

Features of Monitoring Heavy Metals in Soil Cover of Urban Environment

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Abstract— This study analyzes modern approaches to the monitoring systems organization for heavy metals in the soil cover in urban areas. The current situation was considered in individual countries, as well as the organization features of the soil monitoring system in the Russian Federation and the city of Volgograd. The study results showed that in most foreign countries, monitoring of urban soils is currently one of the priority areas. The research system has a high level but is subject to improvement in certain areas. In most cities of the Russian Federation, monitoring researches on the content of heavy metals in soils are the unsystematic and nonperiodic feature and are usually associated with the implementation of thesis research or scientific projects. At the federal level, studies are conducted only in 33 cities, while the lists of identified elements vary significantly depending on the current industry specialization.

Keywords: *ecological monitoring, soil monitoring, heavy metals, urban environment, Volgograd*

I. INTRODUCTION

The problem of a reliable assessment of the actual state and quality of the urban environment, taking into account local technogenic pollution of land ecosystems located near industrial enterprises in urban areas, has become particularly relevant. One of the criteria reflecting the quality of the environment and the level of ecological well-being for the population living in this area is the assessment of the actual state of the soil cover of the territory and the degree determination of pollution with various toxic elements (including heavy metals).

Urban soils, unlike soils of reference sites, function in the changed conditions of a hydrological and temperature regime inherent in the urbanized ecosystems, and also at the

increased level of dust in which is defined by traffic streams, fuel and industrial production. The pollutant flows entering the soils of urban areas together with precipitating atmospheric emissions accumulate there, some of them can be retained in the soil for long years. As a result, they have a significant impact on the processes of soil genesis and the evolution of urban soils.

Heavy metals (HM) are naturally found in the soil, geological and anthropogenic activities increase their concentration in quantities dangerous to plants and animals. Thus, in the cities soils where metallurgical industry enterprises operate, there is a high concentration and high mobility of HM, from which Hg, Pb, Cd, Zn, As are among the priority pollutants. The accumulation of these elements in the environment is the highest rate, that it causes an increase in their concentration in plants.

In the case of technogenic pollution of the natural environment by heavy metals, there are two main ways of their entry into plants: from the atmosphere through the leaf surface, from the soil through the rooting depth. In this case, the leaves can also accumulate HM, taking into account the internal migration of elements, received from the soil.

Even taking into account the fact that most metals are essential trace minerals for normal plant life (for example, Zn, Cu, Mn, Mo), their excess intake with subsequent deposition in tissues can lead to slower growth and development, color change and decay of leaves, malformation of the rooting depth and even death.

Also, plants growing in the urban environment can accumulate elements to toxic levels. Taking into account the cycle of matters and energy, it should be noted that, entering the plant component of biogeocenosis, TM are redirected to

consumers (animals and humans) and reducers [1], and at the same time are characterized by their durability and practical non-derivability from the system: soil-plants-animals-man. Thus, heavy metals, entering the atmosphere with emissions from various sources, settle and fall on the soil cover, where emissions are retained due to biogeochemical barriers. In this case, the soil is the main reservoir, receiving and fixing microelements, and their source for other components of the natural environment, in particular for the biota microorganisms of soil and plants. Entering the plants, HM food chains migrate to the following levels, which, in the case of elevated concentrations, have a toxic effect. Accordingly, in addition to negative impacts on ecosystems, soil contamination by metals, indirectly through plants, can also affect the health of the local population, worsening the quality of the urban environment. This is because both within the city and in the zones of influence of industrial enterprises, the population grows agricultural products for their consumption in private households and suburban areas.

To track the current state of soil cover, including the study of HM, and to predict a situation in the urban environment requires comprehensive regular surveys on federal, regional and local levels, the problem of organizing a regular system of monitoring is particularly relevant. At the same time, the priority task is to analyze the existing situation and the approaches used to organize monitoring researches both in the Russian Federation and abroad.

II. MATERIALS AND METHODS (MODEL)

In the framework of this research was carried out the analysis of modern approaches to the organization of the monitoring system of HM content in urban soils used both in the Russian Federation (including Volgograd) and in a number of foreign countries (Germany, Austria, Sweden, Poland, Romania, Czech Republic, USA, China, etc.). Current information was selected by the analysis method of normative and bibliographic sources, open materials of relevant government bodies, including official statistics, scientific periodical editions, and conference materials.

III. RESULTS AND DISCUSSION

Urbanized and large industrial developed countries have begun to pay attention to urban soils relatively recently. For example, in London and other major cities in the UK, soils were surveyed for the first time for contamination with heavy metals (Pb, Cu, Zn, Cd) and dust, and the relationship between the level of pollution and industrial activity was revealed [2].

In the late 80s-early 90 the 20th century, European countries adopted the monitoring concepts of soil cover. In 1999, the first European seminar was held to discuss the creation of a "European monitoring system and soil evaluation". Country representatives were invited to submit statements on country activities on monitoring and soil evaluation. The seminar revealed a significant difference in the organization level of soil monitoring systems in Western and Eastern Europe countries [2].

In Germany, work in the field of environmental monitoring of soils began in 1985, and since 1987 have become systemic. Thus, in Bavaria were created 238 permanent landfill areas, in Saxony is 25, Baden-Württemberg is 155. Also, a network of 17 areas was

established to study soil pollution by atmospheric emissions. However, the monitoring system developed in Germany was used mainly for the study of forest soils. Also, in 1988 The German soil science society established a "Working group on urban soil research".

In Austria, the methodology for monitoring soil cover was adopted in 1989 of the Federal Ministry of agriculture and forestry. Soil acidity and the average content of trace minerals were used as the studied indicators. As in Germany, the monitoring covered only forest soils. Additional researches were conducted near industrial complexes. Initially, the planned frequency of research was 5-10 years, but due to the high cost, the plan was not implemented.

In Hungary, since 1992, the monitoring system has included 1,000 permanent areas, 800 of them are on agricultural lands and 200 are on particularly sensitive territories (reclamation and degradation lands, area conservations, industrial and urban facilities). Determination of different soil indicators is carried out at intervals of once every 1-6 years.

Belgium had a national soil service from 1945 until the early 1980s. During this period, pedological maps of various scales were compiled detailing soil properties. However, since the 2000s, the soil service has been replaced by soil monitoring based on modern GIS technologies. The periodicity of research is 5-10 years in particularly sensitive territories, including industrial and urban facilities.

The national system of soil cover monitoring in Sweden includes 20 reference territories, where chemical soil test, research of microbiological processes in the soil is carried out.

In Finland, land monitoring has been carried out since 1974. On the country territory, there are 5 permanent plots for monitoring the state of soil indicators. Also, there are separate areas for the identification and inspection of contaminated areas, including urban [3].

In such countries as Moldova [4], Romania [5], Poland [6], Albania [7], the Czech Republic [8] are completely absent from the monitoring systems of urban soil pollution.

In the United States, soil cover monitoring includes a database system for all soil types. At present, the country has databases that include information on more than 14,000 soil varieties. However, in the United States, as in Western Europe, monitoring is mainly aimed at controlling the quality of natural and agricultural soils. Monitoring of urban land is carried out exclusively in urban gardens, parks and other recreational areas [2], although, for example, in New York, studies of the quality of the urban soils began in the 1980s.

Most African countries, except for Libya and Nigeria [9, 10] do not have full or partial environmental monitoring systems of urban lands. The observations carried out in these countries are limited to a single determination of HM concentrations in the suburbs and centers of large cities.

In the Asian region, along with Western Europe, there are large systems of environmental monitoring of urban land. For example, in China, studies [11, 12] emphasize that the soil index of HM in cities has a significant difference in different functional zones, and [13] in industrial and transport zones, HM has the highest concentration and tend to gradually

increase. In Pakistan [14] data on the concentration of HM in urban soils in dynamics are available only in the city of Sialkot. In India [15, 16], Iran [17] and Mongolia [18] are quite well-developed monitoring covering various urban areas such as parks, green areas, roadsides, crowded places and the industrial quarter.

Urban soil monitoring of the Russian Federation, including their HM pollution, is part of the State monitoring of lands of the Unified system of State ecological monitoring. State monitoring is carried out by specially competent federal agencies and state governments of the subjects of the Russian Federation within their competence.

On a permanent basis, the pollution monitoring of urban soils of the Russian Federation with heavy metals is carried out only in settlements in the territory of which there are enterprises of non-ferrous and ferrous industry, energy, machinery and metalworking, fuel and energy, chemical and petrochemical industry, enterprises for the production of building materials, construction industry [19]. Thus, in 2017, monitoring was carried out in 33 settlements belonging to 23 subjects of the Russian Federation: the Republic of Bashkortostan, North Ossetia-Alania, Mari El, Tatarstan, Mordovia, Udmurt and Chuvash republics, Krasnodar and Primorsky Krai, Irkutsk, Kirov, Kemerovo, Moscow, Omsk, Nizhny Novgorod, Novosibirsk, Orenburg, Samara, Penza, Saratov, Ulyanovsk, Sverdlovsk, and Tomsk regions.

Since 2013, the subprogram "State ecological monitoring (state monitoring of the environment)" has been implemented in Volgograd within the framework of the government program of the Volgograd region "environmental protection in the territory of the Volgograd region". However, the subprogramme does not include a section on urban soil monitoring.

The municipal institution "City Department of analytical and operational quality control of environment" carries out ecological monitoring of natural environments according to the developed municipal tasks, including soil monitoring of the urban area. However, within the framework of research, sampling within Volgograd is carried out only in a few points of different functional zones. It can be noted that this approach to the organization of soil monitoring can not be called complex and systematic.

Sufficient monitoring to determine the content of HM in the soil cover of the region is carried out only about agricultural land located outside Volgograd.

Pollution levels of urban soils of HM are established about the existing health-based exposure limits—maximum allowable concentrations (MAC) according to [20] or approximable permissible concentrations (APC) according to [21]. If the soil is contaminated with only one heavy metal, the assessment is carried out according to [22]. If the concentration of heavy metals found in the soil exceeds 1 MAC, then such soil belongs to the unacceptable pollution category.

Soil pollution assessment of cities of HM from the standpoint of negative impact on human health is carried out according to the complex indicator of total soil pollution with heavy metals relative to the background – $Z_s (Z_{bkgd})$, which is calculated by the formula (1) [22].

$$Z_{bkgd} = \sum_{i=1}^n K_{bkgdi} - (n - 1) \quad (1)$$

where n is the number of metals to be determined;

K_{bkgdi} is the metal concentration coefficient equal to the ratio of mass fraction of the i -metal in the soil of the contaminated area to its background mass fraction.

Thus the soil belongs to category of pollution standard at value $Z_{bkgd} < 16$; moderately hazardous pollution at $Z_{bkgd} = 16-32$; dangerous pollution at $Z_{bkgd} = 32-128$; extremely extra-hazardous pollution at $Z_{bkgd} > 128$.

Another complex indicator of the total soil pollution of HM is the indicator Z_c taking into account the clarks of their concentration. The formula of its calculation is similar to the indicator Z_{bkgd} , but the ratio of the actual metal content in the soil to its clark is summed. This indicator is considered a unified indicator of soil pollution with heavy metals.

Currently, the content of Al, Fe, Cd, Co, Mg, Mn, Cu, As, Ni, Pb, Hg, Cr and Zn in gross, mobile, acid-soluble and water-soluble forms in urban soils is controlled at the federal level. According to [23] highly dangerous heavy metals include As, Cd, Hg, Se, Pb, Zn, moderately dangerous include Co, Ni, Mo, Cu, Sb, Cr.

The main disadvantage of the current system of MAC indicators for HM (total and active forms) in the country is that it does not take into account the diversity of soil types of the Russian Federation and their buffering properties [24, 25, 26], and the established MAC values are developed only for one of the hazard indicators for trans-location or general sanitary [27, 28]. Meanwhile, in the regions of the Russian Federation, the background level content of HM in soils differs significantly. Also, different types of soils have different abilities to inactivation HM. The APC indicator developed in 1995 partially solved this problem. The standard was established for the total content of 6 heavy metals (Cd, Cu, As, Ni, Pb, Zn), for each of which three values of the APC of the metal are given, taking into account the granulometric composition and the reaction medium (pH). However, the APC does not take into account the indicators of the harmfulness of heavy metals. It should be noted that for several metals (Fe, etc.), the MAC or APC indicators have not been developed.

The sources of HM in urban soils and the analysis of the total content of several metals are discussed in detail in the works [29, 30, 31, 32].

Traditionally, studies of urban soil pollution HM conducted to a depth of 10 cm. An alternative approach is the content analysis of HM in the entire soil profile, taking into account the fact of uneven distribution of HM and their concentration on various geochemical barriers [33, 34]. Another approach is based on the calculation of the coefficient of radial differentiation (R) of metals in the soil profile [25, 31, 35].

The influence on the properties and stability degree of urban soils to HM is reflected in the works [32, 34, 35, 36].

One of the priority research areas in recent years is the biological activity of HM. The selective ability of HM to accumulate in tissues and organs of animals and the human body, leading to a violation of the structural and functional

state, is shown in [31, 37]. The issues of HM accumulation by plants and lichens in the urban environment have been studied [36, 38, 39, 40]. Researches of adaptation and mechanisms of metal resistance of plants are presented in [41, 42, 43].

IV. CONCLUSION

Thus, only in the United States and Western Europe, there are soil monitoring networks. However, as in Eastern Europe, these studies are conducted mainly on natural and agricultural soils. The monitoring of urban soil pollution is usually carried out in isolated cases and is not a holistic character. Most studies aim is to determine the actual concentrations of heavy metals in urban soils without focusing on their cumulative effect and indirect effects on public health.

In the Russian Federation, there is no unified system for monitoring urban soils. In most cities of the Russian Federation, monitoring researches on the content of HM in soils are the nonsystem and nonperiodic feature and are usually associated with the implementation of thesis research or scientific projects. A similar situation was found in Volgograd. At the federal level, studies are conducted only in 33 cities, while the lists of identified elements vary significantly depending on the current industry specialization.

The choice of sample areas for research and sampling methodology varies greatly from country to country, depending on the approved recommendations for soil monitoring. The most promising and representative is the "envelope" method used in Russia, CIS countries, as well as Mongolia, Poland, Pakistan, and the Czech Republic.

Practically in all considered foreign and domestic researches, the leading method of concentration determination of heavy metals is a method of atomic absorption spectrometry. Its advantages are universality, allowing to determine several elements from one solution by a single method, high expressiveness, and accuracy.

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