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CAN TREES HELP REDUCE LEAD IN URBAN AIR? A CASE STUDY OF GREENING IN A RUSSIAN INDUSTRIAL CITY

Tatyana Krupnova[1], Olga Rakova[1], Susanna Berentseva [1], Svetlana Gavrilkina[2] and Valerii Udachin[2]

[1]Institute of Natural Sciences and Mathematics, South Ural State University, Russia; [2]Ilmen reserve, South Urals Federal Research Center of Mineralogy and Geoecology of the Urals Branch of the Russian Academy of Sciences, Russia

*Corresponding Author, Received: 01 Nov. 2022, Revised: 06 Dec. 2022, Accepted: 15 Dec. 2022

ABSTRACT: Urban trees can be effectively used as a biomonitor and phytoremediator of air pollution, but not all species are equally capable of filtering the air. Lead-containing $PM_{2.5}$ has raised severe public health concerns in industrial cities. $PM_{2.5}$ pollution episodes occur in Chelyabinsk (Russia) because of a zinc production plant located in the urban area. During zinc production from lead-zinc concentrates, the environment around the enterprise may become contaminated with lead. We measured the amount of Pb in $PM_{2.5}$ and Pb accumulated by the leaves of *Betula pubescens*, *Populus nigra L.*, *Acer negundo L.* and *Pinus silvestris L.* from the 32 sites. The lowest value of Spearman's coefficient was found for pine needles. The stomata of the needles were clogged with anti-icing agents that had accumulated over the winter. Pb found in the tree leaves correlated significantly with that found in the $PM_{2.5}$. The correlations of Pb concentration were maximal for birch tree leaves. The leaves of all three species studied − *B. pubescens, P. nigra, A. negundo* − can be used as phytoremediators of Pb air pollution in the Chelyabinsk urban area.

Keywords: $PM_{2.5}$, Air pollution, Lead, Vegetation, Phytoremediation

1. INTRODUCTION

The world's population is expected to increase by 2 billion by 2050 − from 7.7 billion to 9.7 billion − and by the end of the century, despite continuing declines in fertility, it will peak at nearly 11 billion. Until 2009, more people lived in rural areas than in urban areas. Today, cities and towns are home to about 55 percent of the world's population, with urbanization projected to reach almost 70 percent by 2050.

Russian cities are traditionally well greened. Chelyabinsk is a typical Russian industrial city with over a million inhabitants. Its urban area is characterized by the concentration in a relatively small space of a large number of ferrous and non-ferrous metallurgical industries, a developed transport network, and rapid growth in urban construction. All this has led to residents of the city worrying about "black sky regimes" and the uncontrolled removal of green spaces. Despite the clear contribution of urban greening to improving urban quality of life and the existence of demands for urban sustainability, there is a methodological gap in evaluating the effectiveness of urban greening in Russian industrial cities. We used physical and chemical analysis to search for solutions and recommendations for the modern organization of urban greening for city authorities. It is also useful be-cause urban greenery shows positive associations with human health and mortality [1]. Green spaces play an important role in preserving the health of the population in cities. One of the modern solutions for the sustainability of the urban space is the use of urban greening. Trees can give a good spatial coverage and their leaves are excellent air pollutants collectors, they are frequently used for air quality assessments. According to the deposition of the atmospheric particulate matter (PM), especially particles with aerodynamic diameters <2.5 μm ($PM_{2.5}$), on the leaf surface, metals cations are bound by extracellular ligands. The number of studies rose in this field, but the species responded differently to the atmospheric pollution. This is connected with the ability of trees to capture heavy-metal, which has a serious impact on human health [2, 3]. Worldwide lead pollution is on the rise; lead was responsible 900 000 premature deaths [4]. During zinc production from lead-zinc concentrates, the environment around the enterprise may become contaminated with Pb. Lead is known to have many toxic effects in humans and is ranked second in the priority list of hazardous substances compiled by the US Environmental Protection Agency (USEPA). Lead exposure may cause changes in the neurologic system, leading to loss of neurological function [5, 6]. The Pb-containing PM present on and inside leaves were investigated by scanning electron microscopy coupled with energy dispersive X-ray microanalysis (SEM-EDX).

The study addresses the following two research questions:

1) Can trees help reduce lead in Chelyabinsk urban air?

2) What tree species are the best Pb accumulators?

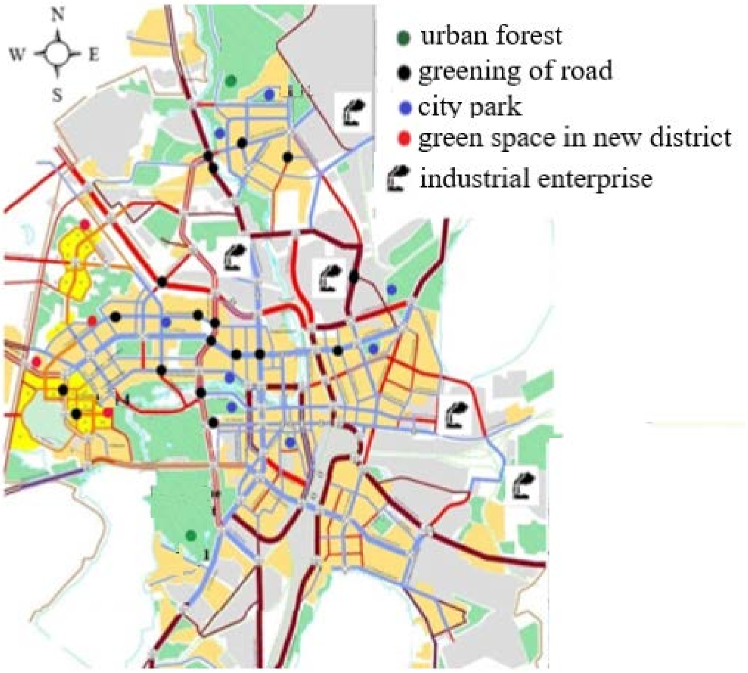

Fig. 1 Map of Chelyabinsk and location of the research sites

2. RESEARCH SIGNIFICANCE

In the present paper we studied the role of tree leaves and needles in the remove of lead-containing PM2.5 from the atmosphere. The foliar transfer of metals and metalloids in plant leaves and needles as a way of urban air purification remain under-studied. This study focused on the foliar uptake of metals from enriched PM2.5 resulting from the different urban anthropogenic emissions including emissions from a zinc production plant located in Chelyabinsk. We chose lead (Pb) as a model element.

3. MATERIALS AND METHODS

3.1 Study Area

The present research studies Chelyabinsk urban greening. Chelyabinsk is the capital of the South Urals region. Chelyabinsk is one of the largest industrial cities in Russia, with a population of more than 1 million people. The city has an unfavourable situation with air pollution and is included in the project "Clean Air".

We chose four types of green area (Fig. 1): urban forest (two sites), the greening of roads (18 sites), established city parks (eight sites) and public residential green spaces in new districts (four sites).

3.2 Sampling and Analysis of $PM_{2.5}$

The $PM_{2.5}$ samples were collected on 37 mm polycarbonate filters using low volume cascade impactor samplers operated at a flow rate of 16 l· min^{-1} at a height of 2 m (72 h of sampling). These $PM_{2.5}$ samples were collected at each station in July 2022. The loaded $PM_{2.5}$ filters were placed in a PTFE digestion vessel for acid treatment (2 ml hydrofluoric acid and 6 mL nitric acid), then microwave digested (MWS 4 Speedwave, Berghof, Germany) for 2 h after the setup routine for Pb analysis [7]. After digestion, the extracts were filtered using a blue-ribbon filter, and distilled water was added so that the total volume was 25 ml. Pb was analysed using Perkin Elmer ELAN 9000 Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Certified reference soil material GSO 10413-2014 CO was used for quality control. The range of recovery efficiency was 119%. The Pb limit of detection was estimated considering the standard deviation of 10 blank measurements (three times the standard deviation was used). The limit of detection of atmospheric concentrations obtained for Pb in $PM_{2.5}$ samples was 4.2 ng m^{-3}.

3.3 Selection of Tree Types and Sampling and Analysis of Leaves and Needles

Objects of research were tree species widely found in Chelyabinsk: *Betula pubescens, Populus nigra L., Acer negundo L* and *Pinus silvestris L.* Selected tree species are most widely used for landscaping the city. We collected tree leaves and pine needles from 2–3 trees at each site, 20 leaves or 30–40 pine needles from each tree. We collected samples from the maximum number of branches available evenly around the tree from the lower part of the crown. Visibly damaged leaves or pine needles were not used for the analysis. The details of sample collection and preparing for analysis were given in our previous work [8].

We washed the leaves and pine needles in running distilled water and air-dried them. All samples (leaf powder and pine needles) were digested separately into 10 ml of aqua-regia solution (HNO_3: HCl v/v 3:1) on a hot plate at 120°C for 2 h. After cooling, the solution was filtered through blue ribbon filter paper and deionized water was added to make up a volume of 50 ml. The solutions were analysed for Pb content by mass spectrometry with inductively coupled plasma ICP-MS using Perkin Elmer ELAN 9000. The analyses were performed in triplicate. All reagents were of analytical grade. The Russian national state standard samples (Vinogradov Institute of Geochemistry SB RAS, Russia) of birch leaves (GSO 8923-2007) and a mixture of herbs (GSO 8922-2007) were used to check the accuracy of the Pb content in the leaves and needles. The ranges of recovery efficiency were 98–105 %. The limit of detection of concentrations obtained for Pb in leaves was 0.1 mg kg^{-1} of dry weight (dw).

Small leaf strips or needles (washed with chloroform for top-part epicuticular wax removal before SEM analysis) were cut out from the area between the margin and midrib of leaves. Each sample was fixed on a metallic pin stub, using conductive double-sided tape, and left to dry at room temperature for at least three days. This dehydration is required to avoid sample damage, as water would evaporate too fast at low pressure. Before the microscopic analysis, samples were vacuum-coated with Au to make them conductive in order to prevent a charge build-up. SEM analyses were performed on a Jeol JSM-7001F Scanning Electron Microscopy Complex. Photographs were taken of randomly chosen spots at 500× magnification, at 5 kV.

Microsoft Excel 2013 and SPSS 24.0 software were used to organize and analyse the data. The relationship between the data was determined using Spearmen's test. MapInfo Pro 2019 was used to build the spatial distribution maps of Pb concentrations.

4. RESULTS AND DISCUSSION

4.1 Lead Concentrations in $PM_{2.5}$, Pine Needles and Tree Leaves

The concentrations of Pb were identified in $PM_{2.5}$, pine needles, and tree leaves of three species. The Pb concentrations are shown in Table 1.

Table 1 Atmospheric concentrations (ng·m^{-3}) obtained for Pb in $PM_{2.5}$ samples and concentration (mg·kg^{-1} dw) obtained for Pb in pine needles and tree leaves collected in the Chelyabinsk urban area (n = 32)

Environmental object	Max	Mini	Mean	SD
$PM_{2.5}$	35.0	5.0	18.0	0.5
Pb in pine needles	6.10	0.10	2.80	0.05
Pb in poplar leaves	12.30	0.20	5.50	0.05
Pb in maple leaves	9.50	0.20	4.20	0.05
Pb in birch leaves	15.0	0.3	7.1	0.1
Pb in birch leaves	15.0	0.3	7.1	0.1

Note: SD- Standard deviation. It was the amount of variation or dispersion of a values set.

It is known that the foliar pathway for metal uptake may be predominantly the soil–root pathway in urban and industrial environments [8]. In the present study, some PM are ultrafine, i.e., sub-micronic and nanoparticles were observed by SEM-EDX in leaf surfaces.

The mean concentrations of Pb in different tree leaves, ranging from 2.8–7.1 mg·kg^{-1} dw. It is well known that there is a well-recognized definition of "phytoremediator" of Pb from soils which the Pb concentration in plant leaves is higher than 1000 mg·kg^{-1} dw [9]. In this study, the deposition of lead from air is studied, so these approaches are not applicable. Rachmadiarti et al. [10] showed that *Wedelia triloba (L.) Hitchc.* and Syzigium sp. grown on the main roads absorbed 0.146–0.288 μg•g^{-1} of Pb by leaf surface area and Pb content of both the plants was within the normal range, as the accepted Pb content for many plant species range from 1.0–3.5 μg•g^{-1}. In our study Pb content in tree leaves was higher than for many plant species.

The Pb content detected in leaf samples (mg·kg^{-1} dw.) from urban trees in Chelyabinsk differed by tree species and location (Fig. 2). The highest Pb content was found in birch leaves collected near the zinc production plant, followed by the leaves of same species collected from the urban area near the steel plant. Poplar leaves collected from the Kashtak forest located in the north of the city showed the lowest Pb content, but samples of the same species collected from locations with similarly busy traffic showed intermediate values of Pb content.

Foliar uptake is likely favoured by these PM morphologies. Comparing the capacity of the leaves to adsorb Pb particles across the deciduous tree species investigated. we can state that the most efficient species was the birch followed by the maple and then the poplar (see Table 1).

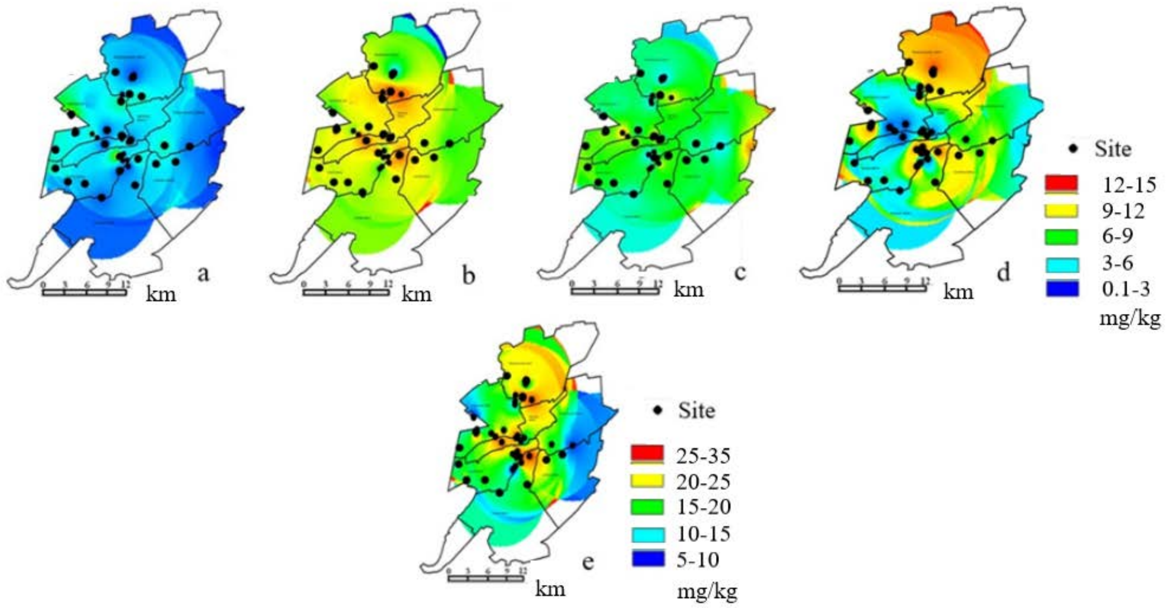

Fig. 2 Spatial distribution maps of the Pb concentrations in (a) pine needles, (b) poplar, (c) maple, and (d) birch leaves, and (e) Pb in $PM_{2.5}$ from all sampling sites. The red and yellow colors on each small map represent relatively high concentration of Pb, while the green and blue colors represent relatively low concentrations, respectively.

Birch tree (accumulated the most PM compared to other tree species because its leaves contain high amounts of cuticular wax.

Our results confirm previous work [11] where it was reported large differences between tree species in heavy metal retaining capacity in foliar dust. It was reported [12] that many factors may affect the air-vegetation transfer including plant characteristics such as functional type, leaf surface area, cuticular structure, and leaf longevity. Rough and hairy leaves accumulate significantly more lead (birch leaves) than smooth leaves (poplar leaves). Maple leaves occupy an intermediate position, they have a larger leaf surface than birch, but more rare and narrow stomata. Compared to poplar, maple has a rougher surface that better holds particles.

It is known that the foliar pathway for metal uptake may be predominantly the soil–root pathway in urban and industrial environments [8]. In the present study, some PM are ultrafine, sub-micronic and nanoparticles were observed by SEM-EDX in leaf surfaces.

Morphological factors such as stomatal index, trichome density, and leaf length affect the efficiency of dust collection by plants. These hypotheses of surface structure were confirmed by scanning electron microscopy (SEM) images of plant surfaces (Fig. 3). Figure 3 shows that the lowest concentration of lead is recorded in pine needles. This is because the absorption of any substances from the surrounding air by pine needles is significantly reduced due to clogging of the stomata with crystals of anti-icing agents that accumulate during the winter. This leads to disease and death of evergreen trees growing along the roads (Fig. 4). The stomata of needles taken further from major roads are less clogged (Fig. 3d).

4.2 Correlation of Lead in $PM_{2.5}$ with Lead Content in Leaves and Needles

We studied the correlations of Pb in $PM_{2.5}$ with Pb concentrations in pine needles and poplar, maple, and birch leaves. Table 2 presents Spearman's correlation coefficients.

Table 2 Spearman's correlation coefficients between lead in $PM_{2.5}$ and lead content in leaves and needles (n=32)

Environmental factor/ object	Spearman's coefficient value
Pb in pine needles	0.31
Pb in poplar leaves	0.58*
Pb in maple leaves	0.63*
Pb in birch leaves	0.71*

Note: * Correlation is significant at 0.001 (two-tailed)

The lowest value of Spearman's coefficient was found for pine needles with Pb in $PM_{2.5}$.

The reason for the absence of a significant correlation was fact that the stomata of the needles were clogged with anti-icing agents.

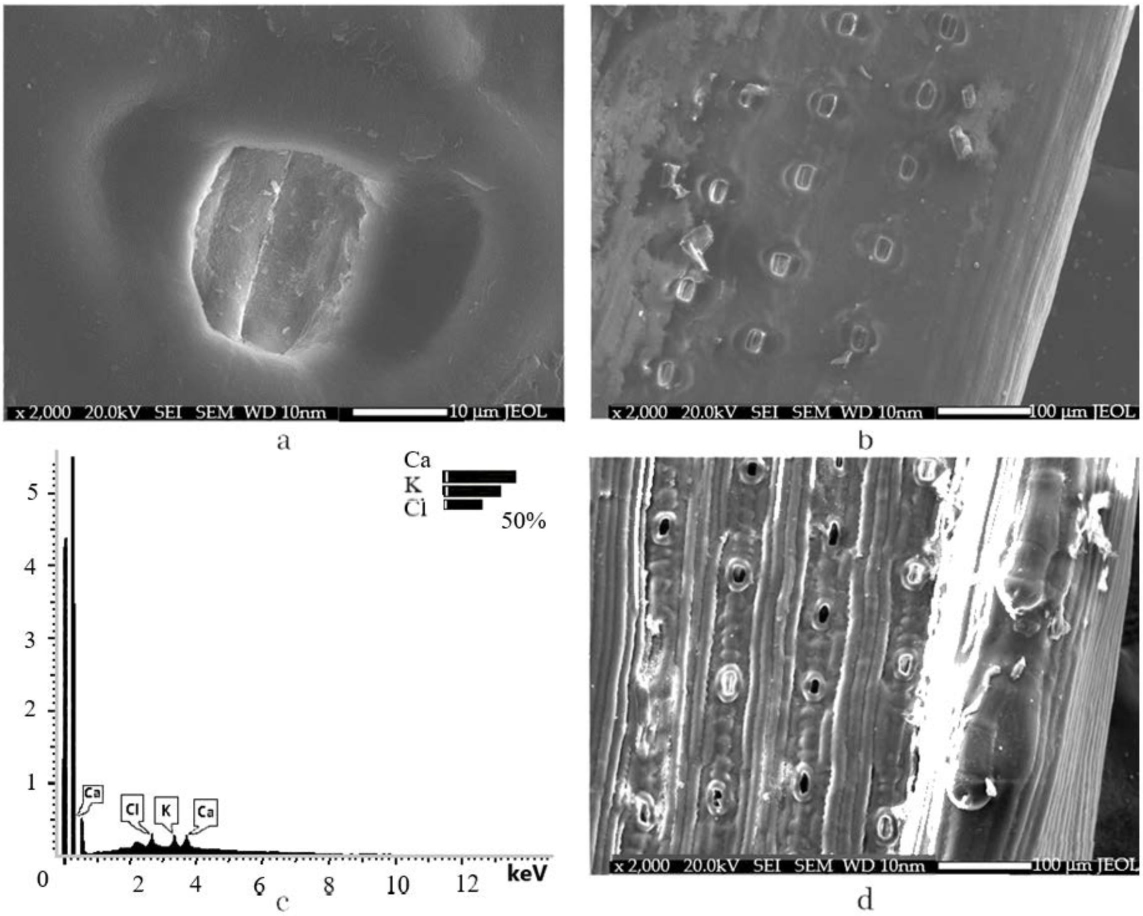

Fig. 3 SEM-images of plant surfaces: (a) salt crystal in the stoma of *P. silvestris*; (b) stomata of pine needles clogged with reagents; (c) spectrum of the composition of salt crystals in stomata of *P. silvestris*; (d) the state of stomata of pine needles collected at a distance from the roads

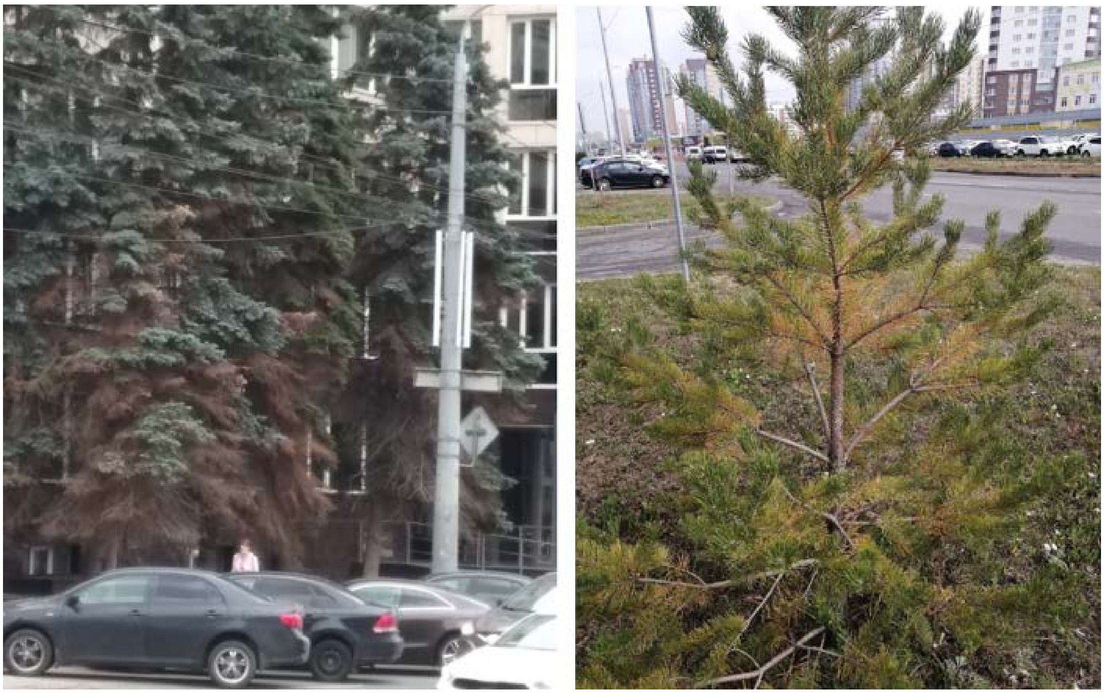

Fig 4 Photos of diseased evergreen trees

It had accumulated over the winter. The correlation coefficients for the leaves fall within the range of 0.58–0.71. Table 2 indicates that Pb concentrations in $PM_{2.5}$ correlate significantly with those found in the tree leaves at the 0.001 level of significance. The correlation coefficients of Pb concentration in leaves and in $PM_{2.5}$ was the highest for birch trees because the birch leaf surface has hairs, and it might favor its metal tolerance and adsorption of fine atmospheric $PM_{2.5}$. Specific leaf surface areas could explain differences in rates of uptake between tree species. Maple leaves exhibit a dissected shape of its leaves with a folded structure. This leads to the formation of more reliable correlations for maple compared to poplar (Fig. 5). However, the correlation is also high for poplar because the leaves have a high wax content [13].

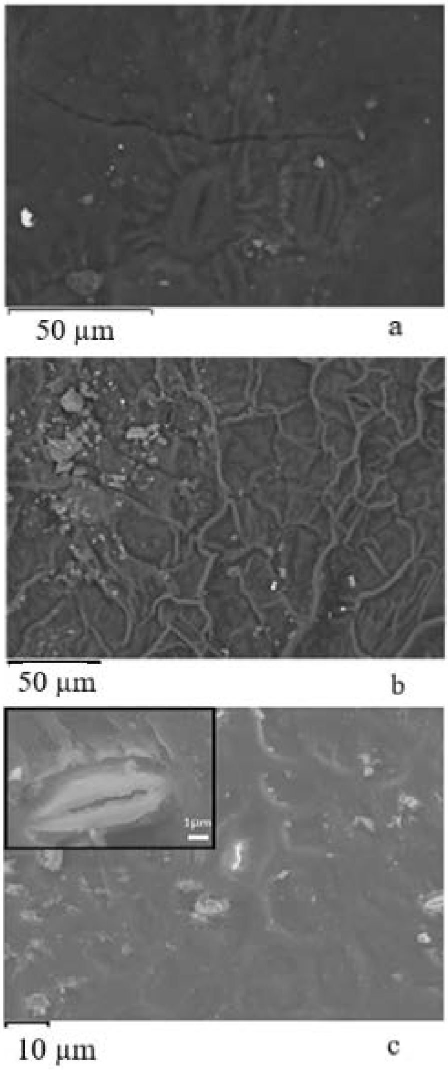

Fig 5 PM near the stomata on a birch leaf (a); PM in the folds of a maple leaf (b); PM on poplar leaves (c)

It may be recommended to treat trees with special injections and droppers link. Due to the high cost, this method cannot be widely used, but in some cases it can take place. For example, if the tree has historical value. In the summer of 2021 residents of the city of Chelyabinsk were outraged by the egregious case of cutting down historical trees in the city center (Fig. 6).

Daurian larches at the intersection of Lenin Avenue and Krasnaya Street were planted in 1905 from 30 seeds brought by a wounded officer–a participant in the Russo-Japanese War. Previously, the larch garden reached the Scarlet Field. Some of the trees were cut down in 2003. After that, the remaining trees were protected. Even during the road revolution, when the roadway was widened, the remaining larches were preserved. However, in June 2021, the trees were cut down due to poor sanitation. Many experts pointed out that such trees with a cultural function could be saved.

5. CONCLUSIONS

This study showed that tree leaves play an important role in the absorption of Pb-containing $PM_{2.5}$ from the air. Birch leaves have the best phytoremediation properties of Pb-rich $PM_{2.5}$ air contamination. Despite the summer period of sampling, the stomata of pine needles taken on the roadside were clogged with anti-icing agents, which prevents the pines from fulfilling their phytoremediation effects. It shows critical need to reduce use of road salt in winter.

In general, urban greening has various functions. It not only forms the urban-ecological framework of the city, but also regulates the urban microclimate, purifying the air in an industrial city, and having an aesthetic, educational, and cultural-historical function. Urban greenery needs to be maintained, protected, and improved. The local city authorities of Chelyabinsk are not making enough efforts to increase the urban green cover. It should also be noted that in the last two years there has been a negative trend in the era of universal urbanization − population decline. Among other things, it can be assumed that it is associated with poor ecology and poor quality of life in the city. Therefore, work towards effective greening of the city could improve the situation. The government and the public should be aware of the scope and function of green spaces and protect them by collecting more data on green cover to enforce laws, increase the role of public organizations and enterprises, and use modern landscaping methods. Such approaches are urgently needed before more green spaces disappear from the cityscape.

Fig. 6 Destruction of Daurian larches

The loss of green cover may exacerbate the city's environmental problems, which are already chronic, negatively affecting the image and viability of Chelyabinsk.

6. ACKNOWLEDGMENTS

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