Assessment of heavy metal contamination of soils in the Republic of Tatarstan using complex pollution indices NPI, RI, BGI

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Abstract. In this study, in most cases in soils susceptible to the accumulation of heavy metals, the highest content of heavy metals was observed in the surface layers of the soil profile. We calculated the values of three pollution indices based on the determination of individual heavy metals (Al, As, Cd, Pb, Sr) and pollutants (Cu, Co, Cr, Zn, Mn, Fe, Mo, Ni) in the territory of the Republic of Tatarstan. The overall degree of pollution and environmental risk assessment were carried out using complex indices NPI and RI. The possibility of accumulation of individual elements in soil horizons was determined using the biogeochemical index BGI. The content of heavy metals in the soils of the Republic of Tatarstan, such as As, Pb, Co, Cu, Fe in the soil horizons was several times higher than the natural content of these metals, which is confirmed by three calculated indicators, taking into account that the values obtained for the O horizon using NPI indices and RI are consistent with each other, and BGI is consistent for individual elements (As, Pb, Co, Cu, Fe, Cd, Cr, Mn and Mo).

1 Introduction

Soil pollution is a type of anthropogenic degradation in which the content of chemical substances exceeds the natural concentrations of toxic elements in the soil [1-2].

The natural cycle of migration of heavy metals begins in the soil, where the main source of migration is the transfer of metals from one place to another. It is the speed of transport through soil layers and the ability to accumulate that determines the accumulation of heavy metals in the soil. In soil layers prone to the accumulation of humus, the majority of toxic elements that pollute the environment accumulate [3].

The entry of heavy metals into the food chain can affect animal and human health. Therefore, high concentrations of heavy metals are a global problem, threatening the safety of food quality [4].

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One of the methods for comprehensive assessment of the degree of accumulation of heavy metals in soil is the use of pollution indices. Various characteristics of soil pollution provide basic data on the content of toxic elements. This, in turn, helps to choose a method for cleaning contaminated areas [5].

The relevance of the study is the need to determine the characteristics of the accumulation of microelements on the territory of the Republic of Tatarstan and the magnitude of potential environmental risks.

The purpose of this work is to assess the accumulation of individual heavy metals in soils using complex soil pollution indices NPI, RI, BGI.

2 Materials and methods

Samples were collected on the territory of the Republic of Tatarstan using an Eidelman soil drill from two soil horizons - Horizon O (0-5 cm.) and Horizon A (5-25 cm.). A total of 4340 mixed soil samples were collected from the entire territory of the Republic of Tatarstan (Predvolzhie (n=720), Zapadnoe Predkamie (n=1490), Vostochnoe Predkamie (n=230), Zapadnoe Zakamie (n=610), Vostochnoe Zakamie (n=1290)).

Sample preparation and elemental status analysis were carried out in accordance with the recommendations of MUK 4.1.1483-03 [6]. Using the ICPE-9000 device, the gross content of individual elements in soil samples was determined.

When measuring the mass fraction of elements and obtaining the final results of the concentration of metals in the solution, we took into account the detection limit of metals according to the current PND F 16.1:2:3:3.11-98, which is suitable for our chosen method of analyzing soil samples [7].

The maps were constructed using the Quantum GIS 3.4.0 program. Madeira using WGS-84 projected degree coordinates and zone 39N.

2.1 Soil pollution indices

2.1.1 Nemerov pollution index

Nemerov pollution index (NPI) allows you to assess the overall degree of soil pollution and includes the content of all analyzed heavy metals, taking into account the contribution of the metal with the maximum concentration in the solution. However, it should be taken into account that the final results of this index are greatly influenced by the number of metals analyzed. NPI includes results from a single Pollution Index (PI) and is calculated using the formula:

$$NPI = \sqrt{0.5(PI_m^2 + PI_a^2)}$$
(1)

Where PI_m is the highest value among all analyzed metals, and is the average value for elements [7].

Based on the NPI results, several levels of soil pollution can be distinguished: 1) NPI \leq 0.7 (no pollution), 2) $0\leq$ NPI \geq 1 (borderline level), 3) $1\leq$ NPI \geq 2 (weak pollution), 4) $2\leq$ NPI \geq 3 (moderate pollution), 5) NPI \geq 3 (heavy pollution) [8].

2.1.2 Potential ecological risk

Potential ecological risk (RI) is an indicator that is used to assess environmental risk caused by the concentration of heavy metals in water, air and soil. RI is calculated based on the sum of the pollution index multiplied by the potential toxicity level of each metal in the environment:

$$RI = \sum_{i=1}^{n} E_r^i \tag{2}$$

Where *n* is the amount of all analyzed metals, and E_r^i is a single environmental risk factor, calculated based on the equation:

$$E_r^i = T_r^i * PI \tag{3}$$

Where T_r^i – The toxicity value of individual elements (As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sr, Zn) is 10, 30, 5, 2, 5, 1, 1, 1, 5, 5, 1, 1 respectively. PI – values of a single Pollution Index (PI) [7, 9].

RI can be interpreted using the following scale of values: 1) low risk (less than 90), 2) medium risk (90 to 180), 3) high risk (180 to 360), 4) very high (360 to 720), 5) extremely high level (more than 720).

2.1.3 Biogeochemical index

The Biogeochemical Index (BGI) helps determine the ability of an O horizon to absorb pollutants. BGI is calculated using the formula:

$$BGI = \frac{C_n O}{C_n A} \tag{4}$$

Where $C_n O$ is the heavy metal content in Horizon O and $C_n A$ is the heavy metal content in Horizon A

3 Results

To comprehensively assess the degree of soil pollution in the Republic of Tatarstan, three complex indices were used: Nemerov pollution index (NPI), Potential ecological risk (RI) and Biogeochemical index (BGI). These pollution indices were calculated for all samples taken from the O and A horizons using the formulas given below. The indices allow for an assessment of the holistic quality of the soil, as well as an assessment of environmental risk.

The NPI summarizes the contribution of all analyzed elements in assessing overall soil quality, taking into account the concentration of the metal with the highest content. This indicator is often used because it is based on the values of the single PI index, which takes into account the average content of chemical elements in the earth's crust and the background in the soil (http://s.kpfu.ru/1ut). However, one should take into account the final value of the index.

Soil contamination on the O and A horizons on the territory of the Republic of Tatarstan varied from clean soil to severe contamination throughout the entire territory. Both horizons were characterized by a predominance of medium and heavy pollution.

RI is an indicator that is used to assess the potential environmental risk caused by pollution due to high concentrations of heavy metals in water, air and soil [9-10]. This complex indicator is also widely used because it takes into account the synergistic effect, toxicity level and sensitivity of heavy metals. Among the disadvantages of this method is the need to use toxicity coefficients for each metal, but not for all metals these values are given in the studies.

The values of potential environmental risk in the O and A horizons were variable. Soils sampled in the O horizon were characterized by moderate to strong environmental risk depending on the RI values. In horizon A, all sampled soils were characterized by low to very high contamination. The data obtained as a result of analysis using the RI index from both soil horizons are consistent with each other. However, higher values of potential environmental risk were observed in horizon A

According to the BGI, heavy metal content in the O horizon can be significantly higher than in the A horizon due to the high content of partially decomposed organic matter, which can bind heavy metals. Using the BGI index, we can calculate the ability of the organic layer of soil to accumulate the heavy metals we studied. The ability to estimate the retention of pollutants in the O horizon is important for determining overall soil quality [11].

BGI helps determine the contaminant absorption capacity of O horizons, values greater than 1.0 indicate high heavy metal absorption capacity of soil O horizons. The studied soils are mainly characterized by clayey granulometric composition (http://s.kpfu.ru/1x1). Clay soil tends to retain most of the pollutants, including heavy metals. However, BGI does not take into account the mechanical composition of the soil, therefore it is an approximate indicator [11].

The biogeochemical index showed that in the Republic of Tatarstan there is an accumulation of As, Pb, Co, Cu, and Fe. As well as small areas of accumulation of Cd, Cr, Mn and Mo (http://s.kpfu.ru/1wo).

4 Discussion

The quality of soil exposed to heavy metal contamination can be assessed by three pollution indicators BGI, NPI and RI. The ability of the organic horizon to accumulate heavy metals in the soils of the Republic of Tatarstan is at an average level. The content of heavy metals such as As, Pb, Co, Cu, Fe in the soil horizons was several times higher than the natural content of these metals, which is confirmed by three calculated indicators, taking into account that the values obtained for the O horizon using the NPI and RI indices are consistent between itself, and BGI - for individual elements. The NPI showed differences in heavy metal concentrations in the O and A horizons. Depending on the sampling point, the O horizon showed moderate, severe, or severe contamination; The degree of heavy metal concentration in the O layer also reflected the RI.

The degree of enrichment of soils in the Republic of Tatarstan with heavy metals was assessed using pollution indices, which in most cases confirm the effect of intrasoil removal of pollutants as a result of anthropogenic activities. However, changes in the content of heavy metals and pollution index values are determined by the external (slope, angle) and internal (texture, carbon and nitrogen content, etc.) characteristics of the soil. Internal natural conditions, such as particle size distribution and soil type, also have a significant impact on the distribution and content of heavy metals in the surface layer. Heavy metals in the clayey soils studied are potentially poorly released into deeper soil layers, which could result in reduced biological activity. The accumulation of heavy metals may also be related to the composition of the plant community, and their entry into the litter could further increase the content of heavy metals in the O horizon.

5 Conclusion

Soil contamination on the O and A horizons on the territory of the Republic of Tatarstan varied from clean soil to severe contamination throughout the entire territory. Both horizons were characterized by a predominance of medium and heavy pollution. Soils sampled in the O horizon were characterized by moderate to strong environmental risk, and all soils sampled in the A horizon were characterized by low to very strong RI values, respectively. The biogeochemical index (BGI) showed that in the Republic of Tatarstan there is an accumulation of As, Pb, Co, Cu, Fe. As well as small areas of accumulation of Cd, Cr, Mn and Mo.

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