Heavy metals in agricultural crops of Rostov region through the example of soft wheat (Triticum aestivum)

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Abstract. In recent decades, the problem of an annually increasing level of anthropogenic impact on the environment has become increasingly important. One of the most dangerous pollutants entering the environment from industrial emissions is heavy metals. This type of pollutant is not subject to biodegradation over time, due to which they accumulate in environmental objects in dangerous concentrations. The resistance of soft wheat (Triticum aestivum) of the Myatlikovy family (Poaceae) to aerotechnogenic pollution in the soil and climatic conditions of southern Russia was studied. The pollution with Pb, Zn, Ni and Cd was established. The average and close correlation was established between the total content and the content of mobile forms of TM in the soil and their content in wheat plants. For the studied plants, the accumulation coefficient (AC) and distribution coefficient (DC) of TM were calculated. The values of the coefficients showed a significant accumulation of elements by plants from the soil, as well as their translocation from the root system to the aboveground part.

1. Introduction

Food security is a high-priority issue for sustainable global development both in quantitative and qualitative context. In recent decades, adverse effects of unexpected contaminants on crop quality have threatened both food security and human health [1]. Excessive accumulation of heavy metals (HM) in crop production, which is used for feed and food purposes, poses a serious threat to human and animal health [2–6]. Unlike organic pollutants, biodegradation of HM does not occur and, therefore, they continuously accumulate in the environment [7–9].

In order to understand the processes of formation of plant adaptation mechanisms to pollution, it is necessary to study the accumulation of HM. The negative effect of HM on plants leads to the decrease in plant productivity (primarily agricultural), disruption of naturally occurring phytocenoses, destruction of assimilation potential of phytomass, disruption of normal organogenesis processes – the appearance of specific teratological changes [7, 10, 11]. The data of histochemical analysis [12] shows that the localization and translocation of HM in the bodies and tissues of plants is species-specific and is determined by the physicochemical properties of the growth medium, metal concentration, and
anatomical, morphological and metabolic features of the species. The study of the distribution of elements allows a better understanding of the internal mechanisms of plant resistance to HM pollution.

The factors affecting the bioavailability of an element to plants include soil organic matter, pH, the concentration of competing ions, the species composition of microorganisms, root secretions and the type of plant. Depending on the genesis and soil properties, they differ in the total content of HM, as well as in the content of their mobile and accessible forms to plants. It is the concentration of mobile forms of metals in the soil that is important with respect to absorption and accumulation in plants [13].

The study of the patterns of accumulation of HM in plants is especially relevant in agricultural regions, which include Rostov region (Russia). Industrial enterprises are closely adjacent to agricultural land, which poses risks to the health of the inhabitants of the region. It is under such conditions that studying the influx of HM into plants is of the greatest importance, making it possible to predict the effects of technogenic environmental pollution.

The resistance of plants to pollution is not constant and changes over time under the influence of unfavorable factors on phytocenoses. In this regard, long-term monitoring research studying the effect of pollutants on plants can solve many problems: to find out the reasons for the different resistance of plants and their adaptation to toxicants; to identify the influence of the most important factors on the translocation of metals to plants; to identify species that can be used for phytoremediation of contaminated lands; to specify the average content and limits of the permissible level of accumulation of HM for various plant species [14].

The purpose of this research is to study the resistance of soft wheat crops to aerotechnogenic pollution in the soil and climatic conditions of Rostov Region (Russia) according to long-term monitoring observations.

2. Methods and materials

Monitoring sites were located at a distance of up to 2.2 km (Fig. 1) in different directions from the branch of OGK-2 Novocherkasskaya power plant (NPP), the largest fuel and energy complex in Rostov Region [12]. Despite its close proximity to NPP, within 2.5 km from the enterprise there were fields sown with oilseeds and grain crops. This led to the choice of monitoring sites (sites No. 1, 2, 3, 4) sown with agricultural crops – soft wheat (Triticum aestivum).

The plants were selected annually during the period 2018–2019 in the first decade of July in the phase of full ripeness of winter wheat, since with it the maximum influx of elements into the plant is confined [15]. Along with plants, soil samples were taken, represented by ordinary carbonate chernozem (Haplic Chernozem), having the following physical and chemical properties: humus content 3.6–4.2 %, pH 7.4–7.7, physical clay 50.6–56.3 %; sludge 40.4–44.6 %, CaCO$_3$ – 0.5–1.1 %, BEC 31–36 cmol kg$^{-1}$, exchangeable bases (cmol kg$^{-1}$): Ca$^{2+}$ 31.0–34.2; Mg$^{2+}$ 5.1–6.3; Na$^+$ 0.03–0.06.

In the samples of plants and soils, such elements as Pb, Cd, Zn, Cu, Ni, Mn, and Cr, which were present in the emissions of NPP, were determined [16]. Mineralization of plant samples was carried out by dry ashing method according to GOST 26657-85. Roots and aboveground organs of plants were separated, washed thoroughly with distilled water, and oven-dried at 65 °C. The plant samples were ground in mill and passed through a 0.25-mm sieve. Copper determination in plant tissues was performed by the combustion method at 450 °C during 6 hrs. The air dried 1 g sample was used, and then the ash was dissolved in 5 ml of 20 % HCl and filtered through 0.45 µm Whatman filter paper.

The total contents of Cr, Ni, Mn, Cd, Cu, Zn, and Pb in soils were determined by the X-ray fluorescence method. Mobile forms of HM were solubilized by 1 N ammonium acetate buffer solution (AAB) with pH 4.8 (soil: solution = 1: 5, extraction time 18 h) capable of solubilizing exchangeable forms of metals, which characterize their actual mobility [17].

The concentrations of HM in soil and plant sample extracts were determined using the atomic absorption spectrophotometer (AAS) (KVANT 2-AT, Kortec Ltd, Russia) with a wavelength diapason of 324.8 nm at room temperature. The AAS was calibrated daily using a standard solution.
The content of HM in soft wheat grain (*Triticum aestivum*) was compared to LOC for food raw materials and food products of the group “Grains (seeds), flour and cereals and bakery products” [18]. The assessment of HM pollution of stems and leaves was carried out by comparison of the concentration of elements in plants with the maximum permissible level (MPL) of metal content in animal feed [19]. Guidance document HS 2.1.7.2041 2006 [20] was used to assess the pollution of HM soils by gross content and mobile forms.

In order to assess the selectivity of HM accumulation by different species of steppe plants under pollution conditions, we calculated the accumulation coefficient (AC) and distribution coefficient (DC). The AC shows the level of element biophility, and its variation shows the level of technogenic load on the soil. The AC is formed by the ratio of the concentration of an element in the plant dry weight to the content of its mobile compounds in the soil [17, 21].

In order to study the migration of HM to various parts of plants, two barriers to the entry of elements were considered: stems and leaves / root system and seeds / stems and leaves. The DC value makes it possible to estimate the capacity of the aboveground parts of plants to absorb and accumulate elements under soil pollution conditions and was determined as the ratio of the metal content in the aboveground biomass to its concentration in the roots. The DC value allowed estimating the barrier functions of plants under contamination [22].

A value of DC > 1 indicates an active translocation of metals from the roots to the aboveground part or from the stems to the grain, the plant is a metal accumulator; DC = 1 indicates the neutral behavior of the plant with respect to metals (indicator), and DC < 1 indicates that the plant excludes metals from absorption, being an exception [23, 24]. The DC values are often the same for the plants of the same species; a change in the value indicates that a plant experiences ecological stress.

The choice of these indicators is reasoned by the fact that, on the one hand, it is necessary to take into account the barrier potential of the soil, and on the other hand, the protective functions of plant itself. The use of these indicators clearly separates the barriers to the entry of HM into plants.

### 3. Results

The soils of monitoring sites, including agricultural land, are subject to continuous long-term aerotechnogenic pollution by emissions from NPP [12]. The maximum permissible concentration exceeding the general content of Pb in the soils of all monitoring sites was found (Table 1).

| Site No | Mn  | Zn  | Cr  | Cu  | Pb  | Ni  | Cd  |
|---------|-----|-----|-----|-----|-----|-----|-----|
| 1 (1.6 PD) | 1036±45 | 152±8 | 132±9 | 66±6 | 98.0±7 | 2.04±0.09 |
| 2 (1.5 P) | 871±32 | 90±5 | 119±8 | 53±2 | 56.1±6 | 1.60±0.05 |
| 3 (2.2 SE) | 928±89 | 102±5 | 112±5 | 40±3 | 60.0±6 | 1.50±0.04 |
| 4 (2.1 S) | 758±28 | 105±9 | 123±5 | 45±3 | 71.0±8 | 1.39±0.04 |
| MPL | 1500 | – | – | – | 32 | – | – |

The content of exchange forms exceeded the MPC for Cr, Pb, and Cd at site No. 1 (Table 2). The high content of exchange forms of HM in the soil of monitoring site No. 1 is reasoned by the greatest degree of anthropogenic load on this site. This is associated with the proximity of the site from the source of emissions – NPP in the predominant direction of the winds. The content of HM in soils decreases moving away from the source of pollution.

The monitoring of agricultural land in the area near NPP, carried out during 2018–2019, showed steady pollution of HM in wheat plants. In wheat grain, MPL is exceeded by 2–10 times for Pb and by 2.5–5.7 times for Cd at all monitoring sites (Table 3). The excess of MPL for forage grasses in wheat straw is observed for Pb and Ni at site No. 1 (1.6 and 2.2 times, respectively) and Cd at sites No. 1 and No. 2 (2.2–5.3 times).
Table 2. Content of the exchange forms of heavy metals in the 0–20 cm Haplic Chernozem layer at monitoring sites, mg/kg (average for 2018–2019)

| Site No | Mn   | Zn   | Cr   | Cu   | Pb   | Ni   | Cd   |
|---------|------|------|------|------|------|------|------|
| 1 (1.6 PD) | 65±6 | 26±3 | 14±2 | 7±1  | 12±2 | 6.2±0.5 | 0.37±0.02 |
| 2 (1.5 P)  | 32±4 | 16±2 | 4±1  | 4±1  | 9±1  | 3.3±0.1 | 0.06±0.01 |
| 3 (2.2 SE) | 97±6 | 3±1  | 5±1  | 5±1  | 7±1  | 3.5±0.1 | 0.10±0.01 |
| 4 (2.1 E)  | 106±7 | 2±1  | 3±1  | 3±1  | 6±1  | 3.7±0.3 | 0.08±0.01 |
| MPL      | 140  | 23   | 6    | 6    | 4    | 0.05   |      |

Table 3. Content of heavy metals in soft wheat plants at monitoring sites, mg/kg (average for 2018–2019)

| No site   | Mn   | Zn   | Cr   | Cu   | Pb   | Ni   | Cd   |
|-----------|------|------|------|------|------|------|------|
| 1 (1.6 PD) | 65/44 | 22/60 | 18/19 | 7/11 | 3.1/2.4 | 6.6/8.4 | 1.63/1.83 |
| 2 (1.5 P)  | 27/44 | 14/32 | 13/15 | 7/10 | 7.0/11 | 2.5/3.8 | 0.54/0.69 |
| 3 (2.2 SE) | 43/57 | 10/72 | 4/7 | 6/8 | 4.2/1.2 | 2.9/2.5 | 0.34/0.41 |
| 4 (2.1 E)  | 19/20 | 6/16 | 10/7 | 2/3 | 3.4/0.8 | 2.6/2.7 | 0.16/0.27 |
| MPL/LOC   | 50/50 | -/-  | -/-  | 30.0/10.0 | 5.0/0.5 | 3.0/- | 0.3/0.1 |

Legend: stems / roots / grain; semibold type indicates the excess of MPL and LOC

The content of Zn and Cr in the generative organs of wheat is higher than in the root system (Table 3), while the content of Mn, Cr, Pb, and Cd differs slightly in plant organs. Pb content in wheat is in the range of 2.8–8.1 mg/kg in straw and 1–5 mg/kg (from 2 to 10 MAC) in grain.

For wheat plants, a close correlation was established (R = 0.58–1.00) with mobile forms in the soil for all the investigated elements.

The calculated AC values indicate a significant influx of Cd, Mn, and Zn in the roots of plants from the soil (Fig. 1). The increase in the mobility of HM in the soil with the increase in the level of pollution contributed to their increase in plants and, as a result, to accumulation in the final product. Pb and Ni are characterized by low AC values compared to other HMs.

AC for soft wheat (Triticum aestivum) is highest for Cd. A number of metals for this indicator are as follows:

Cd> Zn> Cr> Cu> Ni> Mn> Pb (Fig. 1).

It is necessary to note that there is not always a clear pattern in the change in AC depending on the level of anthropogenic load, which is probably reasoned by basipetal accumulation of HM by plants due to foliar contamination.

The calculated DCof stems / roots showed that Cu is the largest translocation from the root system to the aboveground mass of soft wheat (Table 4). Zn and Ni also have higher coefficient values compared to Mn, Pb, Cr, and Cd.
Table 4. DC of heavy metals in soft wheat plants at monitoring sites, mg/kg
(average value for 2018–2019)

| Site No | Mn  | Zn   | Cr   | Cu   | Pb   | Ni   | Cd   |
|---------|-----|------|------|------|------|------|------|
| 1 (1.6 PD) | 0.45/0.68 | 1.06/2.73 | 0.78/1.06 | 0.50/1.57 | 0.79/1.29 | 0.89/0.73 | 0.45/0.35 |
| 2 (1.5 P)  | 0.44/1.44  | 1.08/2.79  | 0.86/1.15  | 0.64/1.67  | 0.52/0.71  | 0.78/1.52  | 0.44/0.85  |
| 3 (2.2 SE) | 1.43/0.81  | 0.57/2.20  | 0.75/2.25  | 3.82/1.17  | 1.16/0.55  | 0.83/0.59  | 1.43/0.76  |
| 4 (2.1 E)  | 0.38/1.32  | 1.43/4.67  | 0.67/0.60  | 4.25/2.50  | 0.96/0.29  | 1.78/0.62  | 0.38/1.69  |

Legend: in the numerator – DC stems / roots, in the denominator – DC stems / grain; semibold type indicates the excess of DC> 1.

The DC grain / stalk values indicate a high translocation of Zn and Cu from the stems and leaves of wheat to the generative organs (Table 4). Various DC values are associated not only with the conditions of anthropogenic load on plants, but also with the genetic characteristics of a plant itself, which determine the need for nutrients [25].

4. Conclusion

The results of long-term monitoring revealed HM contamination with such elements as Pb, Zn, Ni and Cd, of agricultural herbaceous plants growing 1.5–2.2 km from NPP. The content of Pb, Ni and Cd in soft wheat grain exceeds MPL for food raw materials.

A close correlation of HM in soft wheat (Triticum aestivum) with mobile forms of metals in the soil was established, which indicated the predominance of pollutants. The accumulation of elements occurs mainly in the roots of wheat, compared to the aboveground part. However, the distribution of metals in the aboveground part of a plant shows a high translocation of pollutants to grains. This indicates the need for constant monitoring of the safety of agricultural plants growing in impact zones.

Acknowledgment

The research was financially supported by a grant of the President of the Russian Federation MK-2818.2019.5, RFBR No. 19-34-60041 Perspective, No. 19-29-05265 mk.

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