Diversity and Negative Effect of $PM_{0.3-10.0}$ Adsorbed by Needles of Urban Trees in Irkutsk, Russia

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Research Article

Keywords: Urban trees, Pollution by PM, SEM, EDAX, EDS, Negative effect on tree metabolism

Posted Date: July 21st, 2023

DOI: https://doi.org/10.21203/rs.3.rs-3065315/v1

Version of Record: A version of this preprint was published at Environmental Science and Pollution Research on November 4th, 2023. See the published version at https://doi.org/10.1007/s11356-023-30749-5.

Abstract

The study was performed in natural forests preserved within the Boreal zone city, Irkutsk, Russia. Test sites were selected in the forests in different districts of the city, where samples of Scots pine (*Pinus sylvestris L.*) and Siberian larch (*Larix sibirica Ledeb.*) needles were taken to study the adsorption on their surface of aerosol particles of different sizes, in microns: $PM_{0.3}$, $PM_{0.5}$, PM_1, $PM_{2.5}$, PM_5, PM_{10}. Scanning electron microscopy was used to obtain high–resolution photographs (magnification 800–2000x, 16000x) and aerosol particles (Particulate Matter – PM) were shown to be intensively adsorbed by the surface of needles, with both size and shape of the particles characterized by a wide variety. Pine needles can be covered with particles of solid aerosol by 50–75%, stomata are often completely blocked. Larch needles often show areas, which are completely covered with aerosol particles, there are often found stomata deformed by the penetration of PMx. X–ray spectral microanalysis showed differences in the chemical composition of adsorbed PMx, the particles can be metallic if metals predominate in their composition, carbonaceous – in case of carbon predominance, or polyelemental, if the composition is complex and includes significant quantities of other elements besides metals and carbon (calcium, magnesium, potassium, sodium, sulfur, chlorine, fluorine). Since the particles contain a large proportion of technogenic pollutants, accumulation by the needles of some widespread pollutants was investigated. A direct correlation of a highly significant level between the concentration of PMx in the air and the accumulation of many heavy metals in pine and larch needles, as well as sulfur, fluorine, chlorine, has been revealed, which indicates a high cleaning capacity of urban forests. At the same time, the negative impact of PMx particles on the vital status of trees is great, which shows in intense disturbance of the parameters of photosynthesis and transpiration, leading to a significant decrease in the growth characteristics of trees and reduction in the photosynthetic volume of the crowns. We consider that the results obtained are instrumental in developing an approach to improvement of urban forests status and creating a comfortable urban environment for the population.

Introduction

Aerosol particles (Particulate Matter, PMx) of different sizes, different morphological characteristics and diverse chemical composition are currently believed to be among the most common and dangerous pollutants of atmospheric air. PMx can contain almost all known technogenic pollutants, including fluorides, chlorine-containing, sulfur-containing, nitrates, ammonia, heavy metals, polyaromatic hydrocarbons (PAHs), as well as pathogenic microorganisms, viruses, allergens (Baldacchini et al. 2019; Xin et al. 2021; Wang et al. 2021; Tianfang et al. 2022; Leonard et al. 2023). Therefore, the results of the PMx measurement in the air provide quite comprehensive information about the level and nature of its pollution. Such data are especially important for assessing the state of the environment of urbanized territories with high population density. Numerous publications of researchers from many countries great point to the interest in aerosol particles, their origin, composition, morphology, and impact on human health (Mukherjee and Agrawal 2017; Jain et al. 2021; Jirau-Colón et al. 2021; Mei et al. 2021; Xin et al. 2021). The negative impact of PMx on human health has been proven by many studies. For example, suspended particles have been shown to cause exacerbation of respiratory diseases (Jirau-Colón et al. 2021), to spur asthmatic symptoms (Lu et al. 2021), fine particles can penetrate deep into the lungs (Wang et al. 2021) and even increase the incidence of lung cancer (Chu et al. 2021), prolonged exposure to PM can increase the risk of hypertension (Xu et al. 2021). The greatest danger to human health is believed to be represented by particles with a size of ≤ 2.5 μm, which are constantly suspended in the air and are assessed by some researchers as a very high environmental risk factor, ranking fifth in the general list of mortality risk factors (Cohen et al. 2017).

Researchers unanimously agree that one of the most effective methods of reducing urban air pollution is creation of different types of green spaces that serve as powerful phytofilters against PM (Ram et al. 2015; Chen et al. 2020; Letter and Jäger 2020; Wróblewska and Jeong, 2021; Popek et al. 2022). In our opinion, the key ecosystem function of air purification belongs to natural forests as sustainable ecosystems preserved within cities. However, many megacities obviously lack this component of the urban ecosystem, so various types of artificial landscaping are being created there and active research is underway to identify the types of arboreal plants that most effectively absorb PMx (Beckett et al. 2000; Yang et al. 2015; Jin et al. 2021; Mei et al. 2021; Chen et al. 2022; Triratnesh et al. 2022). Such species include *Fraxinus excelsior, Ulmus laevis, Quercus ilex, Pinus nigra, Pinus pinea* (Vigevani et al. 2022). In artificial landings near highways in Norway, *Pinus mugo, Pinus sylvestris, Taxus media, Taxus baccata, Stephanandra incisa, Betula pendula* demonstrated the highest efficiency in PMx capturing (Sæbø et al. 2012). When studying urban trees in Korea, *Quercus salicina and Pinus densiflora* stood out by the largest number of PMx adsorbed by the leaf surface

(Jin et al. 2021). When ranking the most common tree species in cities of the world according to the efficiency of removing $PM_{2.5}$ from the air, it was found that *Platanus acerifolia, Acer saccharinum, Gleditsia triacanthos* exceeded the average efficiency estimate; however, a high potential of evergreen coniferous trees in urban air purification from suspended particles was observed (Yang et al. 2015; Lindén et al. 2023). It is also shown that the efficiency of capturing fine particles rises with an increase in the volume of urban plantings due to additional planting of shrubs (Kim et al. 2017).

We have also previously showed the ability of different types of trees, shrubs, herbaceous plants to accumulate pollutants of various chemical composition in assimilation organs – heavy metals, PAHs, acidogenic gases, fluorides (Kalugina et al. 2018, 2019; Mikhailova et al. 2018; Takahashi et al. 2020). The data obtained are important both for monitoring of environmental pollution and for selecting the species recommended for urban greening. For example, we believe that when creating artificial plantings, it is impossible to do without evergreen coniferous trees, at the same time, we recommend introducing deciduous species into such plantings: *Cotoneaster melanocarpus, Populus suaveolens, Duschekia fruticosa, Sambucus racemose, Populus tremula, Spirea media*, these species can accumulate toxic pollutants in leaves in very high concentrations exceeding the background by 15–22 times.

In this paper, we sum up the results of research of aerosol particles effects on trees growing in urban forests of natural origin. We present real photos of particles of different sizes adsorbed by pine needles (*Pinus sylvestris*) and larch needles (*Larix sibirica*), since there is little information on the status of assimilation organs of trees exposed to aerosol particles pollution. However, this data would be useful to clearly show why photosynthesis process is disrupted and other physiological and biochemical parameters of the tree change. With this in view, we undertook a special study of the adsorption of aerosol particles by needles of two common coniferous species in the urban forests of Irkutsk in order to find out specific features of the particles, their morphology and chemical composition. Accordingly, the purpose of our work was to investigate the distribution of adsorbed aerosol particles on the surface of the needles of urban trees, to identify their chemical composition, to show the variety of their shapes and sizes, to identify their negative impact on tree metabolism.

Material and methods

Study area

The city of Irkutsk is located in Eastern Siberia (boreal zone) and occupies an area of 280 sq. km, about 20% of which are urban forests of natural origin, preserved in forest parks and on the outskirts of the city (Atlas of development of Irkutsk 2011). The coniferous species dominating in the forests are Scots pine (*Pinus sylvestris* L.) and Siberian larch (*Larix sibirica* Ledeb.). To conduct the study, we created 14 test sites in urban forests according to the ICP Forests methodology (Manual on methods and criteria for harmonized sampling, assessment, monitoring and analysis of the effects of air pollution on forests 2010), the 15th background (reference) test site (TS) was located at a distance of 120 km from the city in a forest area with no technogenic pollution (Fig. 1). The size of each TS amounted to 0.1 ha (1000 m^2). Concentrations of aerosol particles of the size range $PM_{0.3}$, $PM_{0.5}$, $PM_{1.0}$, $PM_{2.5}$, $PM_{5.0}$, $PM_{10.0}$ were measured in the air at all test sites using the atmospheric air quality monitor Air detector 2 AM7P, "Environmental Protection Agency", US. PM Detector Biostar air monitor, “BIOTEQ Technologies”, China, was used to measure the AQI index. Based on the data obtained, 8 representative test sites were selected (see Fig. 1), showing stable results on PMx concentration measured over a decade, from July 1 to July 10, 2022. Further studies were carried out at these test sites.

Analysis of adsorbed particles

Samples of pine and larch needles from 6–10 trees of each species were collected at representative 8 test sites and immediately delivered to the laboratory in an isothermal container Mobicool MP30. Samples were prepared from fresh needles by the quartering method (in 10-fold repetition) for the analysis of its surface contamination by aerosol particles by scanning electron microscopy (SEM). Certified equipment of the Limnological Institute of SB RAS (Irkutsk) was used to perform the work: FEI Company Quanta 200 scanning electron microscope with an X–ray microanalysis unit with nitrogen-free cooling GENESIS XM 2 60 – Imaging SEM with APOLLO 10 and an EDAX unit. Qualitative and quantitative microanalysis of PMx particles was performed using energy dispersive X-ray spectroscopy (EDS) and mapping of the distribution of chemical elements on the needles surface.

Spectrograms of chemical composition of the adsorbed particles and high-resolution photographs (magnification from 800 to 2000 times) of surface contamination of pine and larch needles were obtained. To determine the size of the PMx, their chemical composition and concentration, 16000 times increase of the particles was used.

Analytical procedures

Based on the fact that PMx contain a large amount of technogenic pollutants, we investigated the degree of accumulation by the needles of heavy metals (Pb, Cd, Fe, Zn, Cu, Mn, Al, Cr, Ni, Co, Mo, Ti), sulfur, fluorine, chlorine, calcium, magnesium, potassium, sodium using certified methods and equipment of the Center for Bioanalytics of the Siberian Branch of the Russian Academy of Sciences and the Republican Analytical Center of Eastern Siberia. The following equipment was used: atomic absorption spectrophotometer AAnalyst 600 ("PerkinElmer Life and Analytical Sciences", US), optical emission spectrometer ICP-OES Spectro Arcos with spectrum excitation in inductively coupled plasma ("Spectro Analytical Instruments", Germany). All the analyses were carried out in 5-fold repetition, the content of elements was calculated in mg/kg of dry weight of needles.

To identify the negative impact of PMx on trees vital status, a number of physiological, biochemical and morphostructural parameters of pine and larch were determined. As the most representative indicators of trees vital status, the following parameters were selected: level of tree crowns defoliation, shoots length, needles weight, content of pigments (chlorophylls and carotenoids) in the needles, the chlorophyll level in the light-collecting complex (LCC), the intensity and productivity of photosynthesis, the photosynthetic volume of the tree crown, the transpiration rate. Photosynthesis and transpiration parameters were measured in Binder KBW 240 growth chambers for measuring CO_2-O_2 and H_2O gas exchange on cut shoots in experimental vacuum polycarbonate chambers with integrated infrared CO_2 gas analyzer (PTH, Protmex), O_2 gas analyzer (Smart sensor Pro AS8901), air quality monitor (Air Master 2 AM7), temperature and humidity sensors (Elitech RC-5 Data Logger GSP-6, Engbird IBS-TH1). The measurement data were transmitted to the computer monitor. The content of chlorophylls and carotenoids was determined by spectrophotometric method, the optical densities of extracts were measured at wavelengths of 662, 644 and 440.5 nm. The proportion of chlorophylls localized in the light-collecting complex (LCC) was calculated using the Lichtenthaler formula (Lichtenthaler 1987): (Chl *b* + 1.2 Chl *b*)/ (Chl *a* + Chl *b*). The photosynthetic volume of the tree crown was measured using the Huepar HLR1000 laser rangefinder and the Photosynthesis light quantum meter TES 1339P, the calculation was performed using the formula of the volume of a truncated cone with a correction factor for defoliation (Taxation of a single tree 2020).

Statistical analysis

Statistical processing of all the data obtained was performed with the program "Statistical Computing Environment R" and its use in Data Mining (Shipunov et al. 2014). The average values of each parameter and their standard deviations were calculated. To establish correlations between the indicators, the nonparametric Spearman coefficient was used. The equality of the mean values in paired samples was checked using the t-test. The significance of the differences was assessed using the Mann–Whitney criterion (at $P \leq 0.05$). All the values of the indicators given in this paper yielded statistically significant differences.

Results and discussion

Representative test sites selected in urban forests showed significant differences in the concentration of PMx of different sizes in the air and AQI, as well as large differences from the background test site (Fig. 2). Judging by the data obtained, most urban test sites (TS) are heavily polluted with aerosol particles, at the same time, the AQI on them is at least 3–4 times and at most 12–13 times higher than the background. The exceptions are TS 3 and TS 8, which are less polluted, possibly due to their remoteness from sources of technogenic emissions and from highways. It should be noted that in urban test sites, the largest share among polluting suspended particles is taken by small particles ($PM_{0.3}$, $PM_{0.5}$, $PM_{1.0}$, $PM_{2.5}$), while the concentrations of $PM_{5.0}$ and PM_{10} particles are not high, and in the background test site there are no such particles at all. Other authors also report higher concentrations of small particles in polluted urban air (Linh et al. 2023; Vlasov et al. 2023).

The study of pine and larch needles demonstrated that suspended particles are intensively adsorbed on its surface. Heavily polluted pine needles, for example, on TS 1 and TS 5, can be covered with aerosol particles by 50–75%, moreover, complete blockage of stomata is often observed (Fig. 3a, b). Active adsorption of PMx particles on the surface of pine needles is fostered by their morphological features: a significant thickness of the wax layer, the presence of trichomes, a large number of stomata and resin passages. Besides, these features cause a strong connection of polluting particles, especially small particles, with needles, which makes it almost impossible for the particles to wash out by precipitation or to get released by wind currents.

In microphotographs, the surface of larch needles (epidermis and cuticle) looks lumpy, formations in the form of folds and ridge-like protrusions are visible, which contributes to the active adsorption of suspended particles. The areas between the folds may be seen to be almost completely covered with aerosol particles (Fig. 4a). Penetration of particles into the stomata often leads to deformation of the latter (Fig. 4b). Since the covering tissues of larch needles are more thin-walled, they are more vulnerable to suspended particles, especially those containing heavy metals.

X-ray spectral microanalysis of adsorbed PMx was carried out and the percentage of chemical elements in them was calculated (Fig. 5). PMx particles were found to contain carbon, silicon, sulfur, calcium, phosphorus, chlorine, magnesium in the largest amount, a significant proportion of heavy metals (Cd, Pb, Al, Co, Cr, Cu, Fe, Mn, Mo, Ni, V, W, Zn), present in the form of metallized clusters of different-sized particles capable of actively penetrating into tissues through the stomata and cuticle.

The photographs show that the size and shape of the particles are characterized by a wide variety (Fig. 6). The particles with carbon as a dominating component are in most cases of irregular round shape, their surface is not smooth and has through holes. Particles containing metals, as a rule, have a spherical shape and are able to attract each other by their magnetic fields, forming large clusters of PM particles. Polyelement particles may contain up to 10–15 different elements, including C, Si, S, Cl, As, heavy metals.

In addition to the study of the adsorption of suspended particles on the surface of needles, the accumulation of the most common pollutants in pine and larch needles – heavy metals (Pb, Cd, Fe, Zn, Cu, Mn, Al, Cr, Ni, Co, Mo, Ti), sulfur, fluorine, chlorine – was also determined at all TS, these elements often being the components of PMx coming from technogenic emissions of most enterprises, as well as from vehicle emissions. The results showed high HM contents in pine and larch needles, in all cases exceeding background values (Table 1). For example, in pine needles, the lead content is higher than the background by 5–16 times, cadmium – by 3–9 times, chromium by 9–16 times, nickel – up to 10 times, copper accumulates to a lesser extent (the maximum excess of the background is 6.1 times), zinc, iron, aluminum, strontium (max excess background 5.2 times), molybdenum, manganese, cobalt, titanium (max background excess 3.3–4.1 times). The results of the larch needles analysis also indicate a significant accumulation of HM, especially strontium, lead, iron, aluminum, chromium, titanium. High content of lead (exceeding the background by 40 times), chromium (31 times), cadmium (14 times) is characteristic of TS 4 located in the forest near the airport. The lowest content of HM, both in pine and larch conifers, was found on TS 3 and TS 8.

Table 1
The content of heavy metals* (mg/kg) in the needles of Scots pine and Siberian larch on the surveyed test site in the urban forests of Irkutsk

Test site number	Pb	Cd	Zn	Cu	Fe	Mn	Al	Cr	Ni	Co	Mo	Sr	Ti
Scots pine													
1	0.66	0.044	51.22	3.94	295.75	2.34	520.46	0.86	4.14	0.27	0.21	22.75	21.54
2	0.72	0.039	49.12	3.64	283.73	3.45	587.08	0.88	5.70	0.32	0.18	19.70	26.92
3	0.45	0.015	40.07	2.76	203.01	1.36	345.35	0.61	0.78	0.14	0.10	10.63	15.98
4	0.97	0.042	49.57	3.99	351.74	3.77	533.80	1.11	4.05	0.29	0.23	26.05	28.23
5	0.79	0.029	55.77	3.83	313.65	2.73	443.36	0.94	3.91	0.20	0.16	17.59	22.48
6	0.62	0.027	47.87	3.73	276.76	1.99	390.64	0.78	1.30	0.16	0.14	15.89	20.16
7	0.46	0.018	42.17	3.68	242.34	1.87	389.09	0.74	1.09	0.15	0.13	13.94	18.39
8	0.32	0.017	41.45	3.28	209.67	1.32	358.26	0.63	1.01	0.12	0.11	9.17	14.75
Background	**0.06**	**0.005**	**10.97**	**0.65**	**68.81**	**1.02**	**115.42**	**0.07**	**0.54**	**0.08**	**0.07**	**5.04**	**6.81**
Siberian larch													
1	1.15	0.072	31.33	7.58	825.78	6.36	1245.78	1.95	4.96	0.71	0.26	177.27	42.05
2	1.08	0.068	28.71	7.26	772.36	7.65	1179.45	1.86	5.79	0.76	0.22	169.53	45.47
3	0.24	0.021	19.17	3.26	470.12	1.95	722.54	1.27	1.22	0.27	0.14	86.72	19.48
4	1.98	0.084	36.45	8.29	989.45	7.80	1709.12	2.48	7.06	0.85	0.31	186.12	76.37
5	0.97	0.062	30.64	5.59	649.25	5.98	1025.23	1.74	4.64	0.62	0.24	158.10	49.94
6	0.81	0.042	29.74	5.05	639.05	4.35	901.15	1.69	2.18	0.59	0.18	147.62	44.69
7	0.67	0.036	21.35	4.98	630.51	4.22	886.12	1.47	1.68	0.51	0.17	126.92	35.17
8	0.32	0.024	20.18	3.38	497.35	1.86	732.61	1.31	1.28	0.24	0.13	88.627	20.41
Background	**0.05**	**0.006**	**7.15**	**0.78**	**89.78**	**1.38**	**189.45**	**0.08**	**0.63**	**0.09**	**0.09**	**75.04**	**11.51**

* Average values are given; the error of the average value is from 5 to 10%.

Besides heavy metals, concentrations of sulfur, fluorine and chlorine were determined in needles of the conifer trees in urban TS; although these elements are important in plant metabolism (perhaps fluorine is an exception), but with their high content they act as toxic pollutants contained in PM particles. The following parameters were determined: the total content of sulfur (Fig. 7a) and its ionic form SO_4^{-2} (Fig. 7d), the total concentration of chlorine (Fig. 7b) and its ionic form Cl^-(Fig. 7e), the total content of fluorine (Fig. 7c) and its ionic form F^- (Fig. 7f). The data obtained show that in pine and larch needles, the trend of total sulfur accumulation is similar, its level is 2.5–3.5 times higher than the background, while the level of ionic form in larch needles is 9 times higher than the background, in pine needles – 6 times. According to the accumulation of chlorine in the needles, similarity is observed both in the level of total chlorine (exceeds the background by 2.1–2.5 times), and in the concentration of the ionic form (above the background by 12.4–12.7 times). The fluorine content also exceeds the background, in pine needles – by 2.0–3.5 times, in larch needles – by 3.0–6.5 times. The data obtained indicate that the source of these pollutants (HM, sulfur, fluorine, chlorine) in pine and larch needles is PMx, polluting the atmospheric air. To support this conclusion, correlations were calculated between the accumulation of pollutants (on the example of thirteen heavy metals) in the needles and the concentration of different–sized PMx in the air at each TS (Table 2). Correlation analysis confirmed the presence of direct dependencies of a high level of significance ($r = 0.52–0.85$; $P = 0.05$, $n = 24$) between the concentration of aerosol particles and the accumulation of pollutants (HM) in pine and larch needles from urban forests, while in the background TS the correlations between PMx and HM were not statistically significant. These data also indicate the pronounced ability of pine and larch trees to purify polluted urban atmospheric air from suspended particles. Therefore, urban forests have a high ecosystem significance, as they function as natural phytofilters.

However, chronic exposure to aerosol particles negatively affects the status of urban trees themselves, as our studies have shown. The tree crown defoliation level in urban forests in most TS was found to exceed the background, reaching a maximum of 65% for pine and larch (background 10–15%). The length of shoots is smaller, in comparison with background parameters, in pine by 1.5–3.1 times, in larch by 15–44%. Pine shoots have significantly reduced the weight of needles (from 1.3 to 2.3 times) and the number of pairs of needles (from 1.8 to 2.8 times). The weight of needles on larch shoots is in most cases halved. Changes in the photosynthetic volume of pine and larch tree crowns in urban forests are similar, the sharpest decrease in this indicator being observed at TS 2, 4, 5, for pine – by 2.1–2.6 times, for larch – by 2.3–2.6 times. Changes in the parameters considered are less pronounced on TS 3 and TS 8, which are located on the outskirts of the city away from major highways and industrial enterprises.

Table 2

Correlation coefficients between the concentration of PMx particles in atmospheric air in test sites and the content of thirteen HM in pine and larch needles at the test sites in urban forests of Irkutsk

Test site number	**$\sum PM_x$, μg/m^3**	**Correlation coefficients between $\sum PM_x$ and $\sum_{13}$ HM**	
		for pine needles	**for larch needles**
1	3265 ± 126.3	85.1 ± 4.2	87.3 ± 4.2
2	2245 ± 87.6	65.2 ± 3.8	71.2 ± 4.3
3	1023 ± 55.3	53.2 ± 3.6	59.4 ± 3.8
4	2975 ± 112.6	78.2 ± 5.2	80.3 ± 6.1
5	2501 ± 107.8	68.4 ± 4.4	74.5 ± 4.2
6	2185 ± 103.5	72.2 ± 3.6	79.2 ± 3.5
7	1734 ± 69.3	64.4 ± 2.7	68.4 ± 2.6
8	1286 ± 63.5	54.3 ± 3.8	62.3 ± 3.5

It was logical to assume that the identified negative morphostructural changes in trees result from significant disturbances of their metabolism, primarily photosynthesis, respiration, transpiration. A significant disturbance of pine photosynthesis in urban forests is indicated by a drop in its intensity, ranging from 9–46% of background values, productivity – from 6–38% (Fig. 8, 9). Larch studies also detect negative changes in photosynthesis, its productivity is especially sharply reduced on most TS (by 1.6–2.0 times), with the exception of TS 3 and 8, where pathological changes are much less pronounced (Fig. 8, 9). Functional disorders of photosynthesis are largely determined by the changes found in the pigment complex of needles. These changes led to a disturbance in the amount and ratio of different pigment groups. For the studied species of coniferous trees in urban forests, the general trend was a decrease in chlorophyll *a* and carotenoids content, and at the same time an increase in of chlorophyll *b* level in comparison with background indicators (Table 3). In pine needles, the decrease in the content of chlorophyll *a* was maximum 30%, the level of carotenoids decreased more dramatically, by a maximum of 47%. As for chlorophyll *b*, its content in pine needles increased significantly, from 26 to 48% on all TS except TS 3 and 8, where its level increased slightly, only by 8%. Larch needles demonstrated the same tendency in reducing chlorophyll *a* content – its level fell to the greatest extent on TS 1, 2, 4, 5 (by 19–25%), and slightly on TS 3 and 8. Accordingly, pronounced changes in the ratio of chl *a* and chl *b* were observed. The percentage of carotenoid levels drop in general was slightly less than in pine needles – by a maximum of 39%. At the same time, there was a much greater increase in the content of chlorophyll *b* than in pine needles, by a maximum of 63% (TS 1), and a minimum of 10% (TS 3).

Table 3
The content of photosynthetic pigments (mg/g dry mass) in the needles of pine and larch trees growing in the urban forests of Irkutsk

Test site number	Chlorophyll			Carotenoids	% chlorophylls (*a* + *b*) in LCC
	a	*b*	Chl *a*/ Chl *b*		
Scots pine					
1	0.63 ± 0.02	0.34 ± 0.03	1.85 ± 0,11	0.23 ± 0.01	77.1 ± 3.12
2	0.65 ± 0.02	0.31 ± 0.04	2.10 ± 0,12	0.22 ± 0.02	71.0 ± 5.61
3	0.77 ± 0.02	0.25 ± 0.01	3.08 ± 0,13	0.33 ± 0.01	53.9 ± 2.33
4	0.61 ± 0.03	0.32 ± 0.03	1.91 ± 0,16	0.21 ± 0.01	75.7 ± 4.62
5	0.61 ± 0.03	0.33 ± 0.02	1.84 ± 0,07	0.20 ± 0.03	77.2 ± 4.65
6	0.68 ± 0.02	0.33 ± 0.03	2.06 ± 0,14	0.25 ± 0.01	71.9 ± 4.02
7	0.71 ± 0.02	0.29 ± 0.01	2.45 ± 0,15	0.29 ± 0.01	63.8 ± 2.44
8	0.78 ± 0.03	0.25 ± 0.02	3.12 ± 0,12	0.32 ± 0.01	53.4 ± 1.62
Background	0.86 ± 0.02	0.23 ± 0.01	3.74 ± 0,18	0.38 ± 0.01	46.4 ± 1.67
Siberian larch					
1	0.72 ± 0.02	0.31 ± 0.02	2.32 ± 0,11	0.27 ± 0.01	66.2 ± 2.9
2	0.76 ± 0.03	0.29 ± 0.02	2.62 ± 0,12	0.30 ± 0.02	60.8 ± 0.7
3	0.87 ± 0.04	0.21 ± 0.01	4.14 ± 0,13	0.34 ± 0.02	42.8 ± 1.2
4	0.7 ± 0.02	0.31 ± 0.02	2.26 ± 0,16	0.26 ± 0.01	67.5 ± 1.4
5	0.75 ± 0.02	0.28 ± 0.02	2.68 ± 0,07	0.23 ± 0.01	59.8 ± 0.7
6	0.82 ± 0.03	0.26 ± 0.01	3.15 ± 0,14	0.28 ± 0.02	53.0 ± 1.8
7	0.84 ± 0.03	0.25 ± 0.02	3.36 ± 0,15	0.29 ± 0.01	50.5 ± 1.3
8	0.91 ± 0.03	0.23 ± 0.02	3.96 ± 0,12	0.35 ± 0.02	44.4 ± 2.8
Background	0.93 ± 0.02	0.19 ± 0.01	4.89 ± 0,18	0.38 ± 0.01	37.3 ± 1.3

The analysis of the data obtained allows us to conclude that the most vulnerable component of pine and larch pigment complex is chlorophyll *a*. A significant decrease in its level can be caused either by the breakdown of its molecules or by synthesis deceleration under the influence of pollution (Tuzhilkina 2009). The reason for the decrease in carotenoids concentration may be their enhanced use for maintaining the photochemical function of chlorophyll *a*, particularly in case of absorbtion of toxicants from polluted air that initiate the formation of reactive oxygen species (ROS), since carotenoids extinguish the excited triplet states of chlorophyll and ROS (Mulenga et al. 2020). This is exactly the situation we observe in this case – the entry of toxic substances (pollutants) into the assimilation organs of arboreal plants. We have previously found that technogenic pollutants contribute to ROS formation in plant cells (Kalugina et al. 2021). As for chlorophyll *b*, the trend of its change is determined, apparently, by its greater stability, as well as by the performance of a compensatory role in reducing the concentration of chlorophyll *a* under various kinds of negative influences (Khanna-Chopra 2012). The important role of chlorophyll *b* is also indicated by its presence almost exclusively in light-collecting antenna complexes (LCCs). Our calculations demonstrate that a clear increase in the percentage of chlorophylls amount in pine (by an average of 22%) and larch (by an average of 19%) is mainly due to chlorophyll *b*, which allows us to infer that its protective role does grow with pollution of assimilation organs (see Table 3).

Disturbance of metabolism of pine and larch trees is also indicated by such a parameter as a change in the transpiration rate, which, first of all, characterizes the state of their water metabolism (Feklistov and Biryukov 2007). Since transpiration as an energy-dependent process is associated with photosynthesis, it could be expected to decrease in trees in an urban environment, which was proven by our study. A notable decrease in transpiration was found in both species, and the similarity is observed not only in the trend, but also in the degree of weakening of this process in almost all TS (by a maximum of 2.1 times), with the exception of TS 3 and 8, where this indicator changed slightly or remained at the background level (Fig. 10) A significant decrease in transpiration was also anticipated as the needles stomata on most TS are literally "clogged" with polluting suspended particles (PM).

Conclusion

The study of Irkutsk urban forests has shown that Scots pine and Siberian larch trees are polluted by aerosol particles of technogenic origin. In the atmospheric air of the city, the concentration of particles (PMx) of different sizes is high, especially that of finely dispersed particles ($PM \leq 2.5$ microns), and the AQI index can be 12–13 times higher than the background. PMx are intensively adsorbed by pine and larch needles, they can cover the surface of the needles almost completely. The chemical composition of PMx is very diverse, they can be roughly classed as carbonaceous (with a predominance of carbon in the composition), metallic (with a predominance of metals), polyelement (with different elements in approximately the same concentrations: carbon, HM, silicon, calcium, sulfur, chlorine, sodium, magnesium, potassium, fluorine). Direct correlations of a high level of significance between the concentration of aerosol particles in the air and the content of pollutants (HM) in pine and larch needles on test sites in urban forests were identified. These data indicate a well pronounced ability of pine and larch trees to purify polluted urban atmospheric air from suspended particles. Therefore, urban forests have a high ecosystem significance due to their function of natural phytofilters. However, chronic exposure to aerosol particles negatively affects the state of urban trees themselves, as evidenced by the following: decrease in the photosynthetic volume of tree crowns, functional disorders of photosynthesis, decrease in transpiration. Taking into account the results obtained, it is extremely important to find an approach to optimizing the status of urban trees. And in order to improve the city ecological environment, we recommend to expand the area of urban forests by creating artificial plantations that would be similar in structure to natural forest ecosystems.

Declarations

Acknowledgment

We thank M.M. Maslennikova, leading engineer at the Department of Ultrastructure of the Limnological Institute, Siberian Branch, Russian Academy of Sciences, Irkutsk for her help in the studies using scanning electron microscopy.

Ethical Approval

No ethical issues were violated in this study.

Consent to Participate

All authors agree to participate.

Consent to Publish

All authors agree for publication.

Authors Contributions

Tatiana Alekseevna Mikhailova: developed the idea of the paper, wrote the manuscript, **Olga Vladimirovna Shergina:** conceived the study, performed the experiments, data collection, statistically analyzed the data, and drafted the manuscript. The authors read and are in agreement of the final manuscript.

Funding

This work was supported by the Russian Science Foundation, project No. 22-24-00140.

Competing Interests

The authors declare no competing interests.

Availability of data and materials-missing

Not applicable' for that specific section.

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Figures

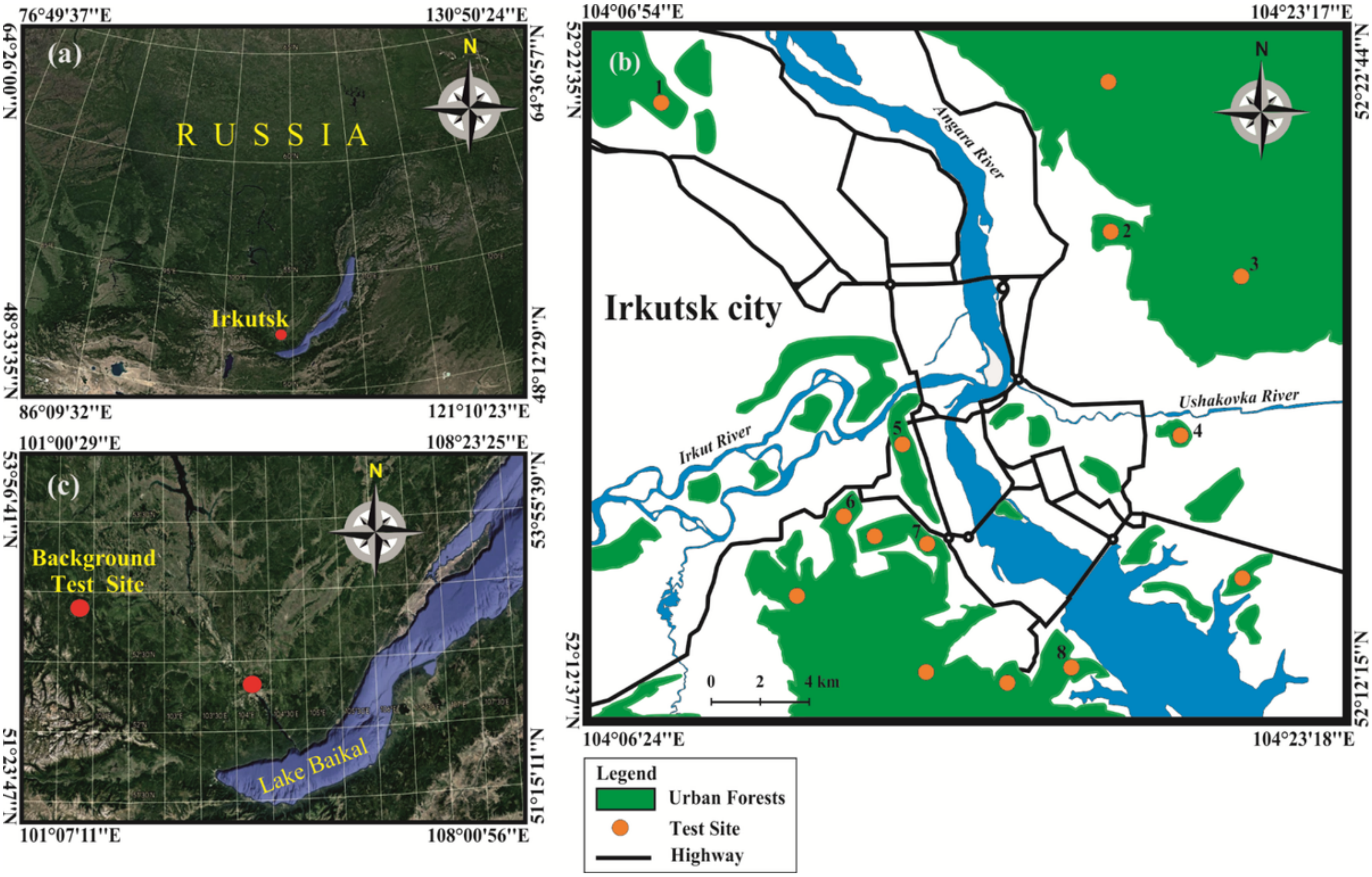

Figure 1

Map of the study area and location of test sites: Irkutsk city on the Russian territory **(a)**; representative test sites in the Irkutsk urban forests **(b)**, coordinates: No. 1 – 52°22'16"N 104°06'37"E; 2 – 52°19'46N 104°20'22"E; 3 – 52°18'17"N 104°21'19"E; 4 – 52°16'53"N 104°21'56"E; 5 – 52°17'04N 104°13'58"E; 6 – 52°15'35"N 104°13'39"E; 7 – 52°14'36"N 104°15'42"E; 8 – 52°13'07N 104°19'33"E; location of the background test site **(c)**.

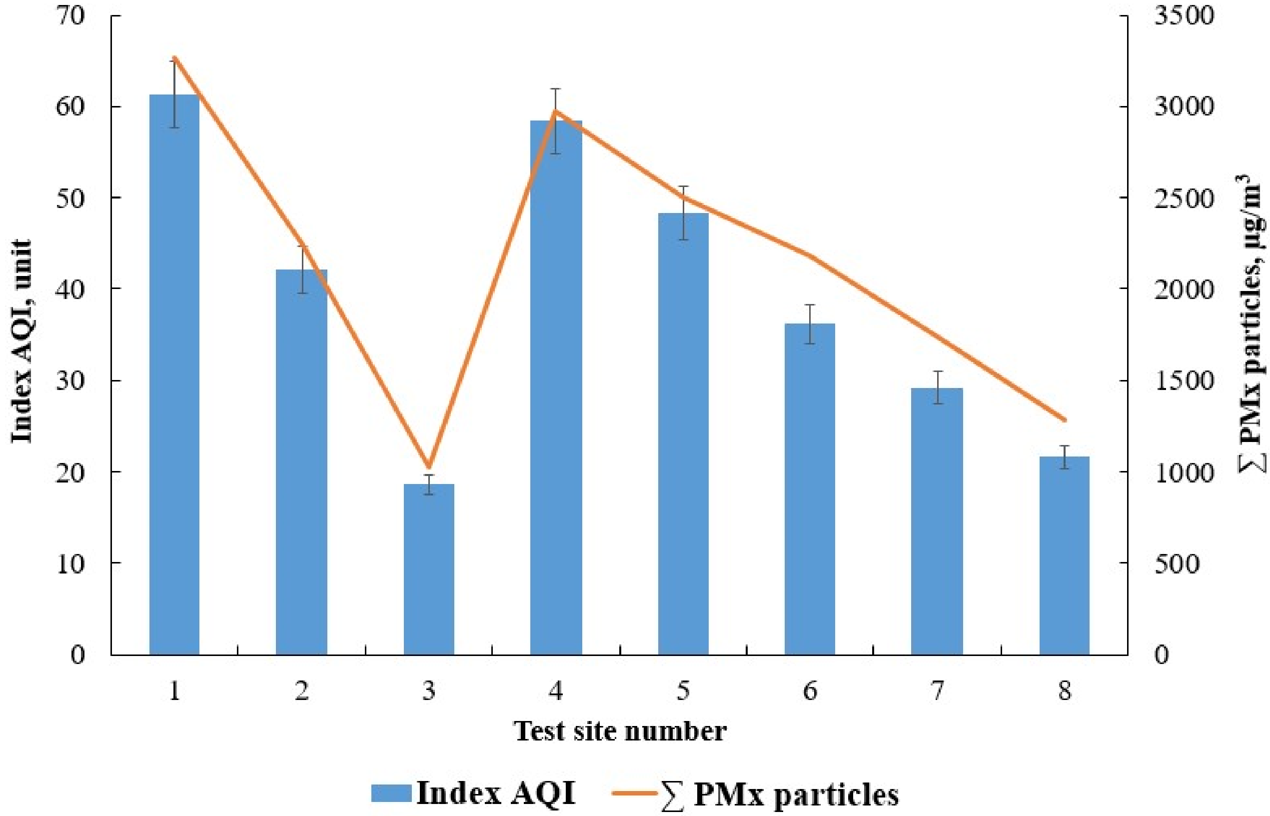

Figure 2

AQI index and concentrations of PMx particles in the atmospheric air (the average values for a summer period) at the test sites in urban forests of Irkutsk.

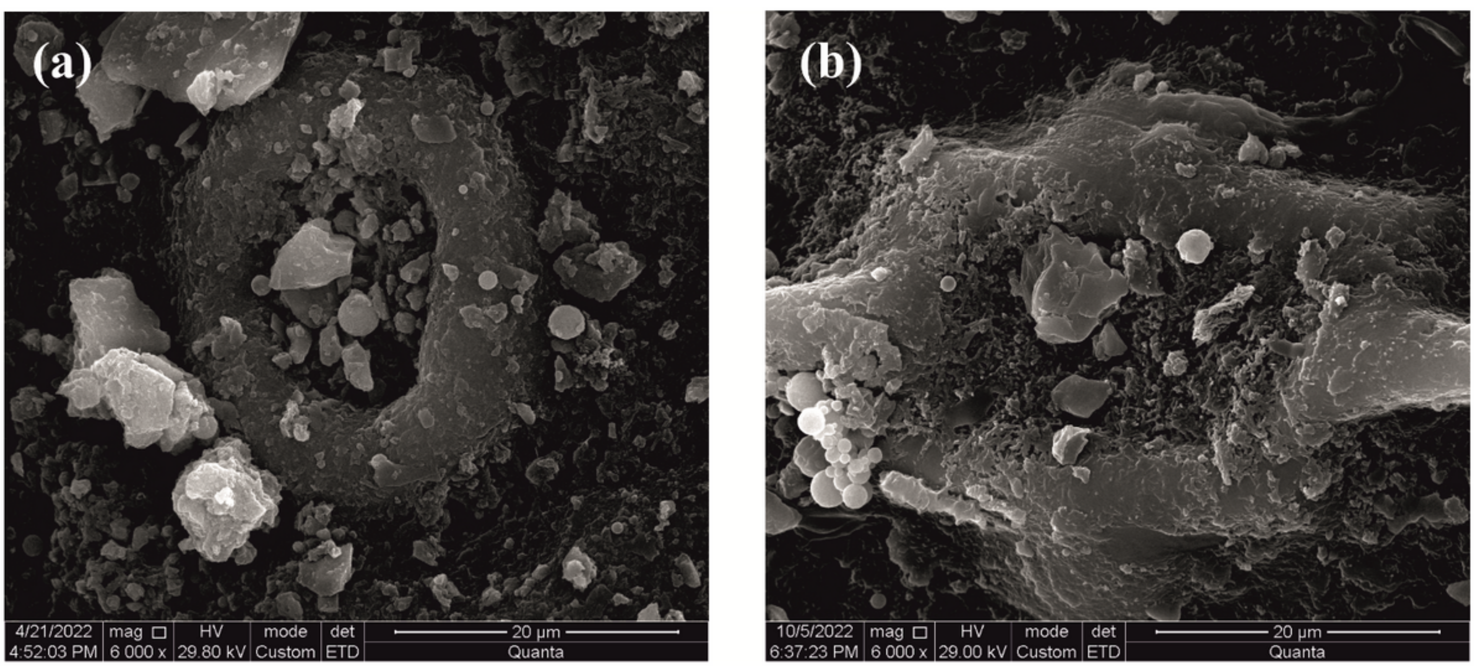

Figure 3

Stomata of pine **(a)** and larch **(b)** needles plugged up by aerosol particles.

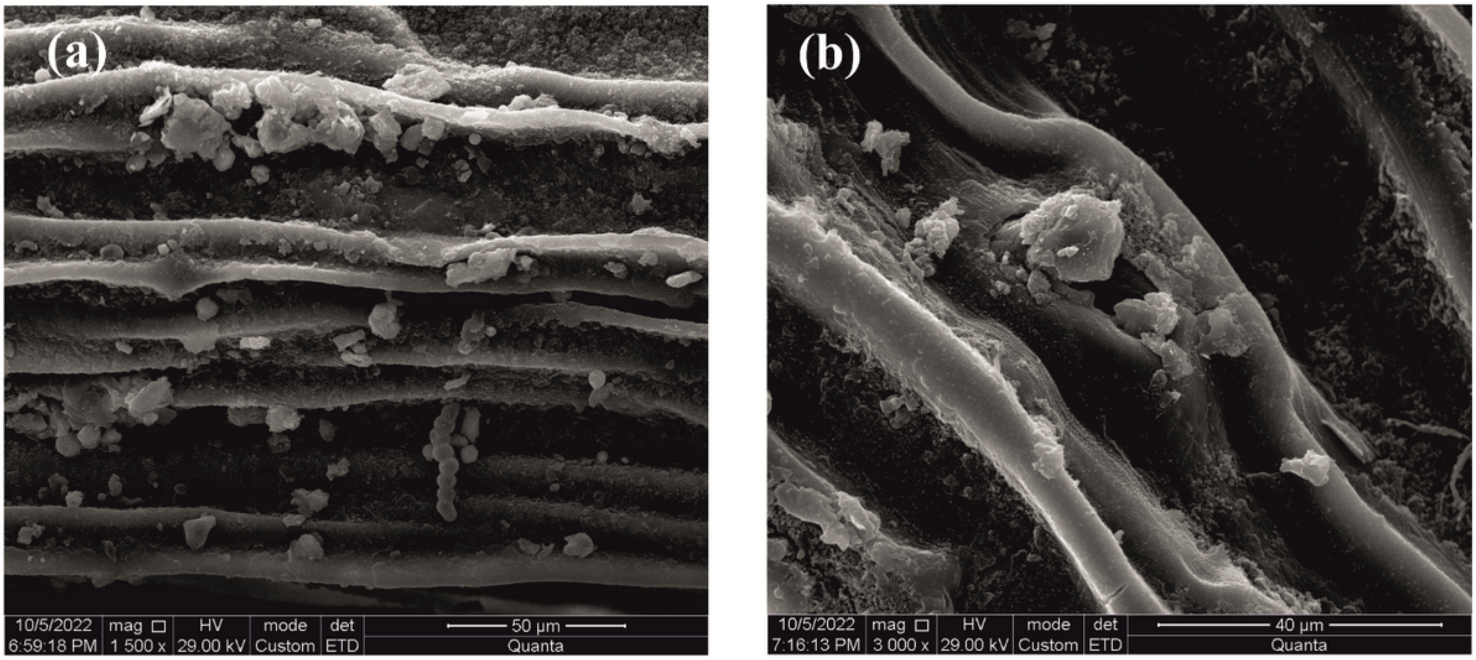

Figure 4

PMx particles on the folded surface of larch needles **(a)**, a stomata deformated **(b)**.

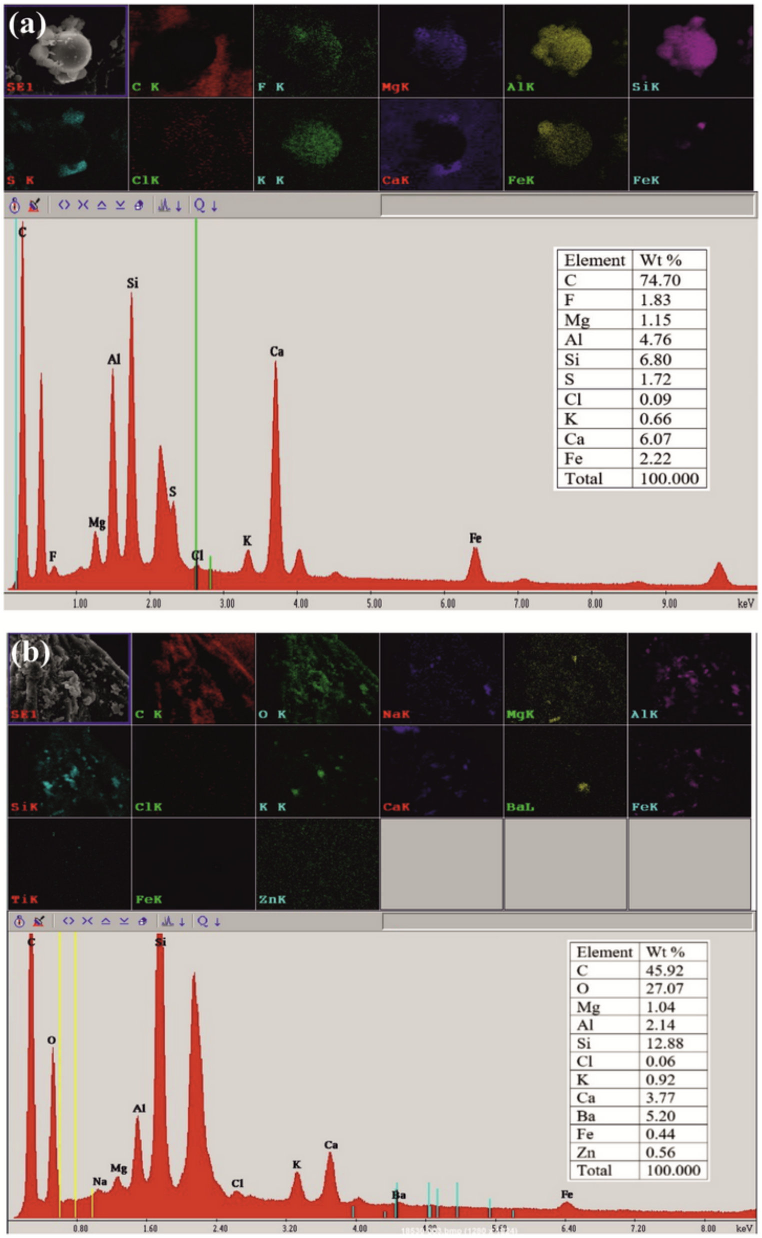

Figure 5

X-ray spectral microanalysis by SEM and EDAX of individual PM particles **(a)**, as an example – larch needle surface **(b)**.

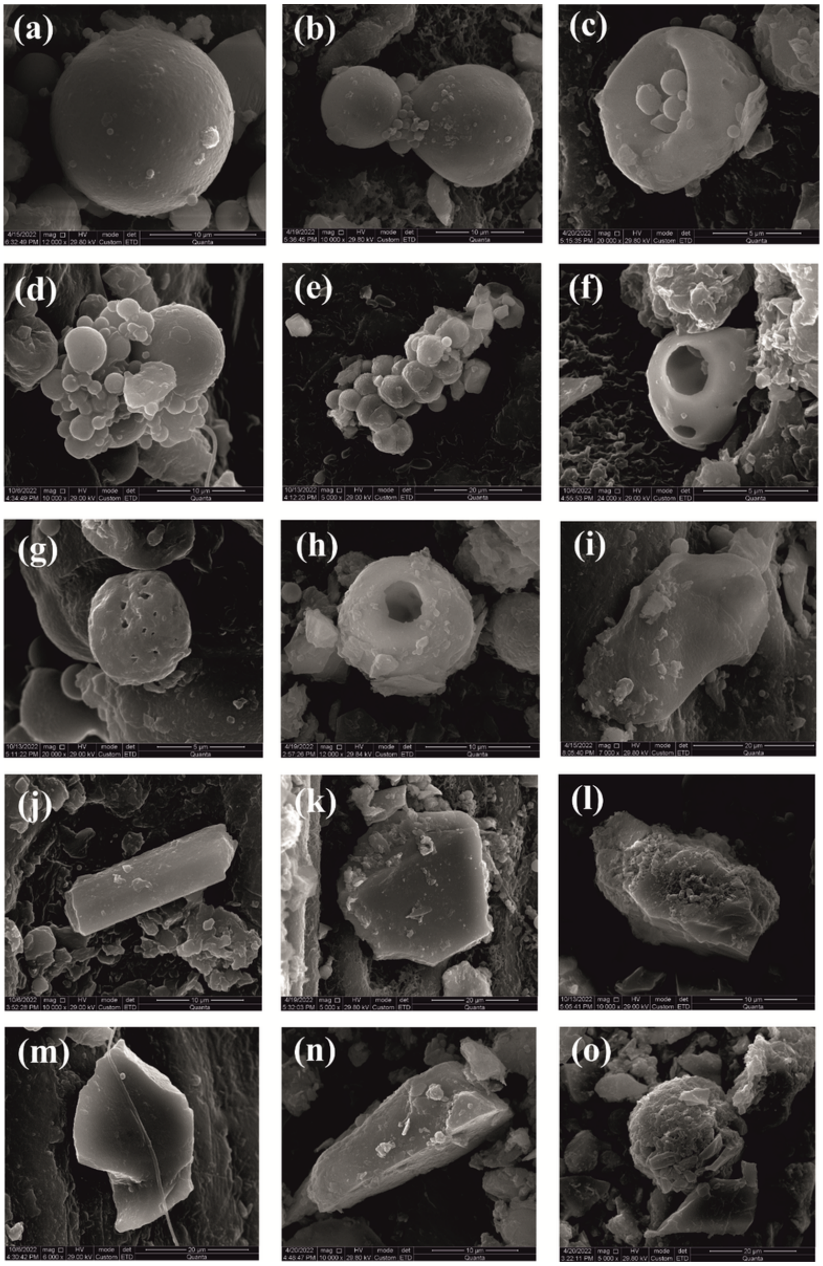

Figure 6

PMx particles of different shapes and chemical composition on the surface of Scots pine and Siberian larch needles of urban trees: **a, b, c, d, e** – metalized; **f, g, h** – carbonaceous; **i, j, k, l, m, n, o** – polyelemental.

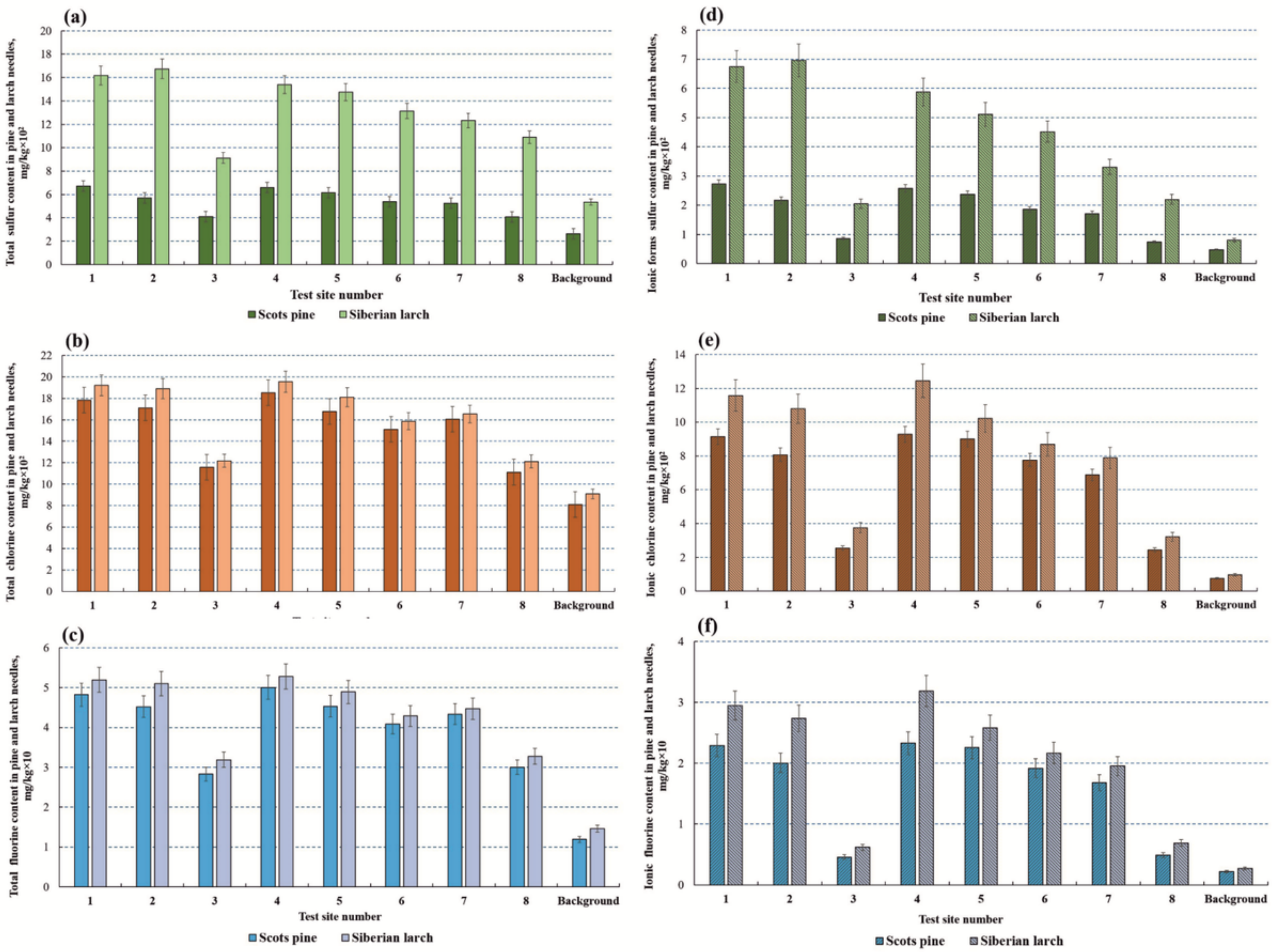

Figure 7

The total content of sulfur **(a)**, chlorine **(b)**, fluorine **(c)** and the content of ionic forms of sulfur **(d)**, chlorine **(e)**, fluorine **(f)** in the needles of Scots pine and Siberian larch.

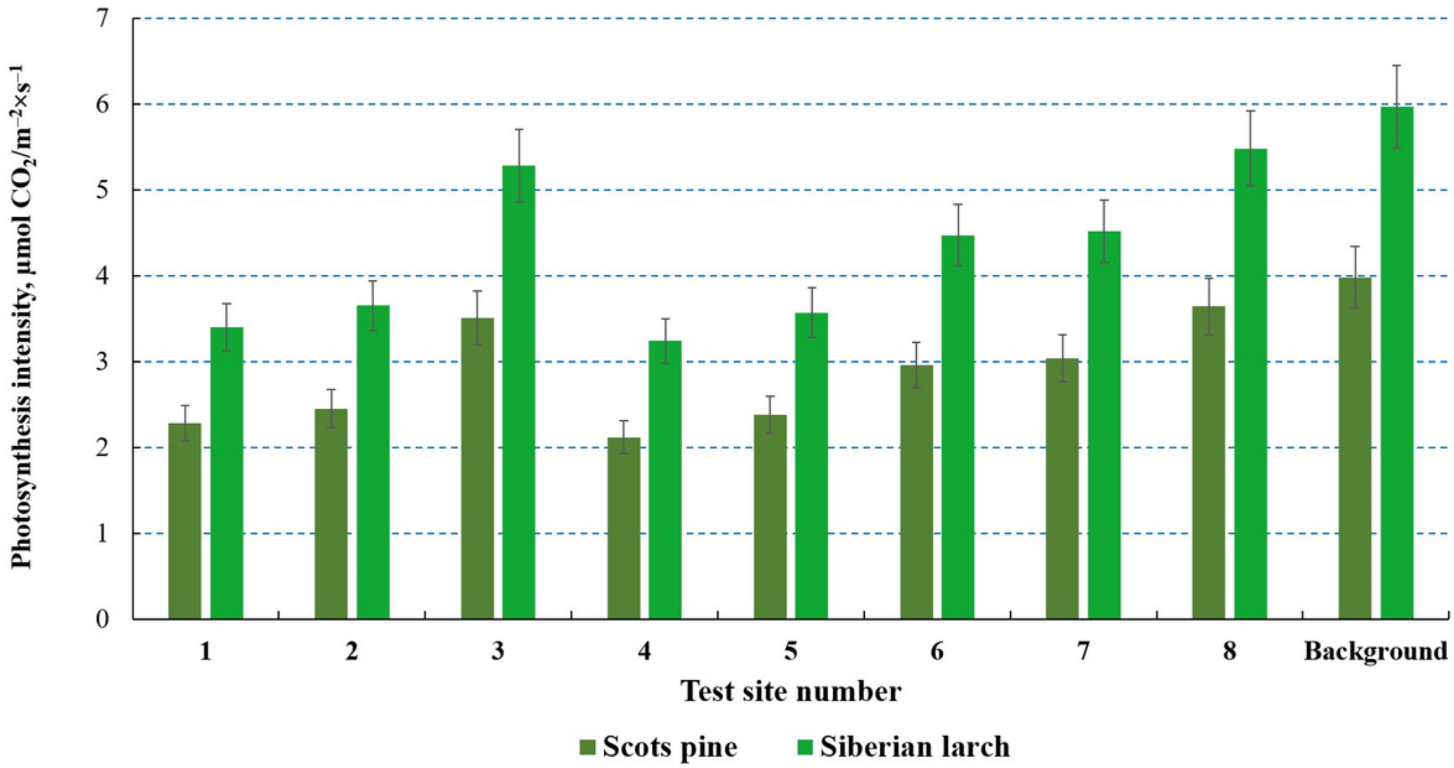

Figure 8

Photosynthesis intensity of Scots pine and Siberian larch in surveyed test sites in urban forests of Irkutsk.

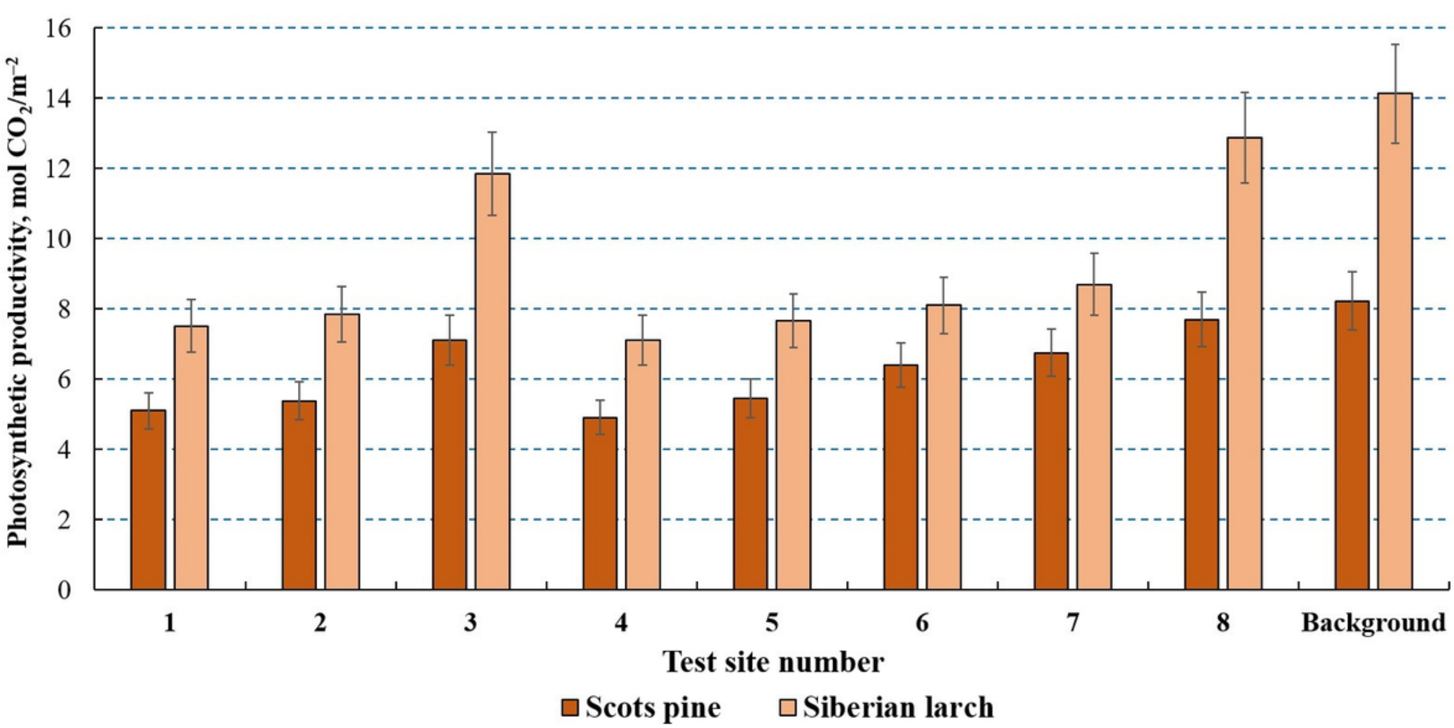

Figure 9

Photosynthetic productivity of Scots pine and Siberian larch in surveyed test sites in urban forests of Irkutsk.

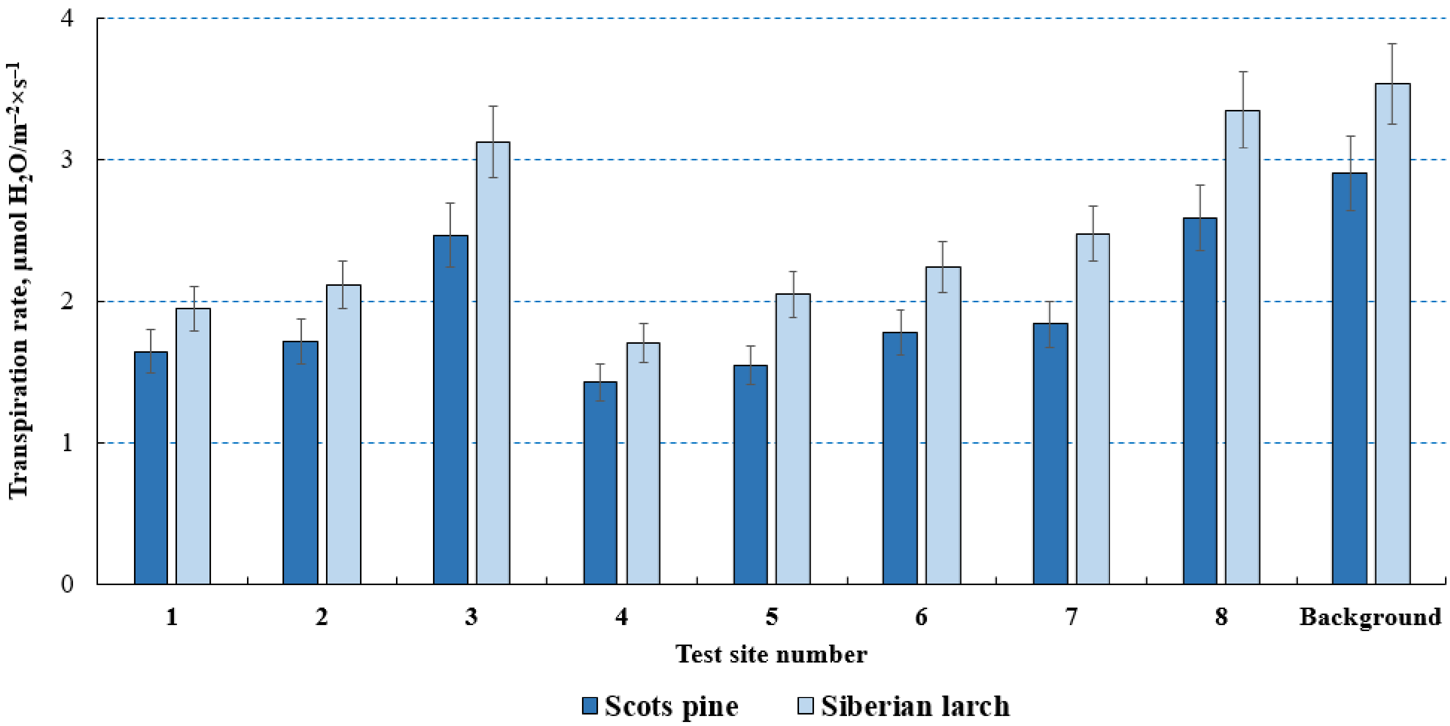

Figure 10

Transpiration rate of Scots pine and Siberian larch in surveyed test sites in urban forests of Irkutsk.