Heavy metals in soil and plants (Agropyron pectiniforme Roem. Et Schult.) of the Pavlodar region (Kazakhstan)

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Abstract. The paper presents the key results of a study on the content of heavy metals (Ti, Mn, Cr, Fe, Ni, Cu, Zn, Pb, Sr) in soil and plant (Agropyron pectiniforme Roem. et Schult.) samples, which are taken in the zone of influence of enterprises of the northern and eastern industrial zones of Pavlodar (Kazakhstan) as part of a study of the state of vegetation in the same territory.

1. Introduction

The city of Pavlodar City (Republic of Kazakhstan) is a large industrial center, forming the territorial industrial complex “Pavlodar-Aksu-Ekibastuz,” which activities are very important for the development of the economy of Kazakhstan. So, among the leading enterprises of the considered region are the Pavlodar Aluminum Plant, Pavlodar Oil Chemistry Refinery (POCR LLP), Kazakhstan Electrolysis Plant (KEP JSC), HES-1, 2, 3, Aksu Ferroalloy Plant, Aksukaya Electric Generation Plant, and many other. The total number of such large enterprises is about 40. According to the development plans of the republic, the number of enterprises will increase. At the same time, the environmental situation is complex, since industrial enterprises in the region have been continuously operating for 60 years; therefore, there is pollution caused by the long periods of activity of enterprises, due to a significant number of enterprises and their emissions and discharges of pollutants.

As a result, a significant amount of emissions containing heavy metals (taking into account the specifics of existing enterprises) enters the environment of the region. The existing environmental situation is well reflected by the distribution of pollutants in the soil cover. At the same time, the rate of movement of the substance in the soil is much lower than in other environments; therefore, the composition of the soil shows not only the current (up to 5 cm in the soil layer), but also long-term pollution processes (in the deeper layers) due to the continuous operation of industrial enterprises. Vegetation, being the most “noticeable” component in the composition of ecosystems, as well as soil, accumulating emissions from industrial enterprises and acting as a buffer and detoxifier, is capable of changing the species composition of the community and/or the state of individual plants to “demonstrate” the presence of anthropogenic impact, fulfilling the role indicator [1]. Therefore, we present the results of a study of the accumulation of some heavy metals in the soils and vegetation of the territory located near the existing enterprises of the northern (HES-2,3, POCR LLP, Kazakhstan Metallurgical Company “Casting” JSC, and others) and eastern (Aluminum of Kazakhstan JSC, HES-1, KEP JSC, and others) industrial zones of Pavlodar, Kazakhstan.
2. Materials and Methods
The object of research was the vegetation cover of the region. The study of the state of cover was carried out in dissertation research in 2006-2009, and further as part of the development of the initiative-search topic, particularly in 2011-2013, 2015-2016. The soil and plant samples for chemical analyzes were taken in 2006, 2011, 2013, 2015-2016 at various distances from the industrial areas of Pavlodar and Aksu [2-5], according to standard guidelines [6], [7].

More than 50 sites were surveyed, they were located at different distances from the leading industrial enterprises of the region. Sampling sites are confined to the predominant plant communities in which detailed geobotanical descriptions were periodically conducted, including assessing the floristic composition, vertical and horizontal structure of communities, the ecological and biomorphological characteristics of individual species (using classical methods adopted during geobotanical studies) [8].

The determination of the content of elements in soil and plants was carried out via the X-ray fluorescence analysis (annealed for soil; with a preliminary ash content for plants) and using a Spectroscan GF-1E spectrometer (Russia, 2000 g/v). The samples were analyzed in the laboratory of the Physical Technical Institute of the Ministry of Education and Science of the Republic of Kazakhstan (Alatau village, Almaty region, Kazakhstan). Comparison of the maximum permissible concentrations of elements with the concentration detected in the soil was established according to the standards of the maximum permissible concentration [9-11], the concentrations of Fe were compared with the background content.

To assess the pollution of the territory, we selected the underground and ground parts of the comb-wheatgrass (*Agropyron pectiniforme Roem. et Schult*). This cespitose grass is found in varying degrees of abundance in most of the study area, often as a dominant in the community, because it is digression-active.

3. Results
Soil samples taken at 23 sites were analyzed. These samples were located at different distances, 0.5-1-3.5-15-20 km to the north, south, east, and west of the enterprises of the northern and eastern industrial zones of Pavlodar, taking into account the rose winds and transport and walking accessibility).

Table 1 shows the maximum levels of heavy metals (Ti, Mn, Cr, Fe, Ni, Cu, Zn, Pb, Sr) from soil samples collected in these areas:

| Soil layer | Ti (mg/kg) | Cr (mg/kg) | Mn (mg/kg) | Fe (mg/kg) | Ni (mg/kg) | Cu (mg/kg) | Zn (mg/kg) | Pb (mg/kg) | Sr (mg/kg) |
|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|
| NIZ 0-5    | 1 4150     | 142        | 735        | 27578      | 34         | 22         | 97         | 27         | 265        |
|            | 2 0.83     | 2.84       | 0.49       | 1.38       | 0.76       | 0.55       | 0.97       | 1.35       | 0.53       |
| 10-15      | 1 3400     | 104        | 675        | 27494      | 35         | 22         | 73         | 20         | 260        |
|            | 2 0.68     | 2.08       | 0.45       | 1.53       | 0.78       | 0.55       | 0.73       | 1          | 0.52       |
| EIZ 0-5    | 1 4150     | 112        | 1005       | 31119      | 32         | 29         | 87         | 46         | 285        |
|            | 2 0.83     | 2.24       | 0.67       | 1.56       | 0.71       | 0.73       | 0.87       | 2.3        | 0.57       |
| 10-15      | 1 4500     | 113        | 885        | 27674      | 34         | 29         | 72         | 44         | 270        |
|            | 2 0.9      | 2.26       | 0.59       | 1.54       | 0.76       | 0.73       | 0.72       | 2.2        | 0.54       |

MPC (in mg/kg)

| Ti (mg/kg) | Cr (mg/kg) | Mn (mg/kg) | Fe (mg/kg) | Ni (mg/kg) | Cu (mg/kg) | Zn (mg/kg) | Pb (mg/kg) | Sr (mg/kg) |
|------------|------------|------------|------------|------------|------------|------------|------------|------------|
| 5000       | 50         | 150        | 19948      | 45         | 40         | 100        | 20         | 500        |

Legend: NIZ – a northern industrial zone (data of soil samples from the impact areas of HES-2-3, POCR, and others); EIZ – an eastern industrial zone (HES-1, Aluminum of Kazakhstan JSC, Kazakhstan Electrolysis Plant JSC, and others); 1 – concentration of elements in the soil (mg/kg), 2 – concentration of elements in fractions of maximum permissible concentration; highlighted – the highest values of each element; * – a background content Fe, mg/kg.
The results of analyzes of soil samples in the table indicate fairly high concentrations of almost all the elements considered. Vegetable samples were collected at the same sites as soil samples. The maximum concentrations (in mg/kg) of Ti, Cr, Mn, Fe, Ni, Cu, Zn, Pb, and Sr in the underground and above-ground parts of the comb-wheatgrass in Table 2.

All the considered elements accumulate more in the underground than in the above-ground parts Agropiron pectineforme (except for a few samples).

Table 2. The maximum content of heavy metals in Agropiron pectineforme (mg/kg).

| Parts of a plant | Ti  | Cr  | Mn  | Fe  | Ni  | Cu  | Zn  | Pb  | Sr  |
|------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| NIZ Below ground | 1   | 1867| 850 | 417 | 13200| 31.7| 7.1 | 778 | 100 |
|                  | 2   | 2.7 | 170 | 1.95| 1.7  | 3.6 | 1.82 | 17.3| 12.2 |
|                  | 1   | 748 | 12.5| 121 | 646.5| 2.0 | 1.3 | 120 | 5.65 |
|                  | 2   | 34  | 2.1 | 1.6 | 2.5  | 2.5 | 2.2 | -   | 20.2 |
| Above ground     | 1   | 1449| 148 | 509 | 10352| 13.9| 5.6 | 92  | 13.9 |
|                  | 2   | 21.4| 23.8| 2.8 | 3628 | 43  | 4.8 | 22  | 4.8  |
| EIZ Below ground | 1   | 470 | 143 | 205 | 353  | 36.2| 8   | -   | 8    |
|                  | 2   | 21.4| 23.8| 2.8 | 53.8 | 8   | -   | 8   | 7.7  |
| Above ground     | 1   | 691 | 5.0 | 213 | 7615 | 8.7 | 3.9 | 45  | 8.2  |
|                  | 2   | 6.0 | 74  | 257 | 0.6  | <LLQ| 0.6 | 14  |      |

Legend: background – 50 km east of Pavlodar; LLQ – a lower limit of quantification; 1 – a maximum content of heavy metals in Agropiron pectineforme (mg/kg), 2 – a share of the background content of the element in plant samples.

4. Discussion

The data of the analytical survey of the soil both in the zone of impact of enterprises in the eastern and northern industrial zones of Pavlodar indicate a significant excess of the maximum allowable concentration of Chrome (Cr), Plumb (Pb) and background values by Ferrum (Fe), Titanium (Ti), Zinetum (Zn), and Niccolum (Ni) content in soil reaches its maximum permissible concentration; slightly more than 0.5 of the maximum permissible concentration content: Manganese (Mn), Cuprum (Cu), and Strontium (Sr).

Significant concentrations in soil samples of Cr and Fe are provided by the activity of the Ferroalloy Plant (Transnational Company Kazchrome JSC), and the remaining elements considered by the cumulative impact of industrial enterprises in the region, since their number and similar composition (for example, for HES) do not clearly define sources, but provide a summation of the pollution fields.

When analyzing the content of metals in the pyrex with a comb-like, it was revealed that this species is characterized by accumulation of heavy metals by an acropetal type “roots>” above the ground parts of plants. It is the territory of influence of the enterprises of the eastern and northern industrial zones of the city of Pavlodar.

The maximum concentrations of Plumb (Pb) and Zinetum (Zn) elements of the first class of danger (hazard class of danger are designated according to M. S. Panin [1]), in the above ground parts of plants registered 1 km north of the HES-2, it is 0.8 km north-east from the HES-2, Pavlodar, for the below ground parts.

Elements of the second class of danger, maximum concentrations of Niccolum (Ni), Cuprum (Cu), and Chrome (Cr) in above ground parts of Agropiron pectineforme were found at a site located 20 km west from the Aluminum of Kazakhstan JSC (12 km north from Transnational Company Kazchrome JSC); Niccolum (Ni) in the below ground parts – 2 km north from the HES-3; in 0.5 km north-east from the HES-3 Cuprum (Cu) was found; and 0.8 km north-east from the HES-2 – Chrome (Cr).

Elements of the third class of danger, maximum concentrations of Manganese (Mn) (completely) and Strontium (Sr) (in the above ground part) in Agropiron pectineforme were observed at a distance of 20 km west from the Aluminum of Kazakhstan JSC (12 km north from the Transnational Company.
Kazchrome JSC); Strontium (Sr) in the below ground part was found 0.5 km north-west of the HES-3, Pavlodar.

The maximum content of Ferrum (Fe) in the below ground parts A. pectineforme was noted 1 km north from the HES-2; Fe in the above-ground parts and Titanium (Ti) completely were also noted at a site 20 km west of the Aluminum of Kazakhstan JSC (12 km north of Transnational Company Kazchrome JSC).

5. Conclusion
High concentrations of the considered elements are found in soil samples collected at a distance of 0.5-1 km from the HES-1 (eastern industrial zone) and HES-2 (northern industrial zone) of Pavlodar, as well as in the territory between the city of Pavlodar and Aksu (a site, located 20 km west of Aluminum of Kazakhstan JSC (12 km north of Transnational Company Kazchrome JSC)).

For Agropiron pectineforme samples, the same pattern was found. A correlation between the increased content of heavy metals in the soil and plant samples of the studied areas was also noted, i.e. the transfer of pollutants from the soil to the plant organism is possible. The fact that the metals in question are obtained from soil by plants is indicated by a significant amount of them in the roots, and much less in its above-ground parts (the aeration mechanism of the intake of pollutants is more developed in broadleaf).

Soil and plant pollution is mainly due to the proximity of sites to industrial enterprises (based on the location of sampling sites, this distance is 0.5-0.8-1 km), as well as the sum of emissions coming from enterprises of industrial zones of Pavlodar (eastern and northern) and the city of Aksu in the environment of the region.

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References
[1] Panin M S 2002 Chemical ecology (Semipalatinsk, Republic of Kazakhstan: Shakarim State University of Semey)
[2] Kanibolotskaya Yu M 2012 Analysis of heavy metal content in plants (Artemisia austriaca Jacq., Agropyron pectinatum, Potentilla bifurca) and soil in Pavlodar region Mongolian Journal of Agricultural Sciences 6(02) pp 101-109
[3] Kozyrenko M, and Kanibolotskaya Yu M 2012 Heavy metals in soil and plants. In Proceedings of the international scientific conference of young scientists, undergraduates, students and schoolchildren: XIV Satpayev's readings (pp. 182-185) (Pavlodar, Republic of Kazakhstan)
[4] Kurmanbaeva A, and Kanibolotskaya Yu M 2014 The main factors influencing the plant communities of the suburb of Pavlodar. In Proceedings of the international scientific conference of young scientists, undergraduates, students and schoolchildren: XIV Satpayev's readings (pp. 191-194) (Pavlodar, Republic of Kazakhstan)
[5] Berikova A T, and Kanibolotskaya Yu M 2017 Anthropogenic transformation of vegetation cover in the impact zone of the Eurasian Energy Corporation JSC and Transnational company Kazchrome JSC. In Proceedings of the IX International Conference Torajgyrovskiye Readings (pp. 75-78) (Pavlodar, Republic of Kazakhstan: Pavlodar State University named after S. Torajgyrov)
[6] Ussr State Committee on Hydrometeorology 1981 Methodical recommendations on carrying out field and laboratory researches of soils at control of environmental pollution by metals (Moscow, USSR: Hydrometeoizdat)
[7] Belyakova E E, Vasilev N N, Grabovskaya L I et al. 1972 Biogeochemical and geobotanical studies (Leningrad, USSR: Nedra)
[8] Lavrenko E M, and Korchagin A A Eds. 1959-1972 Field geobotany (in 4 vol) (Moscow, USSR: Publishing House of the USSR Academy of Sciences)
[9] Kloke A Richwerte 1980 Orientierungssdaten fur tolerierbare Gesamtgehalte einger Elemente in Kulturboden Mitteilunger VDLUFA 1-3 pp 9-12
[10]  Cabinet of Ministers of the Republic of Kazakhstan 1993 *Scientific and methodological instructions for monitoring the lands of the Republic of Kazakhstan* (Almaty, Republic of Kazakhstan)

[11]  Chief State Sanitary Doctor of the USSR 1983 *Sanitary norms of permissible concentrations of chemicals in the soil* SaNiP (May 13, 1983 No. 2546-82)