Heavy metals content in agricultural soils of Vladimir region, Russia

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Abstract. The research presents the results of our field study of the arable layer of agricultural soils in 2017. The study was carried out applying continuous agrochemical testing of the following heavy metals: gross content of Pb, Cd, Cu, Zn, Co, Mn, Ni. Atomic absorption spectroscopy was used to determine heavy metals in soil. The hazard coefficient was used to assess the soil pollution level. Heavy metals concentration in arable soils of the Vladimir region range as follows (min → max): Cd-0.13-0.36 mg / kg; Cu – 2.11 - 10.2 mg/kg; Co – 2.62 – 7.9 mg/kg; Pb – 3.43 - 10.2 mg/kg; Ni – 2.78 - 15.6 mg/kg; Zn – 12.5 – 35.6 mg/kg; Mn - 136 - 541 mg/kg. Calculating the hazard ratio, the series is presented differently: Cu →Pb →Mn →Co→Zn→Ni→Cd. In comparison with background indicators gross content increase of the following elements occurred in the region: Pb (17.2%), Cu (13.5%), Zn (1.3%), Co (17.4%). Cd and Mn slightly decreased. Ni showed no changes. Fertilizers are the main source of HM in the arable layer. The research show that heavy metals gross content in the arable soil layer in the region does not exceed MPC; thus, arable soils in the Vladimir region are slightly polluted with heavy metals and are not harmful to human health.

1. Introduction
Agricultural land monitoring as a part of environmental monitoring, is important for identifying the changes in land conditions, soil fertility assessment, crop production quality and safety. Its primary task is to forecast and develop recommendations to prevent and eliminate the consequences of negative degradation processes, which, firstly, include anthropogenic pollution of soil cover. Soil cover pollution should be considered not only as penetration of some substances and elements into it, but also as natural balance violation, loss of self-recovery and transition possibility to irreversible degradation processes. Along highways and around large industrial enterprises the soil is contaminated with substances spread by air (hydrocarbons, heavy metal compounds (HM), chlorides, fluorides, etc.) [1,2]. Near the warehouses stocked with fertilizers, plant protection products, pesticides, fuels and lubricants soils are contaminated with erosive deposits of these substances as a result of violation of application hygiene, storage and poor sanitary condition of the warehouses. Soil is also polluted with harmful industrial emissions and wastewater.

Since the agricultural soils quality indirectly affects the population health through vege-products, environmental assessment of the arable land is still an important aspect of social and hygienic monitoring [4]. Therefore, the research objective was to assess the anthropogenic pollution of soil arable horizon by heavy metals in the Vladimir region.
2. Materials and methods

The Vladimir region is located in the center of the Non-chernozem zone, in the South taiga forest zone and belongs to the Central economic region of Russia. According to the soil cover characteristics, the region is divided into three main zones. The first is the zone of gray forest soils of Vladimir Opole. The second is the zone of sod-podzolic medium loamy and light loamy soils. The third is a zone of sod-podzolic sandy loam and sandy soils.

The research presents the field research data of Biology and Ecology Department of VlSU of 2017. The study of the regional arable soil layer was carried out applying continuous agrochemical examination of the following HM: gross content of Pb, Cd, Cu, Zn, Co, Mn, Ni. Heavy metals were determined in soil by atomic absorption spectroscopy. Background values of HM were recognized as similar indicators of 2003, presented in the Vladimir region Environmental Atlas [3]. The choice is determined by the identity of the reference sampling sites and the time interval, allowing to trace the dynamic parameters of the analyzed data. To assess the soil pollution level by pollutants the hazard ratio (Hr) was used, which is calculated according to the formula

\[ Hr = \frac{C_i}{APC_i} \]

where \( C_i \) is metal concentration in soil (mg/kg), \( APC_i \) – approximate permissible concentration of heavy metal in soil (mg/kg) [4,5].

Statistical data processing and correlation analysis with Pearson correlation coefficient determination were performed using STATISTICA software. The results with significance level \( p \leq 0.05 \) were considered statistically significant.

The total area of the surveyed area amounted 71946 hectares.

3. Results

The soil is known to serve as a natural barrier to heavy metals (HM) and inhibits their introduction into plants. Environmentally safe products are impossible to produce without taking into account HM migration and accumulation in the soil arable horizon. The content of different HM in the arable soil layer of the Vladimir region is characterized by significant differentiation. This circumstance can be explained by the difference in the industrial development of administrative territories, road networks branching, natural and meteorological features. Moreover, HM content in the arable layer is known to be caused by mineral fertilization.

The HM concentrations in the arable land soil in the Vladimir region range the following way (min → max): Cd – 0.13 – 0.36 mg/kg; Cu – 2.11 - 10.2 mg/kg; Co – 2.62 – 7.9 mg/kg; Pb – 3.43 - 10.2 mg/kg; Ni – 2.78 - of 15.6 mg/kg; Zn – 12.5 – 35.6 mg/kg; Mn - 136 - 541 mg/kg. However, in hazard ratio calculation the series looks different: Cu → Pb → Mn → Co → Zn → Ni → Cd (table 1).

Table 1. Hazard coefficients of gross forms of heavy metals in the arable horizon of agricultural soils of the Vladimir region.

| №  | Sampling area                  | Pb   | Cd   | Cu   | Zn   | Co   | Mn   | Ni   |
|----|--------------------------------|------|------|------|------|------|------|------|
| 1  | Alexandrovsky. loam. pH<5.5    | 0.154| 0.240| 0.120| 0.279| 0.315| 0.187| 0.359|
| 2  | Vyaznikovsky. sandy loam       | 0.204| 0.600| 0.148| 0.313| 0.256| 0.223| 0.459|
| 3  | Gorokhovetsky. loam pH> 5.5    | 0.056| 0.100| 0.038| 0.089| 0.196| 0.248| 0.118|
| 4  | Goose-crystal. sandy loam      | 0.107| 0.440| 0.064| 0.227| 0.105| 0.169| 0.139|
| 5  | Kameshkovsky. sandy loam       | 0.156| 0.560| 0.088| 0.331| 0.230| 0.241| 0.371|
| 6  | Kirzhachsky. sandy loam        | 0.256| 0.260| 0.142| 0.369| 0.208| 0.361| 0.320|
| 7  | Kovrovsky. sandy loam          | 0.179| 0.520| 0.088| 0.344| 0.146| 0.161| 0.317|
| 8  | Kolchuginsky. loam. pH> 5.5    | 0.114| 0.260| 0.147| 0.274| 0.276| 0.244| 0.335|
In comparison with the background indicators in the region the gross content of the following elements increased: Pb (17.2%), Cu (13.5%), Zn (1.3%), Co (17.4%). The content increase of these elements in the arable soils of the region can be associated with their introduction primarily with potash, phosphorus, nitrogen fertilizers and pesticides. These fertilizers are applied as it is required to maintain sod-podzolic soils fertility, which are basic of arable lands of the Vladimir region (up to 60 %), to support soil microelement composition with such elements as potassium, phosphorus, nitrogen, necessary for agricultural plants nutrition and their productivity increase. At the same time, mineral and especially organic fertilizers are known to be the source of heavy metals in soil, even at moderate dosing, so the long term fertilizing causes total increase and accumulation of HM in soil. Such factor is worth mentioning as the increased intensity of cars and trucks traffic on regional roads and roadside territories pollution (and in some cases they are arable lands) with heavy metals, especially lead and zinc [6]. The increase of Pb concentration in arable soil compared to the background was detected in 13 of the 16 districts, most likely due to the anthropogenic nature of pollution and, in particular, air pollution increase by vehicles and industry. The greatest contamination level of arable soils (hazard ratio) was detected in Kirzhach, Vyazniki, Petushki areas. It should be noted that these areas, adjacent to the Federal highway M-7 and characterized with high traffic load, are industrially developed areas, and the soils in these areas are the least resistant to heavy metals pollution, as they are sandy loam.

Soil copper contamination is part of the general trend agricultural soils contamination with heavy metal, due to the long-term use of copper-containing pesticides (copper sulfate, copper hydroxide chloride, copper bicarbonate, etc.). D.), fertilizers (containing copper sulfate, copper dihydrogen phosphate), uneven application, overdosage, storage, disposal, violation of the generally accepted sanitary standards. Copper content excess in the arable soil horizon was observed in the Vladimir region in 10 districts, compared with the background, and the average concentration in the region increased by 13.5 %. The greatest increase of Cu is observed in Sudogda, Selivanovo, Vyaznikky, Kirzhach, Kolchugino, Alexandrov district. The highest risk ratio of soil pollution with Zn was observed in Petushki, Sudogda and Kirzhach areas on sod-podzolic sandy loam soils and amounts 0.369-0.447, the lowest are in Gorokhovets, Sobinka, Yuriev-Polsky, Suzdal areas, represented by loamy soils, where it amounts 0.089-0.162. Zn accumulation in arable sandy loam soils can be assumed to be caused by the fact that Zn in such soils exists in an inaccessible form for agricultural plants, and is poorly absorbed by them, due to long term soil liming, phosphorus over-fertilizing. Anthropogenic zinc in soils is largely fixed with the help of iron hydroxides, phosphates, and is a part of phyllosilicates [7]. Zn migration in such form is hindered, as it is sedentary, without entrainment with plants consequently it is accumulated.

In loamy soils, zinc is more mobile, more accessible to plants, it migrates along the soil profile and is ablated with plants as a micronutrient. Here no accumulation occurs, it is just necessary to maintain its balance in the soil with zinc fertilizing. The highest contamination level of arable soils with cobalt

| Region                        | Pb  | Cu  | Zn  | Co  | Pb  | Cu  | Zn  | Co  |
|-------------------------------|-----|-----|-----|-----|-----|-----|-----|-----|
| Melenkovsky. sandy loam       | 0.179 | 0.400 | 0.107 | 0.296 | 0.138 | 0.197 | 0.281 |
| Murom. loam. pH <5.5          | 0.112 | 0.250 | 0.111 | 0.183 | 0.200 | 0.203 | 0.198 |
| Petushinsky. sandy loam       | 0.184 | 0.540 | 0.094 | 0.447 | 0.216 | 0.091 | 0.305 |
| Selivanovsky. sandy loam      | 0.153 | 0.480 | 0.158 | 0.333 | 0.128 | 0.102 | 0.270 |
| Sobinsky. pH> 5.5 loam        | 0.078 | 0.140 | 0.061 | 0.123 | 0.296 | 0.113 | 0.149 |
| Sudogda. sandy loam           | 0.134 | 0.460 | 0.203 | 0.376 | 0.128 | 0.096 | 0.290 |
| Suzd. loam pH> 5.5            | 0.058 | 0.150 | 0.077 | 0.162 | 0.316 | 0.203 | 0.195 |
| Yuryev-Polsky. loam pH> 5.5   | 0.067 | 0.180 | 0.077 | 0.155 | 0.308 | 0.203 | 0.184 |
| by region                     | 0.14 | 0.35 | 0.11 | 0.27 | 0.22 | 0.19 | 0.27 |
is detected in Suzdal, Yuriev-Polsky, Alexandrovo, Kolchugino districts, which is primarily connected to the intensive land use in the area and, as a consequence, with more active fertilization of arable land. Besides all these agricultural areas have loamy soils, richer in humus thus complicating cobalt migration along the soil profile, binding it, stimulating its accumulation in the upper arable horizon. The risk factor of arable soils contamination in these areas is 0.276-0.316. At the same time the areas where arable soils are represented by sandy loam soils (Sudogda, Selivanovo, Kovrov Melenki, Gus-Khrustalny), depleted in organics, non-leaching the soil, Co content increase is negligible. The contamination risk factor of such soil is 0.105-0.146. On average, Co content in arable soils in the region has increased not only as a result of reclamation measures, but as well due to the technogenic soil pollution, associated with the industry and vehicles traffic.

A slight decrease in the gross content was detected for Cd and Mn. According to the hazard degree, cadmium belongs to the 1st class of highly hazardous substances and its content control in the arable soil is an important component of agricultural monitoring. Cd is introduced into arable soils basically with phosphorus (phosphate fertilizers). It is a concomitant admixture of phosphate ore, which concentrate is used to produce fertilizers. Due to the decrease in the phosphate fertilizing (lack of funding), on average, this element content decrease is observed in the arable soil horizon of the region. As mentioned above, heavy metals in different soil types behave differently. HM distribution and migration along the profile depends on soil agrochemical properties (humus content, medium reaction, mechanical composition). Thus, let’s take Cd for example, despite the fact that its gross content in the whole region decreased, it turned out that in sandy loam soil areas, its content, on the contrary, increased. It can be explained by the fact that sandy and sandy loam soils have the lowest buffering, which is determined primarily by the granulometric composition and acid-base properties of the lithogeochemical group of soils and, as a consequence, is characterized with the worst chemical contamination resistance, in particular cadmium. In such soils, Cd is a sedentary element, so pollution remains for a long time and, as a result, it is accumulated.

The carried out spatial correlation analysis made it possible to reveal high positive statistically significant correlations between the concentrations of most elements (table. 2). Such elements as Pb, Cu, Zn, Co and Ni can be assumed to penetrate into the arable horizon jointly (as impurities with organic, mineral, complex fertilizers; with industrial emissions into the atmosphere; with vehicle exhausts). Mn is an exception, as this element has no dependencies with any of the analyzed HM, it probably gets to the arable layer in a different way. Probably the principle source of its introduction into the arable layer is manganese fertilizers. Taking into account the high price of these fertilizers (manganese sulfate costs about 170 rubles/kg), compared with phosphorus and potassium, they are more rarely introduced into arable land, so now Mn content in the arable soil tends to decrease in the region.

Nickel penetrates into the arable soil both with the fertilizers in the form of impurities, and as harmful industrial emissions and exhaust gases from transport, especially diesel. The arable sod-podzolic sandy loam soil are characterized with the increased Ni content (Vyazniki, Gorokhovets, Gus-Khrustalny Melenki, Kirzhach districts) because of low self-cleaning ability of the soil type. At the same time the regions with sod-podzolic loamy soils, where arable lands are located, its content reduced. However, on the whole, Ni content, compared to the background indicators has not changed in the region.

| Pb   | Cd   | Cu   | Zn   | Co   | Mn   | Ni  |
|------|------|------|------|------|------|-----|
| Pb   | 1.0000 | 0.1712 | 0.6544 | 0.6913 | 0.8179 | 0.2747 | 0.7814 |
| p= --- | p=0.526 | p=0.006 | p=0.003 | p=0.000 | p=0.303 | p=0.000 |
| Cd   | 0.1712 | 1.0000 | 0.4485 | 0.5232 | 0.5409 | -0.3494 | 0.5426 |
| p=0.526 | p= --- | p=0.081 | p=0.038 | p=0.031 | p=0.185 | p=0.030 |
4. Conclusion
The research demonstrates that HM gross content in the arable soil layer in the region does not exceed MPC; thus, arable soils of the Vladimir region refer to slightly polluted areas judging by the heavy metals content and they cause no danger to human health. The principal source of HM in the topsoil is fertilization, therefore, it is required to control fertilizing expediency, proper application and dosage to improve sanitation and reduce the risk to the population health.

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