APPLIED PROBLEMS OF ARID LAND DEVELOPMENT

Accumulation of Heavy Metals by Forb Steppe Vegetation According to Long-Term Monitoring Data

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Abstract—The steppes of the northern Azov Region are extremely favorable for agriculture. Thus, the foremost problem is the cultivation of ecologically safe products under conditions of technogenic pollution. We have studied the effect of aerotechnogenic emissions on the accumulation of heavy metals (HMs) in haplic chernozem, haplic chernozem (stagnic), and calcaric fluvic arenosol and steppe plants *Poa pratensis* L. and *Elytrigia repens* (L.) Nevski. of the families Poaceae and *Achillea nobilis* L. and *Artemisia austriaca* Jacq. of the family Asteraceae) according to the data from 17 years of monitoring. The accumulation of Pb, Zn, Cd, Cu, Mn, Cr, and Ni in soils and plants under the effect of power plant emissions has been established. The proportion of loosely bound compounds of heavy metals in the polluted soils is 28–52% of the total content. In the monitored plots with the highest technogenic load, the content of Pb, Cd, Cr, and Ni in the studied plants exceeds the maximum permissible level for forage. It has been revealed that HM accumulation in the aboveground part of plants and their roots depends on the amount of pollutants and the biological features of each species. The plant species of the family Poaceae accumulate less microelements in their aboveground part than *Asteraceae*.

Keywords: microelements, aboveground part, roots, soil, pollution, accumulation, aerosol emissions **DOI:** 10.1134/S2079096118030058

INTRODUCTION

The Azov region is a unique area in which natural steppe vegetation has survived. The plant cover is represented by herb–bunchgrass and dry herb–bunchgrass plant communities (Blazhnii et al., 1985; Plashkov and Zozulin, 1986). There are very few studies on the accumulation of heavy metals (HMs) in steppe herbaceous plants in the south of Russia. At the same time, there are many industrial enterprises (electricpower enterprises, smelters, and ore-mining enterprises) in the northern Azov Region that are sources of environmental pollution. One of these enterprises is a first-class enterprise, a Novocherkassk Power Plant (NPP); its emissions constitute over 70% of the total emissions in Rostov oblast (*Ekologicheskii vestnik Dona*…, 2017). The NPP emissions contain a large amount of HMs, such as Pb, Cd, Zn, Cu, Ni, Mn, and Cr (Minkina et al., 2013).

Metals can accumulate in plants, because they are absorbed by leaves after pollutant particles settle on the plant surface (Xiong et al., 2014). The role of the air or soil source in metal accumulation depends on many factors: the volume and composition of emissions, the presence of other metals, the soil properties, the duration of pollution, specific plant features, the vegetation period, or the content and composition of metal compounds in the soil (Deng et al., 2004; Motuzova et al., 2014). An understanding of the possibility of metal absorption and accumulation by different plant species will provide insight into their selection for phytomelioration.

HMs are concentrated in the stems and leaves of plants that grow in areas exposed to industrial and transport effects (Shahid et al., 2013). Therefore, environmental monitoring should pay close attention to the study of the microelemental composition of plants that grow in the vicinity of industrial enterprises and motor roads.

Different plant species accumulate different amounts of HMs in their aboveground part and roots, depending on the level of technogenic load and physiological crop features (Demidchik et al., 2001; Ahmad et al., 2012; Il'in and Syso, 2012). The influence of the morphology of plants on the amount of metals accumulated by them is observed: lamina

indentation, pubescence, the presence of resinous substances, wax, etc.

It was previously shown that the metal content in the underground parts of many plant species is higher than in their aboveground parts (Kashin and Ubugunov, 2012; Minkina et al., 2008; Seregin and Kozhevnikova, 2008; Shahid et al., 2017).

Given the same concentration of HMs in soil, the plants of different species accumulate different amounts of these metals, which is due to the physiological features of plants, i.e., metabolic processes in their tissues and the selectivity of absorption by their roots (Minkina et al., 2008; Seregin and Kozhevnikova, 2008).

Plants can accumulate elements, the content of which in the soil exceeds the maximum permissible concentration (MPC). They can accumulate them for a long period to a certain level. An excess of this level leads to unfavorable changes in physiological plant processes. A serious threat is posed by the absence of any visual signs of plant intoxication, which can be clearly manifested only in the course of time. For this reason, long-term static observations in the technogenic impact area serve as a valuable source of information.

The objective of this study was to use long-term monitoring data to reveal the features of HM accumulation by two species of the family Poaceae (*Poa pratensis* L. and *Elytrigia repens* (L.) Nevski.) and two species of the family Asteraceae (*Achillea nobilis* L. and *Artemisia austriaca* Jacq.), which are widespread in the steppe zone in southern Russia and in the study area.

The following tasks were completed:

(1) establishment of the features of HM accumulation for different soil types and test species, depending on their location with respect to the main polluting object, the Novocherkassk Power Plant;

(2) study of the relationship between the metal content in soils and the test species;

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(3) comparative analysis of differences in HM accumulation by the aboveground part of the test plants and their roots.

MATERIALS AND METHODS

In 2000, monitoring plots were established in fallow sites at different distances (from 1 to 20 km) in the direction from the NPP (Fig. 1). The agricultural use of fallow areas ended about 25 years ago, which led to the recovery of the natural herbaceous layer in this area. Most of the monitoring plots (nos. 4, 8, 9, and 10) are in the northwestern direction from the enterprise, which prevails in the wind rose. Soil samples were annually collected from the upper 20-cm layer in the monitoring plots (from 2000 to 2017) (*GOST*..., 1989). The soils of the monitoring plots are formed by heavy-loamy haplic chernozem (plots nos. 1, 4, 5, 7, 9, 10, and 11), as well as by the light-loamy haplic chernozem (stagnic) (plots nos. 3, 6, and 8) and calcaric fluvic arenosol of the Tuzlov River floodplain (plot no. 2); they are characterized by the properties given in Table 1. Plant samples (the aboveground part and roots) were collected during the mass flowering phase (*GOST*..., 1987), since it is at this stage when the highest entry of elements into plants is observed (Il'in and Syso, 2012). The plant sampling was accompanied by geobotanical descriptions. The roots were extracted together with soil monolith to avoid loss of most of the root system. After the plants were sampled, they were dried to the air-dry state and their aboveground part and roots were separated from each other and ground up. Prior to grinding, the roots were cleared of soil particles.

Herbaceous plants of the family Poaceae (*Poa pratensis* L. and *Elytrigia repens* (L.) Nevski) and family *Asteraceae* (*Artemisia austriaca* Jacq. and *Achillea nobilis* L.), which are dominant in all monitoring plots and are easily distinguishable, were chosen as the objects of research. The families represented by the test species have a number of significant ecological and morphological differences. The representatives of

Fig. 1. Sketch map of monitoring plot locations.

the family Poaceae are characterized by a small number of long thin laminae and a strongly branched fibrous root system, while the species of the family Asteraceae are characterized by the presence of numerous and often broad leaves and a taproot system. It has been established (Poznyak, 2011) that most plants of the family Asteraceae (wormwood, wild marigold, and milk-witch gowan) can accumulate an increased amount of HMs (unlike the family Poaceae (awnless brome)) and are characterized by a wide range of vegetation. Pb, Cd, Zn, Cu, Ni, Mn, and Cr, which are found in NPP emissions, were determined in plant and soil samples (Ekologicheskii Vestnik …, 2017; Minkina et al., 2013). The metal content in plants was determined by the dry-ashing method (*GOST*..., 1985), followed by acid extraction of HMs from the ash with 20% HCl and identification on an atomic adsorption spectrophotometer (AAS; *Metodicheskie ukazaniya*…, 1992).

The total metal content in the studied soils was determined by the roentgen-fluorescence method. To estimate the HM compounds available to plants in the soil, we calculated the content of their loosely bound compounds as the sum of exchangeable, complex, and specifically sorbed metal forms (Minkina et al., 2016). A close correlation was previously established between the content of loosely bound HM compounds in the soils and their content in barley grain and stems and in herbaceous vegetation (Motuzova et al., 2014). The exchangeable, complex, and specifically sorbed forms were analyzed with 1 N ammonium–acetate buffer (NH₄Ac) (pH 4.8), 1% solution of EDTA in NH₄A with pH 4.8, and 1 N HCl, respectively. The methods of their application, including calculation methods, are described in detail in the works of Minkina et al. (2013, 2016).

All studies were performed in three replications.

The pollution of the studied plants was evaluated by a comparison of the concentration of elements in the plants with the maximum permissible level (MPL) of the content of metals in farm animal forage (*Vremennye*…, 1991).

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 (Brooks, 1996; Minkina et al., 2008). Loosely bound HM compounds in soils were used as mobile compounds.

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 is determined as the ratio of the metal content in the aboveground biomass to its concentration in the roots. A similar coefficient was used by Sabinin (1955), Fortescue (1985), Chernykh et al. (2001), and Avessalomova (2007) in their studies. The DC values are often the same for the plants of the same species; a change in the value indicates that the plant experiences ecological stress (Chernykh et al., 2001).

RESULTS AND DISCUSSION

It is known (Muratchaeva et al., 2015) that the effect of anthropogenic factors leads to depletion of the floristic composition, as well as to structural simplification, a decrease in species diversity, the disappearance and replacement of valuable species with high fodder properties by poorly consumed ruderal and weed species, and a decrease in the productivity

Fig. 2. HM content in aboveground parts and roots of two Poaceae species and two Asteraceae species, mg/kg (generalized results for all studied monitoring plots).

and resistance of natural herbaceous vegetation. The data from observations at the monitoring plots showed that the total projective cover is 75–90%, irrespective of the distance to the enterprise (the source of pollution). The height of the grass stand varies from 20 to 70 cm, increasing with distance from the source of technogenic load. The share of plant species of the family Poaceae in the grass stand was 10 to 35% and the share of plant species of the family Asteraceae was 30 to 69%.

The study of the HM content revealed significant differences in element accumulation (Table 2). For all species of the studied plants, the HM concentration increases with proximity to the Novocherkassk Power Plant. The highest accumulation of metals in the monitoring plots within the 5-km zone around the NPP is recorded in the aboveground part of the studied plants and their roots. The highest concentration of HMs in plants was revealed in plots nos. 4 and 5.

In *Elytrigia repens*, Pb, Ni, and Cd exceeded the MPL by 2.9, 3.7, and 3 times, respectively; in *Artemisia austriaca*, they exceeded the MPL by 4.2, 2.6, and 3 times, respectively; and in *Achillea nobilis*, the con-

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tent of these elements exceeded the MPL by 1.9, 2.6, and 6.3 times, respectively. The content of these metals in the aboveground part of *Poa pratensis* L. does not exceed the MPL.

The metals are in the following sequence with respect to their absolute content in the aboveground part of plants (Fig. 2):

Cr: *Artemisia austriaca* > *Elytrigia repens* > *Achillea nobilis* > *Poa pratensis*;

Pb: *Artemisia austriaca* > *Elytrigia repens* > *Achillea nobilis* > *Poa pratensis*;

Zn: *Artemisia austriaca* > *Achillea nobilis* > *Elytrigia repens* > *Poa pratensis*;

Mn: *Artemisia austriaca* > *Achillea nobilis* >*Elytrigia repens* > *Poa pratensis*;

Ni: *Elytrigia repens* > *Achillea nobilis* > *Artemisia austriaca* > *Poa pratensis*;

Cd: *Achillea nobilis* > *Elytrigia repens* > *Artemisia austriaca* > *Poa pratensis*;

Cu: *Achillea nobilis* > *Poa pratensis* > *Artemisia austriaca* > *Elytrigia repens*.

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Fig. 3. HM content in aboveground parts and roots of Poaceae and Asteraceae plants, mg/kg (generalized results for all studied monitoring plots and for species belonging to the same families).

The species of the family Poaceae had a lower HM content than the species of Asteraceae (Fig. 3). The lowest content of all studied metals, except Cu, is recorded in the aboveground part of *Poa pratensis*.

Under the conditions of maximum technogenic load, the metals were distributed with respect to the values of the absolute content in the aboveground part of Asteraceae plants (Table 2) as follows:

• *Artemisia austriaca*: Mn > Zn > Cr > Pb > Cu > $Ni > Cd$:

• *Achillea nobilis*: $Mn > Zn > Cu > Cr > Pb >$ $Ni > Cd.$

The metal content in the roots of the plants under the conditions of maximum technogenic load differs from the content in the aboveground parts (Table 2). For the species of the family *Asteraceae*, this is expressed as follows:

• *Artemisia austriaca*: Cr > Zn > Mn > Pb > Cu > $Ni > Cd;$

• *Achillea nobilis*: $Mn > Zn > Cr > Cu > Ni > Pb > Cd$.

The plants of the family Poaceae have the following sequence:

• *Poa pratensis*: Cu > Cr > Mn > Zn > Pb > Ni > Cd;

• *Elytrigia repens*: Mn > Zn > Cr > Pb > Ni > $Cu > Cd.$

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The roots have a somewhat different accumulation series:

• *Poa pratensis*: Mn > Zn > Cu > Cr > Pb > Ni > Cd;

• *Elytrigia repens*: Zn > Mn > Cr > Ni > Pb > $Cu > Cd.$

Therefore, based on long-term monitoring data, we revealed that different species of herbaceous plants that grow under steppe climate conditions accumulate different HM amounts in their aboveground part and roots, which can be determined by what family they belong to or observed within the same family (Figs. 2, 3).

The species of the family Poaceae are characterized by the dominant accumulation of the studied elements in their roots (Table 2, Fig. 3). The DC values indicate a selectivity and low capacity of their aboveground part to absorb HMs under pollution conditions (Fig. 4). The DC value of *Poa pratensis* is the lowest among the studied plants and does not exceed 1.

In plant species of the family Asteraceae, HMs accumulate mainly in the aboveground part. A certain influence on the features of metal distribution in the aboveground part and roots is probably made by the morphology of plants. For instance, representatives of the family Asteraceae are distinguished by a tall thick stem and a taproot system; their leaves are arranged in

Fig. 4. HM distribution coefficients (DCs) in Poaceae and Asteraceae plants (generalized results for all studied monitoring plots).

several layers and have a larger size than those of the species of Poaceae. The large total area of leaves contributes to the settlement of a greater amount of HMs on them, while the root, which runs vertically into the soil column, has a lower rhizosphere area, which decreases the entry of pollutants from the soil. Since the entry of HMs into plants is influenced by biological factors, the estimate of HM accumulation by different plant species requires an integrated approach that takes into account the features of plant species.

We recorded an increase in the total HM content in the soils of the monitoring plots adjacent to the NPP (Table 3).

The plots that are 5 km northwestwards from the NPP, as well as other adjacent plots, have an excess in the total Pb content in soils over the MPC. The highest content of all studied HMs in soils is revealed within 5 km of the NPP, with the maximum accumulation being recorded in monitoring plots nos. 5 and 6. According to the study of Evdoki-

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Fig. 5. Dependence of HM accumulation by plants on content of their loosely bound compounds in soil.

mova et al. (2014) on the effect of air emissions of the Pechenganikel plant, the acute pollution area was within a 3 km radius of the enterprise.

In plots nos. 9 and 10, which are the most distant from NPP, the total metal content in soils corresponds to the background level, except Pb in plot no. 10, the content of which in the soil and plants exceeded the MPC. This is probably due to its proximity to the highway and the use of previously ethylated gasoline.

HM accumulation differs in different soil types: the total metal content is higher in the Haplic Chernozem (Stagnic) of monitoring plot no. 3 than in the Calcaric

Fig. 6. HM accumulation coefficient (AC) in aboveground parts of plants (generalized results for all studied plots): (a) two species of Poaceae and two species of Asteraceae; (b) families Poaceae and Asteraceae (generalized results for species belonging to the same families).

Fluvic Arenosol of plot no. 2, which is located at a distance of 200 m from plot no. 3 (Table 3). This is due to the higher content of humus, physical clay, and silt particles and a higher cation exchange capacity (CEC) in the Haplic Chernozem (Stagnic) (Table 1).

Without an anthropogenic load, loosely bound HM compounds are 10–20% of the total content in soils (Table 3). The share of loosely bound HM compounds significantly increases with decreased distance to the main source of emission (power plant) (Table 3) and reaches 28–52% of the total content. We found a close relationship between the HM content in herbaceous plants and the content of their loosely bound compounds in the soil: $r = 0.60 - 0.93(t_r > t_{0.5})$. The highest *r* values are characteristic of Pb, Cd, and Cr (Fig. 5).

The accumulation coefficient (AC) calculated for different plant species made it possible to estimate the intensity of the HM penetration from the soil into these plants. All of the studied species of steppe plants (except *Poa pratensis*) actively absorb Cd from soil and accumulate it in their aboveground part, while the rate of Mn absorption and accumulation is the lowest (Fig. 6a). The AC values are higher for the Asteraceae plants than for those of Poaceae (Fig. 6b).

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The AC values for all of the studied HMs were higher in the plots that were distant from NPP than in the adjacent plots (Fig. 7).

CONCLUSIONS

(1) The HM concentration is lower in the aboveground part of species of Poaceae than in Asteraceae. Among the species of the family Asteraceae, *Artemisia austriaca* accumulates the highest amount of Mn, Cr, Pb, and Zn, while *Achillea nobilis* accumulates the highest amount of Cd and Cu. The plants of *Poa pratensis* of the family Poaceae are characterized by the lowest level of metal accumulation among all the test species.

(2) For all of the studied test species, the HM concentration increases with decreasing distance to the power plant. The highest HM content (with Pb, Ni, and Cd, exceeding the MPL for forage) is recorded in herbaceous plants of plots that are northwestwards from the source of technogenic pollution (the NPP) within 5 km of the enterprise. The effect of emissions from the NPP led not only to HM accumulation in plants but also to an increase in the total content and amount of loosely bound HM compounds in the soils of the monitoring plots. A medium and close relation-

Fig. 7. HM accumulation coefficient (AC) in different species of Poaceae and Asteraceae in monitoring plots located at different distances from NPP in the northwest direction.

ship was established between the HM content in all test species and the content of their loosely bound compounds in soil: $r = 0.60 - 0.93$.

(3) The soil properties (content of humus, physical clay, silt, and cation exchange capacity) influence metal accumulation. The total content is higher in the haplic chernozem (stagnic) than in the calcaric fluvic arenosol.

(4) The test species of the family Poaceae accumulate lower HM concentrations in their aboveground

part than the representatives of the family Asteraceae. Among the plants of the family Asteraceae, *Artemisia austriaca* accumulates the highest amount of Mn, Cr, Pb, and Zn, while *Achillea nobilis* accumulates the highest amount of Cd and Cu. *Poa pratensis* L. is characterized by the lowest metal content among all of the studied plant species.

(5) The biological features of the test species influence not only HM accumulation but also their distribution in different plant parts. The greater area of the leaf surface determines the dominant HM accumulation in the aboveground part of Asteraceae plant species as compared to Poaceae species under aerotechnogenic pollution conditions. The distribution coefficient (DC) values are significantly higher among the Poaceae plant species (by almost three times) than among the Asteraceae species.

(6) The lowest capacity of the aboveground part of plants to accumulate HMs from the soil (AC) is characteristic of representatives of the family Poaceae as compared to plants of the family Asteraceae. Of the studied species, *Poa pratensis* is characterized by the lowest AC values for Mn, Zn, Pb, Ni, and Cd, while *Elytrigia repens* has the lowest AC values for Cu.

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