of the urban environment.

The joint-stock company VMP “Red October” [7, 8] was selected as the investigated local object of environmental impact. This enterprise is currently one of the largest producers of high-quality metal-roll special grades of steel for the automotive industry and aviation industry, chemical, oil and power engineering, oil and gas industry in the Russian Federation, and, therefore, is a major source of pollutants (including heavy metals) into the environment.

In accordance with the data on the composition of the company's emissions, three metals were selected for the study - typical representative emissions of this enterprise - zinc, copper, and manganese belonging to hazard classes I, II, and III, respectively, resulting in the study covering all hazard categories of substances in the soil. In addition, for the selected elements, the maximum allowable concentration (MAC) standards have been developed, that is, substances that are rationed by their concentration in soil and are subject to control as part of an environmental monitoring system [2].

Control points for soil sampling were laid in accordance with State Standard of the USSR 17.4.4.02-84 [1] within the territory of the proposed zone of influence of the enterprise. The total distance from “Red October” was 0-4.5 km to the north-west from the enterprise border, which corresponds to 3 times the size of the sanitary protection zone (3 × 500 m) and slightly exceeds it in order to clarify the results. When selecting control points, such factor as prevailing wind direction was also taken into account (based on the analysis of the wind rose of the northern part of Volgograd).

The study of soils was based on quantification of the concentration of labile metal forms and subsequent analytical studies and interpretations of the data obtained. Determining the concentrations
of the investigated elements at each of the sampling point was carried out using the precision atomic absorption spectrometry method [18] with preliminary preparation of samples for the analysis by acid decomposition of solid soil samples in open vessels (based on the sample preparation method used for analytical equipment [6]).

The atomic absorption method is most developed for determining the elemental composition of liquid samples. Accordingly, the method of implementation of the analytical process included two stages. At the first stage, in order to transfer the studied elements into the solution and prepare the working solution for analysis, a sample of a known mass was taken from a solid sample and then dissolved. Then the analyzed solution is directly entered into the atomizer, creating an absorbing layer of atomic vapor and measuring the analytical signal.

The analysis was carried out using an atomic absorption spectrometer "KVANT.Z", the main function of which is to determine the concentration of lots of elements in liquid samples of different origin and composition. The principle of operation of the spectrometer is based on the analysis of the degree of selective absorption of resonant spectral lines by the atomic pair of the element being determined. In addition, each element has its own analytical resonance line, providing maximum absorption of light, the source of which is a lamp with a full cathode for each element being determined (linear radiation).

The process of atomization (conversion of the analyzed sample into atomic vapor) is performed in the analytical cell of the electrothermal atomizer. The graphite furnace is heated to the temperature required for evaporation of the sample and atomization of the element by an electric current.

Due to the presence in the analytical cell, in addition to the atoms of the element being determined, gaseous components capable of absorbing the incident light, nonatomic or background absorption takes place, which, in turn, is a source of systematic measurement error. For the automatic correction of this type of absorption in the spectrometer, the reverse Zeeman effect is used, provided by the placement of a graphite furnace in a longitudinal alternating magnetic field.

The data obtained as a result of measurements make it possible to judge the concentration of the elements being analyzed in the studied environment in a specific area, in this case, in the zone of influence of a local source of environmental pollution (JSC VMP “Red October”).

3. Results and discussion
An isolinear map of the obtained values of the concentration of labile forms of copper in the soil cover in the study area is shown in Figure 1. As a result, soil ranges with different levels of copper, that is, with varying degrees of contamination, were identified. On the presented map, the ranges are displayed as a color gradient, reflecting the levels of copper concentration, correlated with the established MAC.

![Figure 1. The ratio of the actual and regulatory concentration of labile forms of copper in the soil cover in the assumed zone of influence of JSC VMP “Red October”](image_url)
According to hygienic standards 6229-91, the maximum allowable concentration of labile forms of copper in soils is 3.0 mg / kg [2]. The foci of maximum pollution are associated with the activity of steel-smelting shops No. 2 and No. 3 and are located in the immediate vicinity of the border of the Red October production zone; copper concentrations at control points exceed the MAC by a factor of ten (from 2.4 to 20 time). At the border of the sanitary protection zone (500 m from the enterprise), the values fluctuate within 1.5-2.2 MAC. Further, in the north-west direction within the study area, the concentration of copper in the soils in most cases does not exceed 2 MAC, but only in 5 points the copper concentration is within the norm. To the west and north-west of the enterprise, in the extreme Foci of soil contamination with copper with metal concentrations of 5–6 mg / kg are also located in the areas of the study region. These foci are largely limited from the zone of influence of JSC VMP Red October to areas with low copper values in the soil, which indicates the presence of other local sources of exposure that fell into the studied area [5].

The isolinear map of the obtained values of the concentration of labile forms of manganese in the soil cover in the area under study is presented in Figure 2.

Figure 2. The ratio of the actual and regulatory concentration of labile forms of manganese in the soil cover in the potential zone of influence of the JSC VMP “Red October”

The maximum allowable concentration of labile forms of manganese in soils is 140.0 mg / kg [2]. The foci of maximum pollution are also associated with the activities of steel-smelting shops No. 2 and No. 3 and are similarly localized in space. Within the sanitary protection zone, the concentration of manganese at control points exceeds the MAC by an order of magnitude and more: from 1.2 to 6-15 times. From the border of the sanitary protection zone and to a distance of 3.5 km to the north-west of the enterprise, it does not exceed 2 MACs anywhere. At a distance of 3.5-4.5 km, there are 3 cases of excess concentrations above 2 MAC, which is connected with the influence of other local sources of pollution. In general, concentration of manganese in most points does not exceed 2 MAC, but only in 3 points concentration is within the standard [5].

An isolinear map of the obtained values of the concentration of labile forms of manganese in the soil cover in the area under study is presented in Figure 3.
Figure 3. The ratio of the actual and regulatory concentration of labile forms of zinc in the soil cover in the potential zone of influence of JSC VMP “Red October”

The maximum allowable concentration of labile forms of zinc in soils is 23.0 mg / kg [2]. The centers of maximum zinc contamination, as well as with copper and manganese, are related to the activities of steel-smelting shops of the enterprise No 2 and No 3. In the immediate vicinity of the enterprise’s border, zinc concentration varies greatly from values within the limits of the standard to maximum allowable concentrations exceeding 9.4 times. On the border of the sanitary protection zone, the zinc concentration in the soil is already set within the standard or with a slight excess. Further, in the north-west direction within the study area, the concentration of zinc in soils in some cases does not exceed the MAC standard, at 5 points the concentration is below 1.5 MAC. At a distance of 4.5 km, at one point only, an increase in concentration up to 2.6 MAC is observed, which is connected, as in the cases with copper and manganese, with the influence of other local sources of pollution [5].

4. Conclusion

Thus, on the basis of the obtained results, it can be concluded that the actual zone of influence of JSC VMP “Red October”, taking into account the background metal concentrations for the northern part of Volgograd, and also taking into account the prevailing winds, is limited by a distance of 4.0–4.5 km to northwest of the enterprise. The zone of influence, taking into consideration the MAC of metals, instead of their background concentrations, is somewhat smaller and extends 3.5-3.7 km. The first value reflects the absolute zone of influence of the enterprise, where any changes in environmental parameters are observed. The second value determines the zone of influence, where there are noticeable exceedances of standards for the metals content in the soil and negative trends in the state of natural communities, especially vegetation, can be observed and indirectly affect the health and well-being of residents in the area [5].

Thus, the actual state and level of soil contamination with heavy metals are most important for residents of the individual development zone, which occupies 30% of the territory of the Krasnooktyabrsky district (in the zone of influence of the Red October complex) within the boundaries of the region. At the same time, for the entire private sector, elevated concentrations are observed either by one of the studied elements or by their combination, which must be taken into account when growing agricultural products in private farms, since the accumulation of elements to toxic levels in edible parts of cultivated plants is potentially possible.

In addition, several foci of pollution were found within the study area, presumably related to the activities of other sources of anthropogenic impact or unfavorable ecological condition of natural objects, and this confirms once more the relevance of applying soil monitoring data in the areas of actual influence of local industrial facilities in assessing the current quality of the urban environment.
References

[1] GOST 17.4.4.02-84. State Standard of the USSR. Protection of Nature. The soil. Methods of selection and preparation of samples for chemical, bacteriological, helminthological analysis (Standard of 12/12/1984 N 4100) Consultant Plus: inform. system 2018

[2] The List of Maximum Permissible Concentrations (MPC) and Approximately Permissible Amounts (ODC) of Chemicals in the Soil” Consultant Plus: inform. system 2018

[3] Mandzhieva S S 2014 Ecological state of soils and plants in the natural and man-made sphere: monograph Southern Federal University. p. 264

[4] Warm G A 2013 Heavy metals as a factor of environmental pollution Astrakhan Bulletin of Environmental Education 1 182-192

[5] Tikhonov A.A, Bolgov I A 2017 The significance of data on the actual zone of influence of a local industrial facility in assessing the quality of the urban environment (using the example of the Red October metro station) Modern Ecology: education, science, practice 2 108-114

[6] M-MVI-80-2008 2008 Methods for measuring the mass fraction of elements in soil samples, soils and bottom sediments by atomic emission and atomic absorption spectrometry (approved. And put into effect on 06/02/2008 Monitoring LLC) Information system MEGANORM Access mode: http://meganorm.ru/ Index2/1/4293824/4293824289.htm.

[7] Object 18-0134-000164-P JSC “VMK KrasnyOktyabr” VET UONVOS: From -open registry of objects NVOS from 05.14.2018. - Access mode: https://onv.fsrpn.ru/#/public/registry/18-0134-000164-%D0%9F

[8] Information about the enterprise VMK “KrasnyOktyabr” VMK “Kra October October 14.05.2018 - Access mode: http://www.vmzko.ru/spravka.html

[9] C von Brömssen, J Fölster, M Futter, K McEwan 2018 Statistical models for evaluating suspected artefacts in long-term environmental monitoring data Environmental Monitoring and Assessment URL: https://doi.org/10.1007/s10661-018-6900-3

[10] G Tóth, T Hermann, G Szatmári, L Pásztor 2016 Maps of heavy metals in the soils of the European Union and proposed priority areas for detailed assessment Science of The Total Environment 565 1054-1062

[11] G Tepanosyan, L Sahakyan, O Belyaeva, S Asmaryan, A Saghatelyan 2018 Continuous impact of mining activities on soil heavy metals levels and human health Science of The Total Environment 639 900-909

[12] I Sá, M Semedo, M E Cunha 2016 Kidney cancer. Heavy metals as a risk factor Porto Biomedical Journal 1 (1) 25-28

[13] M Woszczyk, W Spychalski, L Boluspaeva 2018 Trace metal (Cd, Cu, Pb, Zn) fractionation in urban-industrial soils of Ust-Kamenogorsk (Oskemen), Kazakhstan—implications for the assessment of environmental quality Environmental Monitoring and Assessment 190(6) 362

[14] N V Stepanova, S F Fomina, E R Valeeva, A I Ziyatdinova 2018 Heavy metals as criteria of health and ecological well-being of the urban environment Journal of Trace Elements in Medicine and Biology 50 646-651

[15] N E Kosheleva, D V Vlasov, I D Korlyakov, N S Kasimov 2018 Contamination of urban soils with heavy metals in Moscow as affected by building development Science of The Total Environment 636 854-860

[16] Qi Wang, Jianfeng Liub, Zhao Chen, Fangbai Li, Huanyun Yu 2018 A causation-based method developed for an integrated risk assessment of heavy metals in soil Science of The Total Environment 642 1396-1405

[17] S Türtcher, P Berger, L Lindebner, T W 2017 Berger Declining atmospheric deposition of heavy metals over the last three decades is reflected in soil and foliage of 97 beech (Fagus sylvatica) stands in the Vienna Woods Environmental Pollution 230 561-573

[18] Shi-Hua Chen, Yi-Xiang Li, Pei-Hua Li, Xiang-Yu Xiao, Min Jiang, Shan-Shan Li, Wen-Yi Zhou, Meng Yang, Xing-Jiu Huang, Wen-Qing Liu 2018 Electrochemical spectral methods for trace detection of heavy metals: TrAC Trends in Analytical Chemistry 106 139-150