Peer-reviewed version available at Atmosphere 2017, 8, 119; doi:10.3390/atmos8070119

Air Pollution Monitoring in the South-East Baltic Using the Epiphytic Lichen *Hypogymnia Physodes*

Yulia Koroleva *, Vladimir Revunkov

Immanuel Kant Baltic Federal University, Kaliningrad 236016, Russia; subjke@mail.ru

* Correspondence: Yu.koroleff@yandex.ru

Abstract

Epiphytic lichens are well-known indicators of air contamination. The chemical composition of lichens is affected by the concentration of pollutants in the environment. Usually, researchers assess long-term variations in trace elements or other pollutants in the study area or identify the spatial features of air contamination. The aim of this study is to create a database of trace element concentrations in the samples of the epiphytic lichen *Hypogymnia physodes* growing in the Kaliningrad region. The database can be used as a 'reference point' for monitoring studies. Another objective is to identify the spatial patterns of iron, manganese, nickel, cadmium, silver, lead, strontium, rubidium, and calcium in the Kaliningrad region. The samples of wild lichens were collected from pine and birch trees 1.2-1.8 m from the bases of the threes, using a regular grid, in August 2010. One-two-year-old thalli were used in the chemical analysis. The metals Ag, Cd, Cu, Pb, Ni, Fe, Mn, and Zn were determined by AAS (Mn, Fe by flame AAS and the others by ETA-AAS) and the elements Sr, Rb, and Ca by X-ray fluorescence. The concentration of metals in the western coastal area (the Sambian or Kaliningrad Peninsula) is higher than it is in the central and eastern parts of the region. Principal component factor analysis was carried out to detect and characterise different pollution sources and to identify the most polluted areas. The factors of metal emission were described. The authors examined the features of the spatial distribution of trace elements. Prevailing winds are form south-west. Therefore, the highest concentrations of trace elements were found on the Sambian peninsula and on the coasts of the Vistula and Curonian Lagoons. The high concentrations of trace elements in the samples of the lichen *H.physodes*, which were observed in the coastal part of the region, are associated with human impact and subsequent pollution. The chemical composition of lichens on the Sambian peninsula may have developed under the impact of both local pollution sources – vehicles, thermal energy facilities, and ports – and such factors as transboundary traffic and sea spray.

Keywords: air pollution; monitoring; lichen; Hypogymnia physodes; trace elements; South-East Baltic

1. Introduction

All living organisms respond to changes in the environment and lichens are no exception [1-3]. Their sensitivity to atmospheric pollution is explained by their physiological features. Lichens are symbiotic associations of fungi and algae – any impact can change the balance between them and thus affect a lichen's viability. Different lichen species can be used to assess environmental contamination [4-6]. The concentration of contaminants in lichens is affected by several factors: the absorption of atmospheric aerosols and gases by the entire surface of thalli and the dehydration of lichen tissues [7-9]. The substrate does not serve as a significant source of metals for lichens. However, this assumption has been questioned in some works [10-13]. The sources of heavy metals, the mechanisms of heavy metal accumulation and detoxification by lichens, and lichen's bioaccumulation capacity have been discussed in a number of works [14-20]. The biochemical composition, physiological processes, anatomical and morphological characteristics, population

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 18 May 2017 doi:10.20944/preprints201705.0138.v1

Peer-reviewed version available at Atmosphere 2017, 8, 119; doi:10.3390/atmos8070119

structure, species composition, and structure of lichen communities change under the influence of pollutants.

The chemical composition of lichens is affected by the characteristics of their habitat. Thus, epiphytic lichens are used as indicators in air quality monitoring [21-26]. Lichens help to determine long-term variations in the level of contamination in the study area, to examine the spatial variability of chemical composition, and to identify the effects of specific pollutants [27-29].

This work aims to create a database of trace element concentrations in the thalli of the lichen *Hypogymnia physodes (L.) Nyl*. in South-East Baltic (Kaliningrad region, Russia). Such a database can be used as a 'reference point' for monitoring, studying, and investigating trends in the concentration of trace elements in the Kaliningrad region.

2. Materials and Method

2.1. Sampling sites

The Kaliningrad region is Russia's westernmost territory situated on the southeastern coast of the Baltic Sea. The region borders Poland in the south and Lithuania in the north and the east. Westerly winds and marine aerosols of the Baltic Sea dominate the climate in the region and determine the atmospheric transport and the deposition of trace elements.

Only 17% of the territory of the region is covered by forests. These are secondary forests, predominantly mixed coniferous-deciduous ones. Most large forested areas are located in the southeastern and southwestern parts of the region.

There are no large industries in the region. The exceptions are agriculture and extraction, the latter producing amber, peat, and oil. The western part of the region is highly urbanised, whereas the coastal part of the Kaliningrad (Sambian) peninsula is home to numerous resorts. The level of human impact is decreasing from west to east. The east of the region is exploited for agriculture.

2.2. Sampling procedure and the method of analysis

The epiphytic lichen *H. physodes* was chosen as a bioindicator of air contamination in the Kaliningrad region. The lichen is widely distributed and resistant to impurities in the air – thus, it has been commonly used in regional studies on heavy metal deposition [30-33].

The samples of the lichen *H. physodes* were collected from 54 forest plots measuring 50*50 m, using the existing monitoring grid (Figure 1). This grid has been employed from 1999 to monitor trace elements in the atmospheric transport and deposition [34-36]. Samples were taken from birch and pine trunks, 1.20 - 1.80 m from the bases of the trees, in 2010. The sampling period was very short – it did not exceed two weeks. The plot location was marked using GPS. The distance from the local sources of pollution, roads, residential housing, and agricultural areas was taken into account [37]. The sampling rules were as follows: 3-5 samples of lichens were taken from one plot (from 3-5 trees); the youngest part (edge) of the lichen thallus was cut; the samples of lichen were packed in a paper bag.

Peer-reviewed version available at *Atmosphere* **2017**, *8*, 119; doi:10.3390/atmos8070119

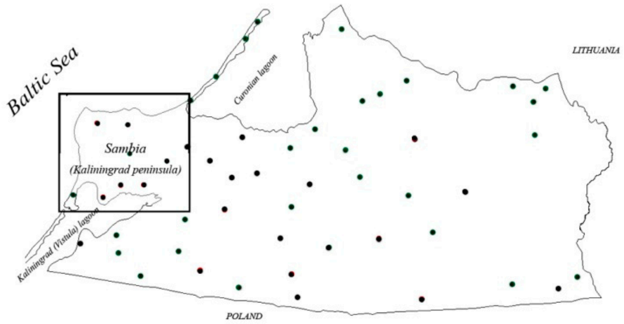

Figure1. Monitoring grid.

The unwashed 1-2-year-old lichen thalli were used in analysis, after being freed from extraneous materials such as tree bark. The samples were dried to constant weight at 40°C for 24 h and later homogenised. A wet digestion of the homogeneous sub-sample was carried out. A sample preparation method was developed. About 0.5 g of lichen was transferred to tubes, and 7 ml of nitric acid were added. Opened tubes were left at room temperature for 12 h, then the temperature was increased to 135°C for 15 min, and the samples were digested for 15 min at 135°C. After that, the solutions were cooled, 2 ml of hydrogen peroxide were added, and the temperature was increased to 190°C. As the volume of acid decreased, the colour of the solution became lighter. The mass obtained was transferred to 25-ml volumetric flasks and filled to mark with osmosis-treated water. For the analysis by X-ray fluorescence, the samples of lichens were dried and pressed.

The concentration of Ag, Cd, Cu, Pb, Ni, Fe, Mn, Zn were determined by AAS (Mn, Fe by flame AAS, and others by ETA AAS) and that of Sr, Rb, Ca by X-ray fluorescence.

2.3. Quality control

The quality control of the sample preparation and AAS and X-ray fluorescence results was ensured by using reference samples (the Canadian waterweed CW-1, SSS 8921- 2007 and the birch leaf LB-1, SSS 8921-2007). In addition, blanks were measured parallel to the decomposition and analysis of the samples.

2.4. Data processing

Spatial distribution and multivariable data can be examined using various statistical analysis techniques and the principal component analysis in order to reveal the underlying deterministic behaviours and thus help to establish a cause-and-effect relationship between the data and environmental problems. GIS software systems – namely, the ArcGis and QGIS Brighton – were used to draw element distribution maps for the Kaliningrad region.

3. Results and Discussion

The concentrations of such elements as iron, manganese, zinc, nickel, strontium, rubidium, and calcium were determined in the lichen samples collected across the study area, whereas cadmium, lead, copper, and silver concentrations were determined only in the lichens of the Sambian peninsula. Tables 1 and 2 show the results of the descriptive statistical analysis of heavy metal concentrations in the samples.

 doi:10.20944/preprints201705.0138.v1

Peer-reviewed version available at *Atmosphere* **2017**, *8*, 119; doi:10.3390/atmos8070119

Table 1. Element concentrations in the *H. physodes thallus* in the Kaliningrad region, µg/g DW.

	mean	SD	SE	CV,%	median	max	min
Fe	446	183	33	41	399	1135	180
Mn	200	135	25	72	187	455	33
Zn	83	47	8	56	78	298	33
Ni	1.30	0.63	0.11	56	1.30	2.43	0.013
Sr	10.1	4.79	0.92	47	8.96	18.6	4.45
Rb	9.74	4.59	0.82	47	10.5	19.9	1.28
Ca	1203	817	140	68	980	2995	219

Table 2. Concentrations of trace elements in the *H. physodes thallus*, in the sambian peninsula, µg/g DW.

	mean	SD	SE	CV,%	median	max	min
Ag	0.051	0.024	0.009	47	0.040	0.095	0.032
Cd	0.194	0.040	0.016	21	0.185	0.263	0.146
Pb	6.57	2.36	0.96	36	7.15	9.03	3.50
Cu	7.91	1.21	0.49	15	7.83	9.94	6.69
Mn	313	253	103	81	259	664	74.2
Ni	1.64	0.549	0.225	34	1.611	2.43	0.941
Zn	79.5	22.7	9.26	29	87.7	100	45.6
Sr	15.0	10.3	4.22	69	10.7	31.5	6.38
Rb	12.2	5.59	2.28	45.8	10.9	22.6	5.69
Fe	610	279	114	45.7	526	1135	339
Ca	1253	0.855	0.349	68	1118	2684	375

The results of chemical analysis were used to draw maps of element distribution in lichens. The prevailing SW winds determine the element distribution in the lichens of the Kaliningrad region. The study areas stretched from west and south-west to northeast. Higher concentrations of such trace elements as cadmium, nickel, iron, copper, and lead were observed on the Sambian peninsula and on the coast of the Vistula and Curonian Lagoons.

3.1. The spatial distribution of elements

The iron concentration in the thalli of *H. physodes* varied from 180 to 1135 µg/g DW. The maximum concentration was observed in the area stretching from the centre of the Sambian peninsula towards the coast of the Vistula Lagoon and the northern coast of the Baltic Sea. High iron levels were observed on the southern coast of the Curonian Lagoon, which lies below sea level. The coefficient of variation was below 50%. Therefore, the iron content in lichens did not change across the studied territory. The high iron concentrations can be explained by the geological features [38] – carrstones and iron-manganese nodules. The high iron levels in soils and water pose a serious challenge to the region. Iron concentrations in lichens decrease from south-west to northeast (Figure 2).

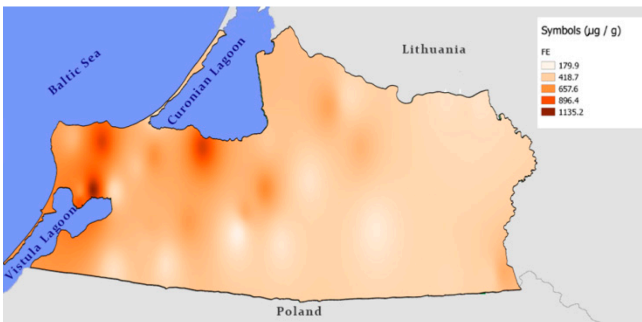

Figure 2. The distribution of iron in the thalli of *H. physodes* in the Kaliningrad region, 2010.

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 18 May 2017 doi:10.20944/preprints201705.0138.v1

Peer-reviewed version available at Atmosphere 2017, 8, 119; doi:10.3390/atmos8070119

The nickel concentrations are estimated at hundreds or even thousands of mass units, depending on the time of exposure and the distance from the source of emission in the contaminated areas of nickel accumulation [25]. The concentrations of nickel in the Kaliningrad region varied from 0.013 to 2.43 µg/g. The coefficient of variation was 56%. The pattern of nickel concentration distribution in the lichens of the Kaliningrad region did not differ from that of iron. The highest nickel concentrations in lichen thalli were observed in the western and southwestern part of the region – on the Sambian peninsula and on the coasts of the Vistula and Curonian Lagoons (Figure 3).

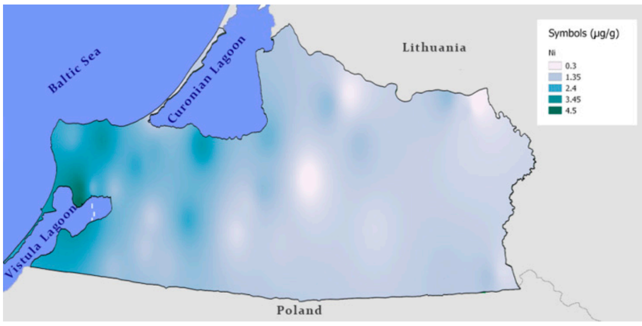

Figure 3. The distribution of nickel in the thalli of *H. physodes* in the Kaliningrad region, 2010.

The average manganese concentration is 200 µg/g DW. The coefficient of variation is 72%, which reflects the heterogeneity of manganese concentration in the lichen thalli. The highest manganese levels (above 450 µg/g) were found on the Sambian peninsula, on the coast of the Curonian Lagoon between the Rivers Deima and Pregolya, and in the region's south-east near Lake Vištytis (Figure 4).

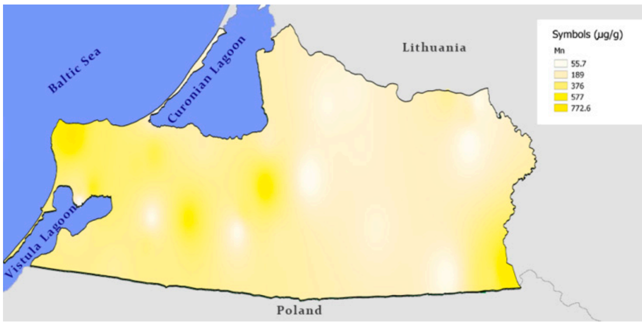

Figure 4. The distribution of manganese in the thalli of *H. physodes* in the Kaliningrad region, 2010.

The concentration of zinc in lichens varied dramatically – from 33 to 298 µg/g, the coefficient of variation was 56%. The highest zinc concentrations were found in the northern part of the region in the River Neman valley (Figure 5).

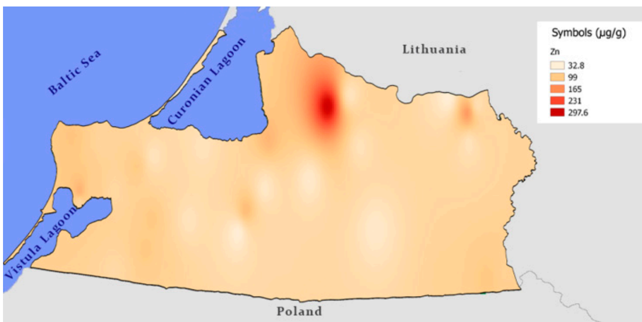

Figure 5. The distribution of zinc in the thalli of *H. physodes* in the Kaliningrad region, 2010.

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 18 May 2017 doi:10.20944/preprints201705.0138.v1

Peer-reviewed version available at *Atmosphere* **2017**, *8*, 119; doi:10.3390/atmos8070119

Strontium is transferred from atmospheric air to water and soils [38]. The corresponding coefficient of variation was below 50%. The concentrations of strontium in *H.physodes* differed slightly across the Kaliningrad region, ranging from 4.45 to 18.6 μg/g. The maximum concentration was observed on the Sambian peninsula and in the River Pregolya valley. The biochemical properties of strontium are similar to those of calcium. Calcium concentrations ranged from 219 to 2995 μg/g (Figure 6). Critical levels of strontium and calcium were not observed. Elevated levels of strontium are usually human-caused (Figure 7).

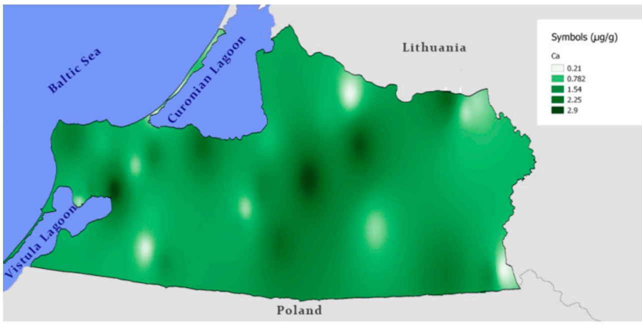

Figure 6. The distribution of calcium in the thalli of *H. physodes* in the Kaliningrad region, 2010.

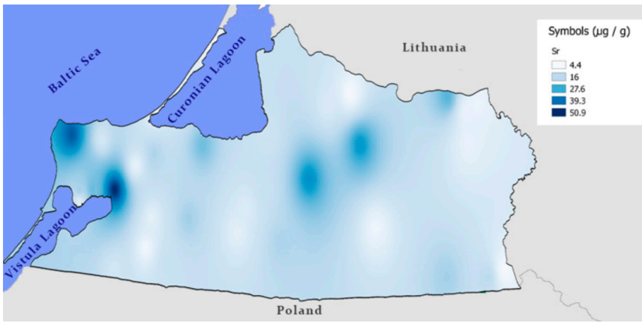

Figure 7. The distribution of strontium in the thalli of *H. physodes* in the Kaliningrad region, 2010.

Similar to the other monovalent cations, rubidium is absorbed by plants [39]. Rubidium can replace potassium in plants cells. The maximum concentrations of rubidium in *H. physodes* (19.9 μg/g) were found in the west of the region – on the Sambian peninsula and the northern coast of the Vistula Lagoon (Figure 8). The coefficient of variation was 47%. The average and median values were equal. There was a significance difference between the extreme values.

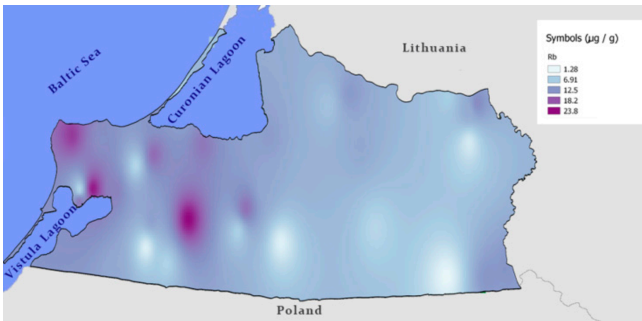

Figure 8. The distribution of rubidium in the thalli of *H. physodes* in the Kaliningrad region, 2010.

The average copper concentration in the lichen *H. physodes* was 7.91 μg/g. The coefficient of variation was the lowest. Sampling homogeneity was confirmed. The maximum copper concentration was 9.94 μg/g (Figure 9).

Peer-reviewed version available at *Atmosphere* **2017**, *8*, 119; doi:10.3390/atmos8070119

The average concentration of lead was estimated at 6.57 µg/g. The samples were homogeneous. The coefficient of variation was 36%. High lead levels were found in lichens in the western and central part of the Sambian peninsula (Figure 9).

The coefficient of variation of cadmium concentration in lichens on the Sambian peninsula was 21%. The samples were homogeneous. The maximum level of 0.263 µg/g was observed in the north-west of the Sambian peninsula (Figure 9).

The average silver content in lichens was estimated at 0.051 mg/g. The coefficient of variation was 47%, which is indicative a relatively high heterogeneity of silver accumulation in lichens in different parts the Sambian Peninsula. The maximum silver concentrations in thalli (0.095 µg/g) were found in the north of Kaliningrad (Figure 9).

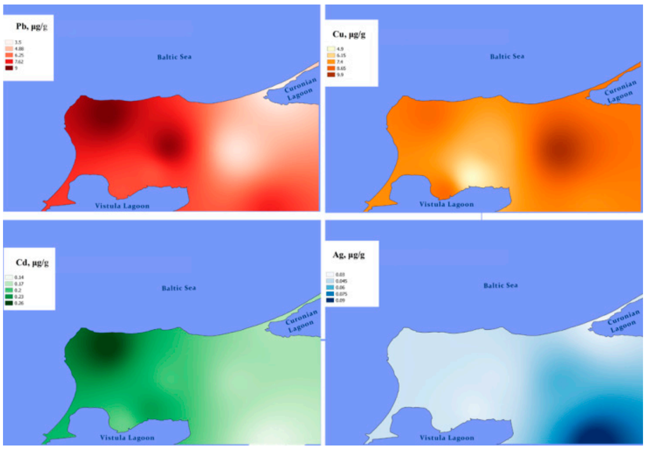

Figure 9. The distribution trace elements in the thalli of *H. physodes* on the Sambian peninsula, 2010.

By concentrations in lichen samples, the elements were ranked as follows: Ca>Fe > Mn > Zn > Sr > Rb > Cu > Pb > Ni > Cd>Ag. Most elements exhibited lognormal distribution (P>0.05), which is characteristic of the lithogenic origin of crustal elements and is reflected in the atmospheric deposition from windblown soil dust. However, such trace elements as Cd, Pb, and Ni did not exhibit the lognormal distribution. Their distribution in lichen samples was influenced by other anthropogenic factors.

To evaluate the degree of contamination in the Kaliningrad region, the contamination factor (CF) [21, 40] was calculated using the formula

$$CF = \frac{C_i}{C_b},$$

where C_i is the concentration of elements in lichens in the study area and C_b the concentration of the same elements in the control areas. The Arctic (Sr and Rb) and Northern Canada (other elements) were chosen as control [41, 42] (Table 3).

Peer-reviewed version available at Atmosphere 2017, 8, 119; doi:10.3390/atmos8070119

Table 3. The contamination factor in the Kaliningrad region

metal	Sambian peninsula		Kaliningrad region	
	CF	classification	CF	classification
Pb	22	C5		
Cd	3.1	C3	-	-
Cu	2.1	C3	-	-
Ni	2.0	C3	1.6	C2
Zn	2.2	C3	1.9	C2
Fe	9.7	C5	7.4	C4
Ca	1.5	C2	1.2	C2
Mn	2.0	C3	1.4	C2
Sr	2.3	C3	1.9	C2
Rb	2.7	C3	2.6	C3

For interpreting the results, six categories corresponding to CF values were introduced. CF 1 means no contamination (category C1); 1–2 suspected contamination (C2); 2–3.5 slight contamination (C3); 3.5–8 moderate contamination (C4); 8–27 severe contamination (C5), and 27 extreme contamination levels (C6) [43].

Thus, the level of trace element air pollution in the Kaliningrad region was estimated at C2, with the exception of Fe and Rb. However, in the western part of the Sambian peninsula, where the factors are higher than in the other areas, it was estimated at C3. The concentrations of lead and iron also considerably exceed control values.

3.2. The principle component factor analysis

To identify the origin of elements in lichen samples, a correlation matrix was calculated. It shows slight correlations <0.3-0.4; high correlations – 0.5-0.75, and significant correlations >0.75 [44].

Table 4. Matrix of correlations.

	Mn	Ni	Zn	Sr	Rb	Fe	Ca	Ag	Cd	Pb
Mn	1.00									
Ni	**0.67**	1.00								
Zn	**-0.38**	-0.20	1.00							
Sr	0.13	0.19	**-0.43**	1.00						
Rb	0.28	0.10	-0.12	**0.42**	1.00					
Fe	**0.65**	**0.46**	-0.10	**0.49**	**0.82**	1.00				
Ca	0.17	0.12	**-0.62**	**0.91**	0.16	**0.30**	1.00			
Ag	**-0.47**	-0.01	0.19	-0.08	-0.24	-0.21	0.01	1.00		
Cd	**0.42**	-0.10	0.04	0.25	-0.05	0.23	0.30	**-0.64**	1.00	
Pb	**0.33**	-0.22	0.29	-0.17	0.07	0.34	-0.05	-0.02	**0.56**	1.00
Cu	-0.13	0.24	**0.45**	**-0.64**	**-0.75**	**-0.59**	**-0.60**	0.09	-0.12	-0.22

There is a significant positive correlation between Ca-Sr, Fe-Rb, Mn-Ni, Fe-Mn, and Cd-Pb. This may be indicative of a common source of contamination. There are four major sources of trace elements, which correspond to the geographic and climatic features of the region - the atmospheric transport from the sea (marine factor), windblown dust from local soils (soil factor), the transport of soluble compounds from atmospheric precipitation, and vascular plant root uptake from the soil and the subsequent transfer to lichens (vegetative factor).

The factor analysis was carried out to ensure consistent interpretation of the findings. The four main factors were derived from the results of factor analysis and they were interpreted as source categories contributing to element concentrations at the sampling sites. The source categories were identified by examining the factor profiles, i.e. the loading of elements and other variables after varimax rotation. The main criterion for selecting the number of optimal factors and models of major source detection is that eigenvalues must be greater than 1.

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 18 May 2017 doi:10.20944/preprints201705.0138.v1

Peer-reviewed version available at *Atmosphere* **2017**, *8*, 119; doi:10.3390/atmos8070119

Table 5. The matrix of element correlations.

	Component			
	1	2	3	4
Mn	0.091	0.266	0.518	0.766
Ni	0.077	0.058	-0.107	0.946
Zn	-0.791	0.039	0.010	-0.271
Sr	0.833	0.379	0.046	0.012
Rb	0.126	0.917	-0.041	0.115
Fe	0.115	0.867	0.221	0.407
Ca	0.920	0.173	0.131	-0.044
Ag	-0.119	0.011	-0.695	-0.238
Cd	0.141	-0.001	0.962	-0.063
Pb	-0.358	0.373	0.640	-0.223
Cu	-0.539	-0.755	-0.084	0.276

The results of factor analysis and the loading values of each element and the association of elements with the factors [45] are analysed in Table 5.

Factor 1 is the strongest and it accounts for 36.2% of the total variance. It is influenced by the high positive loadings of strontium, calcium, and the negative ones of zinc and copper. Strontium is a satellite of calcium in geochemical processes. This may be connected with marine aerosols.

Factor 2 is the second strongest factor, accounting for 19.4% of the total variance. It is influenced by the loadings of rubidium, iron, strontium, and then negative ones of copper. Most likely, the origin of these metals is natural – for instance, uptake by the root system of trees and the subsequent absorption by lichens.

Factor 3 accounts for 15.6% of the total variance. This factor is associated with such elements as cadmium and lead, which are usually responsible for air pollution. At the same time, factor 3 reduces silver concentrations in lichens.

Factor 4, which accounts for 13.5% of the total variance, is connected with the positive loadings of Mn, Ni, and Fe. This factor is associated with a typical crustal composition and it is probably affected by soil particles in lichen samples.

4. Conclusions

The average concentrations of metals in the epiphytic lichen *H. physodes* in the Kaliningrad region corresponded to those of trace elements in the control areas. However, the lichens of the Sambian peninsula accumulate trace elements more intensively. This is explained by the human impact, which translates into higher concentrations of copper, lead, cadmium, nickel, and iron on the peninsula. It is possible that the composition of trace elements in the lichens of the Sambian peninsula is affected by not only local pollution sources, such as vehicles, thermal energy facilities, and ports but also the transboundary traffic and sea spray. The present study is the first step towards lichen-based air contamination monitoring in the Kaliningrad region. It can serve as a groundwork for further research. It is planned to continue studies into trace element concentrations in the lichen *H. physodes* and to establish not only the spatial features but also the temporal dynamics of air pollution in the Kaliningrad region.

Conflicts of Interest

The authors declare no conflict of interest.

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 18 May 2017 doi:10.20944/preprints201705.0138.v1

Peer-reviewed version available at *Atmosphere* **2017**, *8*, 119; doi:10.3390/atmos8070119

References

1. Tyler, G. Uptake, retention, and toxicity of heavy metals in lichens. *Water Air Soil Pollut.* **1989***, 47*, 321–333.
2. Garty, J. ; Karary, Y.; Harel, J.; Lurie, S. Temporal and spatial fluctuations of ethylene production and concentrations of sulfur, sodium, chlorine and iron on/in the thallus cortex in thelichen *Ramalina duriaei* (De Not.) Bagl. *Environ. Exp. Bot.* **1993**, *33*, 553–563.
3. Garty, J. Biomonitoring atmospheric heavy metals with lichens: theory and application. *Crit. Rev. Plant Sci.* **2001**, *20*, 309–371.
4. Chettri, M.K.; Sawidis, T.; Karataglis, S. Lichens as a tool for biogeochemical prospecting. *Ecotoxicol Environ Saf.* **1997**, *38*, 322–335.
5. Nimis, P.L.; Andreussi, S.; Pittao, E. The performance of two lichen species as bioaccumulators of trace metals. *Sci Total Environ.* **2001**, *275*, 43–51.
6. Bergamaschi, L.; Rizzio, E.; Giaveri, G.; Loppi, S.; Gallorini, M. Comparison between the accumulation capacity of four lichen species transplanted to a urban site. *Environ. Pollut.* **2007**, *148*, 468–476.
7. Balabanova, B.; Stafilov, T.; Šajn, R.; Baèeva, K. Characterisation of Heavy Metals in Lichen Species *Hypogymnia physodes* and *Evernia prunastri* due to Biomonitoring of Air Pollution in the Vicinity of Copper Mine. *Int. J. Environ. Res.* **2012**, *6*, 779-794.
8. Tretiach, M.; Baruffo, L. Effects of H_2S on CO_2 gas exchanges and growth rates of the epiphytic lichen *Parmelia sulcata* Taylor. *Symbiosis* **2001**, *31*, 35–46.
9. Adamo, P.; Crisafulli, P.; Giordano, S.; Minganti, V.; Modenesi, P.; Monaci, F. et.al. Lichen and moss bags as monitoring devices in urban areas. Part II: Trace element content in living and dead biomonitors and comparison with synthetic materials. *Environ. Pollut*. **2007**, *146*, 392–399.
10. Chiarenzelli, J.R.; Aspler, L.B.; Ozarko, D.L.; Hall, G.E.; Powis, K.B.; Donaldson, J.A. Heavy metals in lichens, southern District of Keewatin, Northwest Territories, Canada. *Chemosphere* **1997**, *35*, 1329–1341.
11. Osyczka, P.; Rola, K. Response of the lichen *Cladonia rei* Schaer. to strong heavy metal contamination of the substrate. *Environ Sci. Pollut. Res.* **2013**, *20*, 5076–5084.
12. Rola, K.; Osyczka, P. Cryptogamic community structure as a bioindicator of soil condition along a pollution gradient. *Environ Monit Assess.* **2014**, *186*, 5897–5910.
13. Rola, K.; Osyczka, P.; Nobis, M.; Drozd, P. How do soil factors determine vegetation structure and species richness in post-smelting dumps? *Ecol Eng.* **2015**, *75*, 332–342.
14. Bačkor, M.; Loppi, S. Interactions of lichens with heavy metals. *Biol. Plantarum.* **2009**, *53*, 214–222.

15. Garty, J.; Galun, M.; Kessel, M. Localization of heavy metals and other elements accumulated in the lichen thallus. *N Phytol*. **1979**, *82*, 159–168.
16. Goyal, R.; Seaward, M.R.D. Metal uptake in terricolous lichens I. Metal localization within the thallus. *N Phytol*. **1981**, *89*, 631–645.
17. Sarret, G.; Manceau, A.; Cuny, D.; Halowyn, C. van; Deruelle, S.; Scerbo, R. et al. Mechanisms of lichen resistance to metallic pollution. *Environ. Sci. Technol.* **1998***, 32*, 3325–3330.
18. Basile, A.; Sorbo, S.; Aprile, G.; Conte, B.; Castaldo Cobianchi, R. Comparison of the heavy metal bioaccumulation capacity of an epiphytic moss and an epiphytic lichen. *Environ. Pollut.* **2008***, 151*, 401–407.
19. Purvis, O.W.; Pawlik-Skowrońska, B. Lichens and metals. In: *Stress in Yeasts and Filamentous Fungi;* Avery, S.V.; Stratford, M; West, P. van, Eds.; Elsevier: Amsterdam, Netherlands, 2008, pp. 175–200.
20. Bajpai, R.; Upreti, D.K. Accumulation and toxic effect of arsenic and other heavy metals in a contaminated area of West Bengal, India, in the lichen *Pyxine cocoes* (Sw.) Nyl. *Ecotoxicol. Environ. Saf.* **2012**, *83*, 63–70.
21. Conti, M.E.; Cecchetti, G. Biological monitoring: lichens as bioindicators of air pollution assessment - a review *Environ. Poll.* **2001**,*114*, 471-492.
22. Poikolainen, J. *Mosses, epiphytic lichens and tree bark as Biomonitors for air Pollutants – Specifically for heavy Metals in regional surveys.* University Press: Oulu, Finland, 2004.
23. Cuny, D.; Denayer, F.O.; Foucault, B. de; Schumacker, R.; Colein, P.; Haluwyn, C. van. Patterns of metal soil contamination and changes in terrestrial cryptogamic communities. *Environ. Pollut*. **2004**, *129*, 289–297.
24. Pirintsos, S.A.; Matsi, T.; Vokou, D.; Gaggi, C.; Loppi, S. Vertical distribution patterns of trace elements in an urban environment as reflected by their accumulation in lichen transplants. J. *Atmos. Chem*. **2006**, *54*, 121–131.
25. Nieminen, T.M.; Ukonmaanaho, L.; Rausch, N.; Shotyk, W. Biogeochemistry of Nickel and Its Release into the Environment. *Met. Ions Life Sci.* **2007**, *2*, 1–30.
26. Klimek, B.; Tarasek, A.; Hajduk, J. Trace Element Concentrations in Lichens Collected in the Beskidy Mountains, the Outer Western Carpathians. *Bull. Environ. Contam. Toxicol.* **2015***, 94*, 532–536.
27. Boonpragob, K.; Nash, T.H. Seasonal variation of elemental status in the lichen *Ramalina menziesii* Tayl. from 2 sites in southern California — evidence for dry deposition accumulation. *Environ. exp. Bot.* **1990***, 30*, 415–428.

Peer-reviewed version available at *Atmosphere* **2017**, *8*, 119; doi:10.3390/atmos8070119

28. Walther, D.A.; Ramelov, G.J.; Beck, J.N.; Young, J.C.; Callahan, J.D.; Marcon, M.F. Temporal changes in metal levels of the lichen *Parmotrema praesorediosum* and *Ramalina stenospora*, southwest Louisiana. *Water Air Soil Pollut.* **1990**, *53*, 189–200.
29. Cuny, D.; Davranche, L.; Thomas, P.; Kempa, M.; Haluwyn, C. van. Spatial and temporal variations of trace element contents in *Xanthoria parietina* thalli collected in a highly industrialized area in northern France as an element for a future epidemiological study. *J. Atmos. Chem.* **2004**,*49*, 391–401.
30. Král, R.; Kryžová, L.; Liška, J. Background concentrations of lead and cadmium in the lichen *Hypogymnia physodes* at different altitudes. *Sci. total Environ.* **1989**, *84*, 201–209.
31. Paul, A.; Hauck, M.; Langenfeld-Heyser, R. Ultrastructural changes in soredia of the epiphytic lichen *Hypogymnia physodes* cultivated with manganese. *Environ. exp. Bot.* **2004**, *52*, 139–147.
32. Hauck, M.; Huneck, S. Lichen substances affect metal adsorption in *Hypogymnia physodes. J. chem. Ecol.* **2007**,*33*, 219–223.
33. Mikhailova, I.N.; Sharunova, I.P. Dynamics of heavy metal accumulation in thalli of the epiphytic lichen *Hypogymnia physodes*. *Russ J Ecol*. **2008**, *39*, 346–352.
34. Koroleva, Y. Use of mosses Hylocomium splendens and Pleurozium schreberi for an estimation of absolute values of atmospheric losses of heavy metals in Kaliningrad areas. *Vestnik of Immanuel Kant Baltic federal university* **2006**, *7*, 29-34.
35. Koroleva, Y.; Pukhlova, I. New data on heavy metal bioconcentration on the territory of the Baltic region. *Vestnik of Immanuel Kant Baltic federal university* **2012**, *12*, 99-106.
36. Koroleva, Y.; Vakhranyova, O.; Okhrimenko, M. Accumulation of trace elements by wild mushrooms in West part of Russia (South-Eastern Baltic). *Pollution atmosphérique* **2016**, *226*, https://doi.org/10.4267/pollution-atmospherique.4989. Available online: http://lodel.irevues.inist.fr/pollution-atmospherique/index.php?id=4989 (accessed on 15 February 2017).
37. Rola, K.; Osyczka, P.; Kafel, A. Different Heavy Metal Accumulation Strategies of Epilithic Lichens Colonising Artificial Post-Smelting Wastes. *Arch. Environ. Contam. Tox.* **2016**, *70*, 418–428.
38. Vinogradov, A.R. Average contents of chemical elements in the principal type of igneous rocks of the Earth’s crust. *Geochemistry* **1962**, *7*, 555—571.
39. Kabata-Pendias, A.; Szteke, B. *Trace Elements in Abiotic and Biotic Environments*. Mir; Moscow, Russia, 1989.
40. Carballeira, A.; Carral, E.; Puente, X.; Villares, R. Regional-scale monitoring of coastal contamination. Nutrients and heavy metals in estuarine sediments and organisms on the coast of Galicia (NW Spain). *Environ. Pollut.* **2000**, *13*, 534-572.

Peer-reviewed version available at *Atmosphere* **2017**, *8*, 119; doi:10.3390/atmos8070119

41. Chiarenzelli, J.; Aspler, L.; Dunn, C.; Cousens, B.; Ozarko, D.; Powis, K. Multi-element and rare earth element composition of lichens, mosses, and vascular plants from the Central Barrenlands, Nunavut, Canada. *App. Geochem*. **2001**, *16*, 245–270.
42. Darnajoux, R.; Lutzoni, F.; Miadlikowska, J.; Bellenger, J.-P. Determination of elemental baseline using peltigeralean lichens from Northeastern Canada (Québec): Initial data collection for long term monitoring of the impact of global climate change on boreal and subarctic area in Canada. *Sci. Total Environ.* **2015**, *533*, 1–7.
43. Fernández, J. A.; Carballeira, A. Evaluation of contamination, by different elements, in terrestrial mosses. *Arch. Environ.Contam. Tox*. **2001**, *40*, 461–468.
44. Nimis, P.L.; Scheidegger, Ch.; Wolseley, P.A., Eds. *Monitoring Lichens - Monitoring with Lichens*. Kluwer, Dordrecht, Netherlands, 2002, pp.295-299.
45. Steins, E. A critical evaluation of the use of naturally growing moss to monitor the deposition of atmospheric metals. *Sci. Tot. Environ* **1995**, *160/161*, 243-249.