The influence of sample preparation techniques on results of extraction of heavy metals from soil

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Abstract. A study of the composition of mobile compounds of heavy metals (HM) in the area of aerosol contamination by a heat supply company showed an increase in the number of these compounds near the source of contamination. In the group of loosely bound compounds, the largest part is represented by specifically sorbed compounds. Sample preparation (the degree of sample grinding) had a noticeable effect on the extractability of Zn, Cu, and Pb from the soil. During the sifting of a soil sample through a 0.25 mm sieve, the extraction of mobile forms of HM increases significantly (by 7–16 %). Thus, with an increase in the specific surface of soil particles, the extracting ability of the reagents increases. It is necessary to take into account the sample preparation used in each fractionation method to evaluate the results and compare them.

1. Introduction

When fuel is burned by heat supply companies, the chemical waste is contained in aerosols, as a result of which the content of heavy metals in fly ash is several times higher than in raw materials. Coal dust generated after combustion contains Fe, Cu, Zn, Mn, Pb, Cd, Cr, Ni, Co, V, Ti, Br, Zr, as well as organic pollutants.

The assessment of the ecological state of soils subject to HM contamination involves determination of an increase in the total concentration of elements and their mobility. The assessment of mobile forms of TM compounds accurately reflects their bioavailability.

The soil is a polydisperse system consisting of particles of different sizes. With an increase in the dispersion of soil particles, its total surface increases, which plays the main role in all physicochemical reactions between solid and liquid, solid and gas phases. The size of soil particles significantly affects the bioavailability and potential toxicity of metals [1–6].

The extractability of TM depends on the degree of grinding of the sample, since grinding causes the release of clay particles and primary minerals from organic and oxide films, increases the specific surface area, thereby changing the characteristics of the sample [2, 3]. According to [1, 7–10], in granulometric fractions isolated from soils, HM concentrations increase with a decreasing particle size. The degree of dispersion of particles and their bioavailability depend on the degree of dispersion of the particles.

We studied the forms of compounds of Cu, Zn and Pb in soils, near the heat supply enterprise. These metals are priority pollutants in Rostov region [11, 12].

The purpose of the work is to study the effect of soil sample preparation on the content and composition of loosely bound compounds of Cu, Pb and Zn in ordinary chernozem under the aerotechnogenic contamination.
2. Methods and materials

Emissions of Novocherkasskaya HEP account for 1 % of the total volume in the Russian Federation (RF) and up to 58 % of the volume of emissions in Rostov Region, of which the main part (99 %) is in Novocherkassk and its environs.

HEP emissions consist of ash, sulfur dioxide, nitrogen oxides, soot (over 30 t/year), hydrogen fluoride (7 kg/year), vanadium pentoxide (about 8 t/year), iron oxides (over 5 t/year) and heavy metals (Cu, Zn and Pb), chromic anhydride (about 0.1 t/year), etc. The ash contains up to 85 % of chemical elements that were initially present in initial coal [11].

Samples were taken in the northeast direction at a distance of 1.6 and 15 km from the emission source. Soil located near the enterprise (1.6 km) is affected by aerosol contamination – polluted soil taken 15 km away has no negative impact. The soil cover is represented by Haplic Chernozem. The soil samples have the following physicochemical properties: pH – 7.4–7.6; 54.3–55.3 % of physical clay (particles with a diameter of <0.01 mm), 31–31.4 % of sludge (particles with a diameter of <0.001 mm), the content of organic carbon is 4.2–4.5 %; carbonates – 0.7 %; EKO soil – 32–34 cm (+) · kg–1.

Different sample preparation includes the content of different particle size fractions of soils (Fig. 1), which are characterized by different ability to absorb elements.

![Figure 1. Fractions of particle size elements](image)

To compare the equivalence of alternative methods of soil sample preparation, we performed a comparative analysis of the results of HM extraction from samples of ordinary carbonate chernozem prepared in different ways: general and special.

General preparation includes grinding air-dry soil in a porcelain mortar with a pestle with a rubber (rubber) tip and sifting through a sieve with holes of 1 mm. Special preparation involves grounding the soil into small portions in an agate mortar and sieving it through a sieve with a hole diameter of 0.25 mm. The weight of the soil was 5 g [13].

To determine the mobile forms of metals, three parallel extracts [13] characterizing the complex state of HM in the soil were used:

1) 1 n AAB ammonium acetate buffer with a pH of 4.8 (soil: solution ratio = 1:10, extraction time 18 hours), capable of converting into the solution exchange forms of metals characterizing their “actual” mobility;
2) a 1 % solution of EDTA in AAB with a pH of 4.8 (soil: solution ratio = 1:10, extraction time 18 hours), which, presumably translates relatively fragile complex compounds into the solution.
3) Acid-soluble metal compounds extracted with 1N HCl solution (soil: solution ratio = 1:10, extraction time 18 hours) characterize the potential stock of mobile metal compounds in the soil. They are presumably represented by metal ions capable of exchanging and specifically adsorbed compounds, including those retained by amorphous oxides Fe and Mn, as well as carbonates. Based on the difference between the metal content in HCl and AAB extracts, the amount of specifically adsorbed metal compounds was calculated.
The content of Zn, Cu, and Pb in soil extracts was determined by the AAS method. The gross metal content in the soil was determined by X-ray fluorescence using the MAKC-GV spectroscan.

3. Results
In the unpolluted soil, the total Zn content is $84.3 \pm 6.1 \text{ mg/kg}$, Cu – $45.3 \pm 6.1 \text{ mg/kg}$, Pb – $27.0 \pm 2.3 \text{ mg/kg}$, which corresponds to the background level (Minkina et al. 2014). In the polluted soil, the metal content increased: Zn – $112 \pm 10.2 \text{ mg/kg}$, Cu – $72.1 \pm 6.4 \text{ mg/kg}$, Pb – $68.0 \pm 7.0 \text{ mg/kg}$.

Table 1. Content of exchange, complex and specific compounds of tm extracted from soil using different preparation techniques, mg/kg

| Soil Sample | Exchangeable compounds | Complex compounds | Specific sorbed compounds |
|-------------|------------------------|------------------|--------------------------|
|             | <1 mm*                 | <0.25 mm         | <1 mm                    | <0.25 mm |
| unpolluted soil | 0.3±0.1       | 0.6±0.1          | 0.4±0.1                  | 0.7±0.1   |
| polluted soil    | 10.7±0.9       | 16.9±1.2         | 7.3±0.7                  | 14.4±1.2  |
| unpolluted soil | 0.3±0.1       | 0.7±0.1          | 0.3±0.1                  | 0.7±0.1   |
| polluted soil    | 2.5±0.3       | 5.1±0.8          | 7.3±1.0                  | 10.4±1.0  |
| unpolluted soil | 0.6±0.1       | 1.3±0.2          | 0.8±0.2                  | 2.3±0.2   |
| polluted soil    | 2.4±0.2       | 4.2±0.5          | 6.3±0.7                  | 13.1±1.1  |

* – soil passed through a sieve with a diameter of 1 mm and 0.25 mm

To evaluate the movable metal compounds, the method of parallel extracts was used. A group of loosely bound compounds is retained on the surface of soil particles by the organic and mineral components of the soil in an exchange and specifically sorbed state. This group includes exchange, complex and specifically sorbed metal compounds. The latter can be considered transitional between firmly and loosely bound forms [13]. The determination of loosely coupled HM compounds is most important from an environmental point of view, since they are absorbed by plants and migrate to other adjacent environments.

In the unpolluted soil, the content of Zn, Cu, and Pb is distributed in the following sequence: exchange <complex <specifically sorbed (Table 1, Fig. 2).

In the polluted soil, the share of loosely bound HM compounds increases (Table 1, Fig. 2). The share of the most mobile exchange forms of metal in its composition increases as well (Fig. 2). The content of exchange forms is higher than that of complex compounds. The loosely bound HM compounds are represented by specifically sorbed forms, but their share decreases due to an increase in the share of exchange and complex forms (Fig. 2).

The main difference between Zn and other metals is that during contamination its significant part is fixed due to the ion exchange, therefore Zn is less firmly fixed in the soil. So, in unpolluted soil, the share of Zn exchange forms is 0.4–0.7 %, in the polluted soil, it increases to 9.6–15 % (Fig. 2).

The significance of organic substances in the fixation of Pb and Cu ions is caused by the high ability of HMs to form intracomplex compounds (chelates). Cu and Pb form chelate complexes with functional groups of aromatic rings. This is reflected in the greater share of complex compounds in Cu and Pb.

For the extraction of HM from soils, various sample preparation techniques are used. To determine chemicals in order to control general and local contamination, the soil is sieved through a sieve with a hole diameter of 1 mm. In sequential fractionation by the Tessier method, the soil sample is sifted through a sieve with a hole diameter of 0.25 mm [12].
Figure 2. The content of Zn, Cu and Pb compounds in the soil at different levels of contamination and sample preparation methods, % of the total content

When the soil is sifted through a 0.25 mm sieve, the extractability of Zn, Cu, and Pb is higher due to an increase in the specific surface of the particles. These differences were observed both in the unpolluted soil and at different levels of contamination.

A similar pattern is valid for three forms of metal (Table. 1, Fig. 2). The clay fraction is characterized by the highest concentrations of metals, which is due to the high adsorption capacity of its secondary clay minerals, coagels of sesquioxides and silicic acid, crystallized oxides of iron and aluminum, and humic substances of lower condensation [11].

The differences in the values of extraction of Zn, Cu and Pb from the unpolluted soil prepared using the general and special sample preparation methods were as follows: for exchangeable compounds – from 0.3 to 2.6 %, for complex compounds – from 0.3 to 5.5 % and for specifically sorbed – from 0.7 to 5.2 %. With an increase in the degree of the anthropogenic load, an increase in the number of HM extracting compounds from soil samples passing through a sieve with hole diameters of 1 mm and 0.25 mm is observed. Thus, an increase in the dose of Zn pollution led to an increase in the number of all metal compounds to 41.2 %, with an increase in the dose of Cu to 22.7 % and Pb to 28.2 %. At the same time, differences remain in the greater extractability of metals from soils containing fractions of particles of less than 0.25 mm. In case of Zn contamination, differences in
the relative metal content in soils reach 15.6 %, in case of Cu contamination – up to 6.7 % and in case of Pb contamination – up to 10.0 %. Therefore, with an increase in the specific surface area of soil particles, the extracting ability of the reagents used increases significantly (Fig. 2).

4. Conclusion
Thus, under the influence of aerosol emissions from NHEP, the total content of metals in soils adjacent to the emission source significantly increases. In the group of loosely bound compounds, the predominance of specifically sorbed forms was identified. Zn is characterized by the greatest increase in exchangeable forms, and Cu and Pb form complex compounds.

A significant effect on the data of parallel hoods has the state of the analyzed sample. During the sifting of a soil sample through a 0.25 mm sieve, the extraction of mobile forms of Zn, Cu, and Pb increases. To analyze and compare the results of fractionation of HM compounds, it is necessary to take into account the sample preparation technique.

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