# MONITORING AIR QUALITY USING LICHENS IN CHELYABINSK, RUSSIAN FEDERATION

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**ABSTRACT:** Air pollution in large cities is one of the most serious ecological problems, because emissions always go into the atmosphere. One of the specific methods of pollution monitoring is lichen indication. The aim of the study is to evaluate the quality of the atmospheric air of Chelyabinsk city (Russian Federation). The results were obtained from samples collected in June-July 2015. The trees for the lichen sampling were chosen from the areas with different pollution levels: relatively clean, moderately polluted, hardly polluted. For the purposes of the comparison lichens were measured in Ilmen reserve, as the protected relatively clean territory. Using the method of lichen indication mapping we identified an indicator species *Parmelia sulcate*. Based upon epiphytic lichen distribution in sampling areas we distinguished several zones of atmospheric pollution: polluted zone, relatively clean zone, the cleanest zone. Lichen biodiversity and their projective cover are stated to decrease as the anthropogenic load is increasing. In urban and anthropogenic environment lichen population density is declining more intensively than the number of species. Also we measured elemental composition of lichens by X-ray fluorescence (XRF) analysis. We have studied the presence of heavy metals. Zink oxide, chrome and mangan oxide rate in the samples from environmentally troubled areas near steel factories and the power plantis almost twice higher.

Keywords: Lichens, Monitoring Air Quality, Bioindication, X-Ray Fluorescence Analysis

# 1. INTRODUCTION

In urban ecosystems most of the pollutants are spread by air. It calls for air emission monitoring. Today lichen indication is a priority area of modern eco-toxicological and monitoring researches. It is one of the promising and most developed ways of eco-monitoring which lets assess the industrial impact on the environment (including urban ecosystems) on a reliable and cost-efficient basis [1], [2].

There are several advantages of using lichens as bioindicators. First, these objects let forecast the pollution level in time, assess the dynamics of air quality. Secondly, there are many indicator values to assess the environment on the basis of lichen population [1], [2]. Due to the absence of root system lichens have atmospheric nutrition and their element composition reflects the integrated composition of chemical elements in the air in gaseous, dissolved, or particulate forms.

Lichens are a symbiosis of mycobiont and photobiont. They have been proved to be excellent bio-monitors because of their ability to accumulate chemical elements in concentrations exceeding their physiological needs and keep them in their thallus (body) for a long time. Since lichens have atmospheric nutrition, they get substances from wet and dry fallouts absorbing them by the whole thallus surface. That makes it possible to use lichens in large-scale mapping [3], [4].

Lichens are found in almost all geographical regions because they are resistant to extreme nature conditions. Today in Russia the use of lichens as bioindicators for the study of the dynamics of atmosphere pollution has been proved in some researches [5]–[7]. For the last 15 years in many cities of the Russian Federation lichens have been studied in detail. Romanova and Sedelnikova [8] examined the lichen population of large and small cities of Siberia. Biazrov [3], Anishchenko and Azarchenkova (Safrankova) [4] investigated the lichens of the South and North-West of Russia. They revealed bioindicators and biotic diversity indicators, measured lichen indication indices and zoned the territory according to the air pollution level [8], [9]. The comparative analysis of lichens growing in Tomsk Oblast allows for the conclusion that lichens form the areas of oil and gas exploration complex and Tomsk-Seversk industrial agglomeration has geochemical peculiarities [10]. Lichens data on the average content of chemical elements on the territory of Western Siberia are scarce and limited to a few metals [11].

The substances increasing atmospheric acidity and speeding up oxidizing, such as sulfur dioxide (SO<sub>2</sub>), nitrogen oxides (NO, NO<sub>2</sub>), fluoro- (HF) and chloride hydrogen (HCl), ozone (O<sub>3</sub>) are primarily known to have a destructive influence on lichens. Pollutants together with precipitation and dust penetrate into thallus from air. Among ecosubstrate groups, epiphytic lichens are the most sensitive to the change of chemical substances concentration in air. Lichens are stated to accumulate heavy metals from precipitation 2–5 times faster than higher plants, with epiphytic lichens being more intensive in the process than soil lichens [12]–[15].

There is no data concerning the use of lichens as air quality indicators in South Ural (Russia). Today such studies are of special importance because many large industrial cities with an intensive traffic are situated on the territory of South Ural. Chelyabinsk region (South Ural, Russia) has such specific industries as coal and nuclear energy facilities, steel mills, which are the sources of various gaseous and particulate pollutants into the atmosphere. These contaminants include a wide range of chemical elements, including rare and radioactive. These features of the region determine the need for air monitoring and analysis of atmospheric emissions.

Chelyabinsk, for example, is a large industrial city with a steelworks, three power stations and other industrial facilities. The present study contains an X-ray fluorescence analysis of lichen element composition in some sites of Chelyabinsk. Numerous studies shown the need to study regional geochemical background at evaluation of the effectiveness of the anthropogenic load [16]. That is why the Ilmen State Reserve (located near Chelyabinsk) was taken as the unpolluted control site.

The aim of the paper is to study the potential use of lichens as biomonitors of urban air quality as exemplified by Chelyabinsk.

# 2. METHODS

## 2.1 Methods of Sampling

The research methods included describing the structure of epiphytic lichens along the gradient "pollution source – background". Sampling sites of  $20x20 \text{ m}^2$  were laid in the vegetation period of June – July 2015 on the territory of Chelyabinsk and the Ilmen State Reserve (the control site) (Fig.1). The territories under research varied in the degree of anthropogenic influence. We described the lichen synusiae from four aspects at the height of 1.0–1.5 m from the base of the tree trunks. All the epiphytic lichens met on the sampling trees were considered. The samples were hermetically packed in plastic bags. In the laboratory we removed bark, needles and other impurities from the samples and dried them.

The species activity was assessed on the basis of its occurrence on the sampling trees and its projective cover. A five-grade scale was used to measure each species activity: 5 – highly active (it is rich in frequency of occurrence on all the sampling trees, and covers the tree trunks and/or lower branches to 50 %); 4 – active (it occurs on most of the sampling trees, and covers the trees to 10 %); 3 – moderately active (its frequency of occurrence is 50–30 %, but it has a low level of cover (5-1 %); 2 – low active (its frequency of occurrence is 30–10 %, and it covers the trees to less than 1 %); 1 – not active (it rarely occurs (less than 10 % of trees), just small thallus, its projective cover approaches zero) [17].

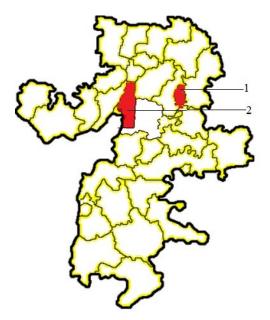


Fig.1 Map of Chelyabinsk region: 1 – Chelyabinsk city, 2 – Ilmen State Reserve

### 2.2 Methods to Assess Occurrence

The software used in the work included Microsoft Word, Microsoft Excel, GRAPHS. The following statistical parameters of element distribution were calculated in terms of the obtained results: mean, standard error, standard deviation.

## 2.3 X-Ray Fluorescence Analysis

Air dried lichen samples were burnt in a muffle furnace at 550 °C. The lichen ash was ground in a mortar. The finely ground rock powder, mixed with a small amount of polyvinyl alcohol dissolved in water, was compressed using a hydraulic press into a pellet.

XRF patterns were registered in the lab of Center for Nanotechnology at South Ural State University. Rigaku SuperMini200 XRF Spectrometer was used for XRF analysis. The relative standard results deviation was not more than 5 %.

#### **3. SITE CHARACTERISTICS**

Chelyabinsk city is situated in forest steppe zone of South Ural. It is a large industrial city with a developed traffic network. There are studies showing the effect of the speed of vehicular traffic to emissions. The higher the average speed of vehicles, the lower the emission of air pollutants [18].

To analyze the chemical composition of lichen thallus we selected average samples from the typical habitats within the urban ecosystems: Site 1 is a city pine forest; Site 2 is a city park; Site 3 is the territory of the steelworks; Site 4 is the territory of a transport hub in the city centre; Site 5 is the territory near a power station (Fig.2).



Fig.2 Map of Chelyabinsk city and location of the sampling stations (Site 1–5)

The city pine forest (Site 1) is a relict pine forest at the western part of Chelyabinsk. It stretches from North-East to South-West for about 5.5 km. Its width is about 2 km. The Victory Park (Site 2) is a city park which occupies more than 19 hectares. The Chelyabinsk steelworks (Site 3) is one of the largest steel manufacturers in Russia. Its area is more than 22 km<sup>2</sup>. The transport hub (Site 4) in the city centre covers the city major avenue with adjusting highways. The territory of the power station (Site 5) is to the South-East of Chelyabinsk.

The Ilmen State Reserve is located on the eastern macroslope of South Ural. It's a part of the South Ural physiographic region of the Ural highlands. The Ilmen State Reserve is of an utmost importance as a gene bank preserving flora. It serves as a standard of undisturbed and relatively undisturbed vegetation communities of the South Ural pine and birch forests that are seriously damaged nearby. The Reserve is a refuge for many endemic and extinct plants and for rare and protected species. The scientific and production center of the South forestry in Ilmen State Reserve was Site 6. It was the control site.

# 4. RESULTS AND DISCUSSION

Using the method of lichen indication mapping on the territory of the Ilmen State Reserve (Site 6) we identified an indicator species *Parmelia sulcate* [19]. To detect the chemical composition more than 300 samples of *Parmelia sulcate* were gathered and described. To map the zones of urban pollution we relied on the lichens idiosyncrasies to accumulate pollutants in thallus [20]–[22]. We found out *Parmelia sulcate* in all the sites. But we should admit that there are few lichens on the territory of the city (Site 3, Site 4, Site 5).

That species, at the same time, is dominant in epiphytic lichen population in the background zone (Site 6). It is rich in occurrence with the rate of 3–5. Based upon epiphytic lichen distribution in sampling areas we distinguished several zones of atmospheric pollution. The first (polluted) zone includes the territory near the steelworks (Site 3), the territory of the power station (Site 5) and the transport hub (Site 4). The second (relatively clean) is a park territory (Site 2). But as far as the park is located in the anthropogenic zone of the city, the values under research are close to the limits. The third (the cleanest) zone corresponds to the background territory (Site 6) and the city pine forest (Site 1).

Lichen biodiversity and their projective cover are stated to decrease as the anthropogenic load is increasing. Lichenometry survey showed that the average cover degree of points, located close to the railroad, was 9.2–19.0 %. The maximum cover degree (67.0–82.8 %) and maximum score of 5 were registered in the points far from the railroad. Previous studies have shown that the intensity of human impact affects the projective cover of lichen trees [23].

The list of epiphytic lichens of the South part of the Ilmen State Reserve includes 31 species of 18 genera, 10 families. The basis of the epiphytic lichen flora under study (51.6 % of the whole species composition) is made by taxons of *Lecanorales* order (16 species of 9 genera, 4 families). The second in species diversity is *Caloplacales* order including 10 species of 6 genera, 3 families that accounts for 32.3 % of the whole species composition. *Stictalis* order includes 16.1 % of epiphytic species [23].

*Parmeliaceae* family (4 genera, 9 species, 29.0 %) is the most numerous in species diversity. *Phisciaceae* family (4 genera, 8 species, 25.8 %) is a bit less as well as *Usneaceae* family (3 genera, 4 species, 12.9 %). Other families are not diverse (3.3 % each) containing only a single genus each [23]. Lichen indication mapping of the researched territory of the Ilmen State reserve was applied to identify *Parmelia sulcate* as an indicating species. Epiphytic families ratio is graphically represented in Fig.3.

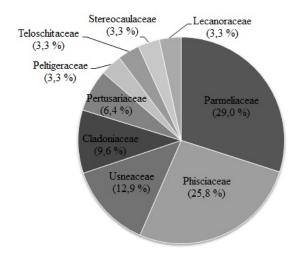


Fig.3 Epiphytic families ratio

In urban and anthropogenic environment lichen population density is declining more intensively than the number of species. For example, in the city pine forest and the city park lichen population density is rather high, but the average projective cover of lichen synusiae is essentially lower than on the background territory (the Ilmen State Reserve) (Fig.4). In addition, the share of the trees without lichens is much bigger (64.2 %) in contrast to the background lichen communities of the Ilmen State Reserve where that value doesn't exceed 12 %.

Within the city the share of the trees with lichens is definitely rich. The city pine forest has the largest number of the trees with lichens (82 %), the city park – 46 %. There are far fewer such trees in the buffer zone of the steelworks (27 %) and the adjusting territory of the power station (14 %). Lichens occurred there in small thallus on 1-2 trees of 10. Lichens were rarely found (10 % of trees). They are in a poor condition.



Fig. 4 Average projective cover of lichen synusiae in the city pine forest (a) and in the Ilmen State Reserve (b)

Some authors in their works insist not to overestimate the role of lichens as bioindicators. Byazorov says empirical indices and correlation with the concentration of some xenobiotics are locally important. He also notices that regularities set in some regions can't always work in others [2], [3], [9]. There isn't enough data about the impact of some elements where there are other elements in the environment. And there is little information about the pollutant transformation under the environmental factors. Some organic compounds may form from 16 to 20 transformation products some of which may be more toxic and harmful than the original substance [3]. For example, the engines of modern cars emit a lot of organic compounds such as benzene, toluene, phenol, which as a result of active chemical interactions can quickly turn into substances more toxic than the original.

To make the comparative analysis more reliable we used *Parmelia sulcate* as the species occurred in all the sites, as morphological and physiological properties of each species influence the accumulation of elements in lichen thallus. The ration analysis of oxides in mixed sampling of epiphytic lichens in summer showed that lichen accumulation of mangan, zink, cuprum and chrome might be related to the environmental load. The average rate of copper oxide and silver oxide in samples is small (Table 1).

But cuprum and silver in lichen even in small concentrations are known to make cell membrane more permeable and therefore they "push off" potassium more intensely than other metals. In fact the increase of cumulative percent of these oxides in samples leads to the decrease of potassium oxide rate.

Zink oxide rate in the samples from environmentally troubled areas is almost twice higher (Fig.5). For example, zink oxide rate of the background territory is 0.86 %, that rate in lichen samples gathered from the trees of the territory near the power station is 1.74 %. Chrome and mangan oxide in the anthropogenic sites is two and more times higher.

Oxide	Sites					
	1	2	3	4	5	6
MgO	0.94	2.26	3.12	2.13	2.79	1.6
$Al_2O_3$	8.21	17.52	10.67	14.51	16.43	9.6
$SiO_2$	16.70	31.89	28.53	27.13	19.54	16.34
$P_2O_5$	3.37	2.93	1.74	2.13	2.67	4.98
$SO_3$	3.66	3.58	7.04	3.29	5.28	4.15
Cl	0.72	0.48	1.34	0.71	1.30	0.78
$K_2O$	6.51	6.49	3.24	4.23	5.32	9.67
CaO	34.65	10.74	8.65	9.76	12.74	23.64
TiO <sub>2</sub>	2.50	1.6	3.24	3.12	2.95	2.85
MnO	1.00	0.45	1.96	2.01	2.04	0.87
$Fe_2O_3$	18.46	20.33	25.56	26.41	24.45	23.10
ZnO	1.02	1.02	1.56	1.43	1.74	0.86
SrO	_	_	_	_	_	0.11
Ag <sub>2</sub> O	0.51	0.33	0.42	0.31	_	0.41
CuO	_	0.33	0.51	0.49	0.47	0.63
CrO	1.70	_	2.10	2.11	2.14	0.36
$ZrO_2$	0.05	0.05	0.23	0.16	0.14	_
$Y_2O_3$	_	_	0.09	0.08	_	0.05

Table 1 The content of oxide in the sol lichens

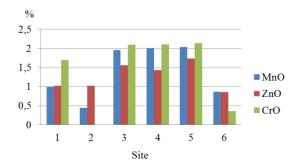


Fig.5 The content of oxide (MnO, ZnO, CrO) in the sol lichens

Three zones different in chrome and mangan rate are distinguished: relatively clean (to 0.9 %) – the background territory; moderately polluted (from 1.0 % to 1.9 %) – the city pine forest; significantly polluted (from 2.0 % to 2.9 %) – the territory of the steelworks (3), transport hub in the city centre (4), power station (5).

## 5. CONCLUSION

The chemical lichen monitoring revealed a trustworthy difference between the rates of metal oxides in lichen thallus gathered on the territories of the Reserve and the city. To detect the degree of pollution chrome and copper oxide rates in *Parmelia sulcate* thallus may be used. The use of these oxides to give a similar characteristic of the territory pollution based on other lichen species considers revising.

The study revealed the main regularities of the lichen distribution on the territory of Chelyabinsk.

Environmental assessment of the territory of Chelyabinsk was conducted. Zones of significant pollution covering not only the surrounding areas of industrial objects and highways but also parks and residential areas are characterized by a comparatively large territory. The results indicate strong negative effect of atmospheric pollution on most natural and artificial plant communities located within the city limits. With the increase of anthropogenic load there is a tendency towards the decrease of lichen species diversity and the amount of trees with lichens. The projective cover of lichen groups and the amount of trees with lichens are more informative, in comparison with species diversity.

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