Heavy metal composition in the *Plantago major* L. from center of the Murmansk City, Kola Peninsula, Russia

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ABSTRACT

*Plantago major* is an indicator of environmental pollution in the city. The plant grows along the traversed paths, close to the sidewalks. Contaminating substances accumulate on the leaves of the plantain. In the summer of 2016, samples of plants were collected in the central Murmansk region for analysis using a scanning electron microscope to identify dust particles on their surface, and to study leaves using the ICP-MS method to determine the heavy metals content. A relatively serious concentration of lead, zinc, copper, nickel as well as high arsenic and chromium content has been demonstrated in the city center, along with ties with human activities (vehicular traffic). High iron content is associated with peat soils used in the city for fertilization. The remaining metal content is relatively low.

Keywords: *Plantago major*; Pollution; Environment; Geochemistry.

1. INTRODUCTION

The city of Murmansk is located on the Kola Peninsula, being the capital of the region and the district (oblast) [1]. It is a center of scientific, cultural and industrial character. It is an important inter-regional and international communication hub. The city has the northernmost port, not frozen in winter. It is used for communication between northern Russia and the rest of Europe, America and through the northern route with Asia [1-3]. A road connecting Russia with Finland and Norway runs through Murmansk. The transport of fertilizers, coal, ores as well as numerous goods including food is transported through the seaport and further by the
railway or road line. Through the railway line running each day, wagons with fuel from refineries to military ports. There are also several combined heat and power plants in the city. The city is located in the close vicinity of Kola Gulf, extending to the nearby hills, where there is a beautiful, scenic view of the area (Fig. 1). Plant vegetation period is relatively short (from May to the end of October) [4-6].

Due to its nature, the city of Murmansk faces many problems resulting from human activities [7-11]. The big transshipment port located in the city may be a potential source of pollution, as are transit and transit roads passing through the city [12-17]. Urban means of transport require urgent attention, they are modernized in some way, although it still requires many amendments. There is a large infrastructure in the city, however, due to severe climatic conditions it undergoes rapid corrosion, leaving its geochemical trace in the ground [12]. This is also manifested in the form of particulate matter which settles and contributes to geochemical changes [10, 13, 18-21]. Plaster tests carried out in 2015-2017 have shown a lot of pollution originating from the corrosion of city infrastructure, suspended dust and road transport [22-23]. The crystal substrate of Archean granite-gneisses (contents a several ore minerals) may also have some impact on the pollutants (in weathering processes).

2. METHODS

The fieldwork was carried out in the 2010-2016 period [7, 22-24]. It was make an inventory of Plantago major location, photographic documentation and leaf samples from 28 locations were taken (Table 1). In the next stage, these samples were brought to the Department of Geology and Protection of the Lithosphere at the Maria Curie-Sklodowska University (UMCS), where after drying they were subjected to observations using a binocular loupes as well as the Leica DM2500P optical polarization microscope. Subsequently, these samples were subjected to tests using a scanning electron microscope Hitachi SU6600 with the use of which micrographs of backscattered electrons and micro-area studies were performed. Then the samples were analyzed in order to determine the content of selected metals in the analyzed samples a high resolution absorption spectrometer (ICP-MS) was used in the Department of Hydrology UMCS. Samples of Plantago major leaves have been subjected to analyzes, which were previously dried, milled and dissolved using royal water (nitrohydrochloric acid). In the first stage of the study calibration curves for metal ions was prepared determining and tested samples. Absorbance was measured parameter. Its quantity value changed during the measurement, a signal as a peak. Result analyses were held in a specialized program Cs Aspect, wherein the measured absorbance values were read out as the concentration [mg/l], in relation to a calibration curve. The results are shown as the arithmetic mean of obtained values. The results were developed mathematically using Microsoft Excel and Surfer®.

3. RESULTS

This plant (Plantago major L.) is characteristic of habitats associated with significant anthropopressure. The plant grows usually on lawns, squares and places with increased pedestrian traffic. Analyzes of the area of research as well as adjacent areas indicate that plant does not occur in the natural environment of the region and has been dragged by a human [25]. The plant practically does not occur in Murmansk near urban green areas. As a perennial plant, each year Plantago produces fresh shoots for
flowering and seed formation. During the growing season, it is exposed to various factors related to human activity. It absorbs various substances which, in the form of solid, liquid or gas, get to the surface and into the plant through the root system as well as from the ground part. Particular attention should be paid to relatively large leaves that collect various substances on their surface. They collect dust and other persistent pollutants that are related to human activity. Therefore, grandmother is an indicator of environmental pollution in the place where it grows.

The analysis of dust collected on the surface of the plantain leaves is illustrated below (Fig. 2), where the metallic admixtures found on the surface of *Plantago major* leaves are marked in red.

Studies in the micro-area of dust collected on *Plantago major* leaves collected in Murmansk showed the occurrence of oxides of metals such as titanium, iron, lead, copper (Fig. 3, Table 2). The presence of sulphides, sulfates of phosphorus compounds and halides as well as soot were also found. These results are described below.

In the case of titanium, its content was found in three samples (03 Mu, 10 Mu and 21 Mu, Table 1), of which the highest (4.54 wt.%) was measured in a sample of 10 Mu. Iron compounds (oxides and hydroxides) were found in 11 samples in quantities of 25 to 57% by weight. The highest values were recorded for samples 23 Mu, 24 Mu, 21 Mu, 18 Mu and 03 Mu respectively: 57.78; 57.14; 52.82; 49.98 and 48.35 [wt.%]. In addition, in the sample of 03 Mu and 23 Mu iron sulphide (pyrite) was also found. Lead oxides were found in four samples of 15 Mu, 06 Mu, 18 Mu and 04 Mu with values of 73.06 respectively; 67.41; 18.93; 11.26 [wt.%]. Malachite was found in a sample of 23 Mu. In addition, in the samples 08 Mu, 15 Mu, 09 Mu and 18 Mu, sulphate (gypsum) was found. Chlorine compounds were found in samples 18 Mu, 20 Mu and 08 Mu. In the sample 4.46 [wt.%] Content of phosphorus was found in the samples 08 Mu, 10 Mu, 24 Mu, 11 Mu, 18 Mu, 03 Mu, 26 Mu and 21 Mu there was a significant accumulation of carbon (soot) with a quantity of 40.79; 33.38; 31.34; 26.17; 24.84; 24.21; 23.05; 22.88 [wt.%].

ICP-MS examinations carried out on *Plantago major* leaves showed the presence of a number of elements. The following elements were analyzed: Li, Be, B, Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Ag, Cd, Cs, Ba, La, Hg, Tl, Pb, Th, U (Fig. 4, Table 3). All contents of the examined elements are given in ppm.
In the case of lithium, its highest content was found in the samples Mu 21, Mu 25 (Fig. 2, Table 1), respectively 11.83 and 11.04, and the lowest in the sample 0.138 Mu 27. The most beryllium was measured in the samples 01 Mu and 02 Mu, respectively: 0.369 and 0.204, the lowest 0.006 in the sample 20 Mu. The highest content of boron was found in samples 28 Mu and 23 Mu respectively: 901.4 and 607.2, lowest 50.64 in the sample 06 Mu. In the case of aluminum, the highest content of this element was found in the samples 21 Mu and 28 Mu respectively: 493.75 and 193.25, lowest 43.9 in the sample 01 Mu. Vanadium in the largest amounts was measured in samples 21 Mu and 20 Mu respectively: 27.95 and 13.62, lowest 1.139 in the sample 11 Mu. In the case of manganese, the most element was found in samples 10 Mu and 08 Mu, respectively: 1139 and 882.9, least 85.62 in the sample 18 Mu. The highest concentration of iron was measured in samples 28 Mu and 21 Mu respectively: 1217 and 1190, lowest 87.17 in the sample 27 Mu. Most gadolinium was in the samples 10 Mu, 26 Mu and 28 Mu respectively: 6.893, 6.865 and 6.219, the least 2.325 in the sample 06 Mu. Rubidium was shown in the highest content in samples 14 Mu and 09 Mu respectively: 1340 and 418.7, lowest 10.67 in the sample 06 Mu. In the case of strontium, the most of this element was determined in the samples 26 Mu and 28 Mu, respectively: 3432 and 1408, the least 155.7 in the sample 20 Mu. The concentration of cesium is highest in the samples 14 Mu and 23 Mu respectively: 1,396 and 1,247, the lowest 0.001 in the sample 20 Mu. The most bar was found in 10 Mu and 26 Mu samples respectively: 475.4 and 426, and at least 140.3 in a sample of 20 Mu. In the case of lanthanum, the highest content of this element was found in the samples 06 Mu and 03 Mu, respectively: 0.532 and 0.275, the lowest 0.029 in the sample 11 Mu. Tal at the highest concentrations was tested in samples 14 Mu and 01 Mu, respectively: 0.533 and 0.236, the lowest 0.022 in the 18 Mu sample. In the case of thorium the highest...
concentrations were determined in the samples 01 Mu and 02 Mu, respectively: 1.535 and 0.936, the lowest 0.086 in the sample 20 Mu. The highest uranium values were found in samples 01 Mu and 02 Mu respectively: 0.154 and 0.153, lowest 0.06 in the sample 05 Mu.

In the case of a total content of heavy metals (Cr, Co, Ni, Cu, Zn, As, Ag, Cd, Hg, Pb), the highest contents were found in the 21 Mu (1446 ppm) 19 Mu sample (1050 ppm) and 28 Mu samples (836 ppm) and 07 Mu (816 ppm), 25 Mu (815 ppm) and also in samples of 11 Mu (595 ppm), 02 Mu (592 ppm) and 23 Mu (507 ppm). The lowest values of these metals were found in the samples 13Mu (119 ppm) and 06 Mu (146 ppm), as well as 12Mu (191 ppm), 27 Mu (2019 ppm), 24 Mu (234 ppm) and 01 Mu (246 ppm). In the remaining samples, these values are in the range of 256-498 ppm (Fig. 4).

Figure 4. Sum of element concentration in Murmansk Plantago major plants samples measured using ICP-MS.

Figure 5. Range of measuring element concentration in Murmansk Plantago major plants samples measured using ICP-MS.

In the case of the assessment of the content span of the elements, the greatest differences were found in the case of cesium reaching a multiplicity of 1396, although in this case the amount of this metal in the samples is still not large (1.396 ppm 0.001 ppm). Another case is a rubidium with a
multiplicity of 126 and a content of 10.67 to 1340 ppm. Among the heavy metals, the greatest multiplication is for lead in the amount of 86, for contents varying in the range: 1.137-98.18 ppm. In the case of this metal, it should be noted that its high content is a sign of significant environmental pollution.

Then, the following times were found: Li - 86, Be - 61, U - 26, V - 24, Tl - 24, Fe - 22 and Sr - 22. In the case of heavy metals after the above-mentioned lead it is respectively: Co - 21, Cd - 16, Ag - 15, Cu - 14, As - 13, Zn - 12, Ni - 12, Cr - 9 and Hg - 7. For other elements it varies from 18 for lanthanum to 3 for barium and gadolinium (Fig. 5). It is worth mentioning that in the case of Zn, Cu, Ni and Co the maximum values from 890 ppm (Zn) to 90 ppm (Co) significantly exceeding the norm, for As reach 7 ppm, for Cr 9 ppm which is also dangerous content, while for Cd and Hg these values they are no longer big and amount to 2 and 0.1 ppm, respectively.

Analyzing the spatial distribution of examined elements in plant samples (see atlas in graphical annex, Fig. 6), it can be stated that in the case of heavy metals the highest concentrations of lead are found in the northern part of the city near the port, in the case of zinc as well as cobalt and cadmium at its southern part in the area of Lenina and Polarnye Zori streets. For arsen, the highest contents were found in the south-west of the city for Papanina Street 11 and in the Chumbarova-Luchinskovo area. The content distribution for mercury is similar, while in the case of nickel the highest contents were found in the southern part of the city near Polarnye Zori street and the intersection of Liebknieht and Cheluskintsev streets and in the northern part of the city in the Chumbarova - Luchinskovo area. In the case of other elements, the location of the highest values is similar to the above-described heavy metals. In the reconciliation of Cheluskintsev and Polarnye Zoi and Lenin streets, the highest traffic volume takes place, similarly in the port areas where there are numerous industrial plants and ship repair and demolition zones (in the transshipment port there was no possibility of taking trials). The lowest metal content was found in the central-western part of the city near Liebkniehta 46, Papanina 11 and in the southern part of the city near Kirova 62a. These are locations away from heavy traffic and industrial zones where there are residential houses.

4. DISCUSSION

Murmansk is a specific city. It is the capital of the region with the largest concentration of people on this latitude. It is also an industrial center with an important port, where reloading of metal ores, coal, fertilizers, food and goods related to the development of technology takes place. The port's facilities are extensive, with numerous warehouse zones scattered in various parts of the city [22]. To this picture come issues of wheel and railway transport, areas of abandoned coasts with decaying ships and old buildings deteriorating in the city. The polar climate significantly shortens the time of vegetative and bacterial vegetation, preserves and slows the processes of soil bioregeneration. An additional factor is the relatively shallow substrate of crystalline rocks that are the carrier of non-ferrous metals and shielding the penetration of pollutants into the soil. These factors cause Murmansk to be in a more difficult position compared to other European cities [16, 26-28]. Until recently, the issue of nature conservation and ecology was not a priority in Murmansk, which is also clear today [4-6]. Screening tests of the substrate and the facade of the houses conducted jointly by the authors showed in Murmansk a significantly increased amount of lead reaching 3158 ppm in the area of Vodoprovodny Pereulok street, 17 ppm arsenic in the Siemionovski Lake region, zinc in the amount of 920 ppm in the Vorovskogo Street area, nickel in the area Siemionovski Lake 170 ppm, Chrome in the area of Askoldovec street 110 ppm, cadmium up to 60 ppm in the area of Cheluskintsev, Papanin, Liebkniht streets [22]. Such high levels of heavy metals in urban infrastructure facilities must also affect its accumulation in plants [4, 5, 7, 16, 26]. The examined Plantago major samples show a certain variability of the content of elements per balance both in the plants themselves and in the spatial distribution of the city [27, 29]. This is due to the properties of the substrate and the work carried out by man (various types of infrastructure, soil fertilization) as well as the property of the plant itself, which has a natural predisposition to absorb certain metals and geochemically elements determined with them.

It is known that the content of heavy metals in plant tissues depends on many external factors.
(soil acidity, humus and oxygen content, moisture content) and internal factors (life forms, physiological traits from species, age of plants) [30, 31]. In particular, birch has been shown to intensively accumulate zinc and copper, spruce-zinc and manganese as well as Siberian pine-lead [32]. In many respects, the content and mobility of heavy metals in soil depends on the parent rock [33]. The increased content of iron oxide in some samples is most likely caused by renovation and installation works in the summer (welding, metal cutting). The high content of cesium and rubidium is due to its chemical nature: these are alkali metals that form monovalent cations, like potassium ions. As it is known, potassium is a deficient element in the soils of the Kola Peninsula, which is why the plants created mechanisms that ensure sufficient absorption of these elements. The cesium content in the soil on which the grandmother samples tested grew, probably, was not high, and the absorption is very intense, so even a small increase in the alkali metal content in the soil causes a jump in their concentration in the leaves. Compared to the transition element ions, cesium and rubidium cations are less toxic, so their accumulation in large quantities does not lead to the death of the plant. Less pronounced variations in mercury content compared to other metals are explained, on the one hand, by the less frequent presence of this metal even in disturbed ecosystems. On the other hand, mercury cannot accumulate in significant amounts because it is so toxic that it kills even at low concentrations [34].

Plantago major is a plant that can grow in very different climate zones, so it can be studied and compared with each other. Examination of this plant gives good correlations between environmental pollution and the amount of metals in the leaves of this plant. This has been demonstrated in many works [26, 28], where in Plantago major the highest concentration was found for Zn and Pb from Albania, through the cities of Romania, Poland to the north. Plantago major showed the ability to absorb metals, and the concentration of metals in the leaves showed a good correlation with the concentration of metals in the soil. A comparison of this plant [4], with samples of Scots pine (Pinus silvestris L.) and toadstool caps (Amanita muscaria) showed that the highest concentrations of cadmium, lead and zinc were found in the leaves of broad-leaved plantain, broad-leaved plantain roots and toadstool mushrooms.

The high concentration of iron compounds in plant tissues, in our opinion, is associated more with natural factors than anthropogenic ones: peat soils in the Murmansk region are commonly used for gardening and urban greening, usually contain excess iron, both in the free state and in forms of chelating complexes. Significant lead content results from its high content in roadside soils. It is generally believed that the main source of lead in soil is road transport, since lead tetraethyl was previously used to increase the octane number of gasoline [35]. At present, the use of this carcinogenic organometallic substance has significantly decreased, but lead accumulated in previous years is poorly mobile in the soil and is very slowly washed away. Given the presence of iron chelating complexes, this process is slowing down even more [36].

Divalent cations of heavy metals are actively absorbed by plants "by mistake," because they are equal in their charge to calcium ions. Transshipment of coal and the work of coal-fired boiler plants makes a significant contribution to the replenishment of the soil pool of heavy metals including, lanthanum, cadmium, lead and many others. The significant content of lead, nickel, zinc and a number of other metals in the tissues of the creature can also be partially explained by the long-term transport of compounds of these elements in the composition of aerosol pollution from the metallurgical enterprises of the Monchegorsk and Pechenga regions. Comparison of heavy metals in different parts of the city reveals the highest concentrations in the streets adjacent to the port. In our opinion, the source of these compounds is coal dust, which spreads in accordance with the wind rose. In addition to carbon itself can contain arsenic, lead and other dangerous pollutants. Metal oxides, which are processed in large quantities in the installation of metal structures, have a larger particle, so they do not extend beyond the limits of the port. Pollution by coal dust is a relatively new phenomenon, therefore toxic substances are concentrated in the upper layers of the soil and do not yet have a disastrously harmful effect. Heavy metals in the soil are inactive, which further concentrates them in the upper layers of the soil, not allowing them to migrate downward. Separate sharply distinguished
values of heavy metals can be associated with the effect of random causes: improper disposal of batteries and household batteries, the use of paints, cement mixtures with a high content of heavy metals, etc. Halogenides of various metals in large quantities fall into the soil with reagents against icing of roads in winter [37, 38]. As a rule, metal anions are more mobile in the soil because soil colloids have a negative surface charge. After snowfall, it melts in spring, these ions move quickly to deeper layers of soil, they have a limited effect on plants such as Plantago major, which has a fibrous and surface root system. In general, it is obvious that Plantago major is very resistant to heavy metals and dust on the leaves. Nevertheless, as a result of the measurements, the ability to excessive accumulation of heavy metals, characteristic of some plant species that concentrate contamination a thousand times, has not been revealed [2]. Many members of the Brassicaceae Burnett family have such a clear ability to absorb heavy metal ions from the soil, it is possible to use them for phytoremediation of areas exposed to pollution [39, 40].

The results can be used to create ecological urban lawns, responsive to soil contamination and adapted to the relatively short vegetative period of plants in the polar zones of Murmansk. In many works it has been shown [16] that the study also pointed to the tolerance of plants to heavy metals, which indicates that Plantago major has the potential to be used in the phytostabilization process.

5. CONCLUSION

The Murmansk Plantago major L. plant samples may have grown after the snow in infiltration of contaminated meltwater, dust are deposited on the leaf surface (sulphides, gypsum and copper carbonates, lead oxides, titanium) in areas of human activity.

Studied plants have serious concentration of lead, zinc, copper, nickel as well as high arsenic and chromium content. Metals such as Cu, Ni, Cr, Zn can also come from the penetration of corrosion products of the city infrastructure (trolleybus wires, signs, handrails, etc.). The lead and soot content on the leaf surface results from increased vehicular traffic, as well as old out-of-date transport stock.

The results of the Plantago major L. plant samples allowed distributing the content of individual elements identified during the study in urban space. Studies have shown a significant increase in the content of heavy metals in the southern and northern parts of the city, which is associated with increased human activity. This circumstance indicates the need to improve the ecological status of the urban environment of Murmansk.

CONFLICTS OF INTEREST

The authors have no conflict of interest to declare.

AUTHORS' CONTRIBUTION

MAH: sampling collection, result interpretation, microanalysis. MYM: discussion part. SC: ICP analysis. GVZ: introduction, conclusion and references. RD: language and environment information. OAI: sampling collection and field documentation. All authors read and approved the final manuscript.

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