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GEOCHEMISTRY

Geochemistry of Terricolous Lichens in the White Sea Catchment Area

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Abstract—This paper presents new data on the multielemental composition of terricolous lichens in the White Sea catchment area. The content of 51 chemical elements was determined in 31 samples using modern analytical methods. It was shown that the chemical composition of terricolous lichens varies widely and depends on many factors. The lithogenic dust plays the main role in accumulation of Ti, Cr, Co, Ga, Fe, Zr, Nb, Ga, Th, U, and REE. Long-range transport from remote pollution sources is important for Pb, Zn, Cd, Bi, Hg, and Se. The Kostomuksha ore dressing mill provides the local enrichment of the lichens in Fe, whereas the Monchegorsk copper–nickel enterprise affects large distances and additionally enriches the lichens in Cu, Ni, Co, Pb, and Cd in comparison with the background regions. The marine impact is reflected in elevated contents and enrichment factors in Na, Mg, and the Na/K ratio.

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Atmospheric transfer is important for the introduction of substances including toxic metals into the environment. The lichens are significant bioindicators of chemical elements during atmospheric transfer [1, 2]. They, being a symbiosis of the fungus and green algae or cyanobacterium, have no roots and feed mostly from the atmosphere. The surface of the lichens is rather large, which makes them natural biosorbents [1].

The multielemental composition of the lichens has been studied in many countries to estimate the degree of atmospheric pollution; however, such works are few in number [4–7] for the territory of the White Sea catchment area [3–7].

Our study is devoted to the microelemental composition of the terricolous lichens sampled in 2004–2006 in the White Sea catchment area on the territory of Murmansk and Arkhangelsk oblasts and the Republic of Karelia. The sampling locations are shown in Fig. 1. Thirty-one samples of the terricolous lichens including 28 *Cladonia*, 2 *Flavocetraria*, and 1 *Alectoria* lichen species (Table 1) were collected.

The lichens were sampled into sterile polyethylene packages using disposable polyethylene gloves in order to prevent pollution. The averaged lichen samples were collected from an area of 10–20 m^2. The upper parts (3–7 cm) of the lichen thalluses were sampled for the analysis. The samples were dried at a temperature of 30–35°C in the laboratory. The dried samples were cleaned from fragments of other plants or soil particles using plastic pincers. Then the samples were powdered in an agate mortar.

The content of 51 chemical elements was analyzed in the powdered samples at the Laboratory of Mechanisms and Transfer in Geology (Toulouse, France). Mercury was determined using atomic absorption on a Milestone DMA-80 express-analyzer without preliminary decomposition by the method of [8].

To determine other chemical elements, the samples were completely decomposed in acids, which included the subsequent processing of the sample in savillex (teflone) vessels with especially pure H_2O_2–HNO_3–HF–HCl–HNO_3 reagents in a clean room of the A 10 000 class.

The contents of Na, Mg, Al, K, Ca, Mn, Fe, and Sr were analyzed on an Ultima 2 ICP-OES spectrometer (HORIBA Jobin Yvon, Great Britain). The contents of other elements were determined on an Agilent 7500 ICP-MS spectrometer. The accuracy of analyses was controlled by international CRM 482 (lichen *Pseudevernia furfuracea*) and SRM 1515 (apple-tree leaves) standards. The relative deviation of the contents of

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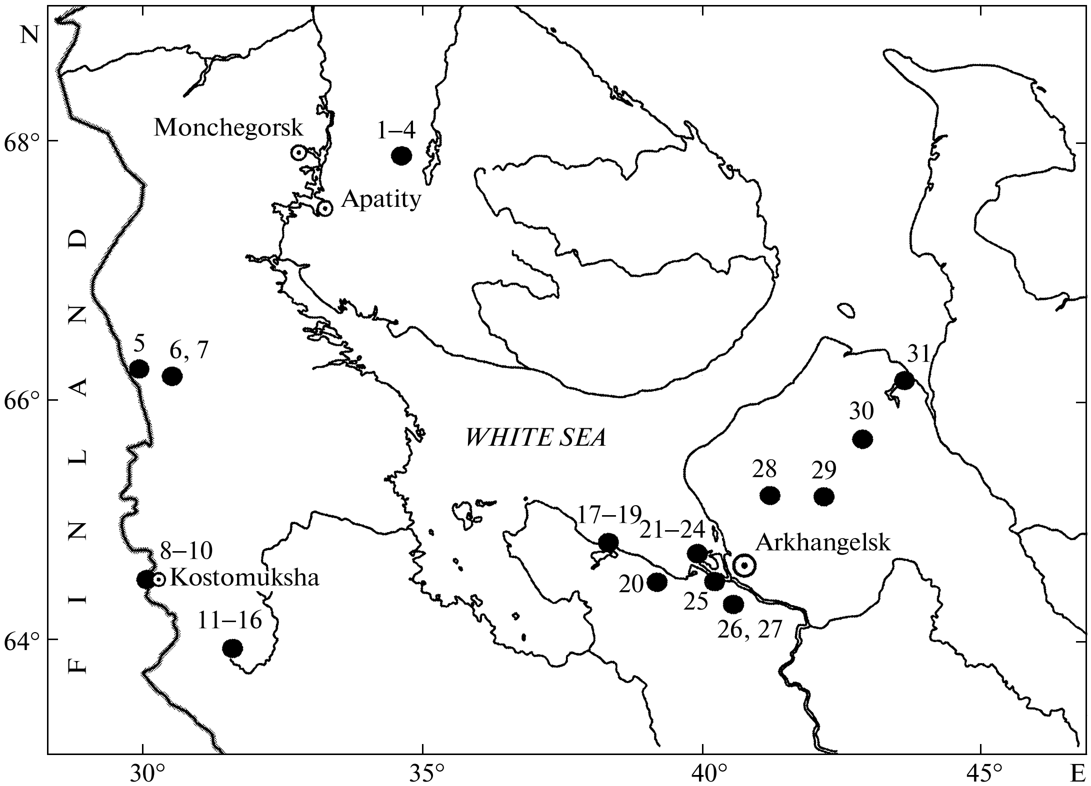

Fig. 1. Location of the sampling points of terricolous lichens in the White Sea catchment area in 2004–2006.

certified elements was 10–15%. The method is described in detail in [9].

The results of chemical analyses are shown in Table 2. To identify the lithogenic, marine, biogenic, and anthropogenic contribution to the formation of the lichen elemental composition, we calculated the enrichment factors (EF) relative to the average composition of the continental crust by the following formula:

$$EF = (El/Al)_{sample} / (El/Al)_{Earth's\ crust},$$

where El and Al are the contents of chemical element and Al in the lichen samples and in the upper part of the continental crust [10].

Three groups of samples were distinguished by their multielemental composition: (1) samples from the Lovozero tundra located in the central part of the Kola Peninsula (nos. 1–4); (2) samples taken at a distance less than 1 km from the Kotomuksha ore dressing mill (nos. 9 and 10); and (3) other samples.

The EF values of Ti, Cr, Co, Ga, Fe, Zr, Nb, Ga, Th, and U are <10 in the majority of the samples, which indicates a mostly lithogenic source of these elements. The highest EF values (locally, in unit samples) are typical of K, Mn, Fe, Ni, Cu, Zn, Se, As, Sr, Mo, Cd, Sb, Hg, Pb, and Bi (Fig. 2).

Almost all lichen samples were significantly enriched (EF >10) in K, Mn, Zn, Se, Rb, Mo, Cd, Sb, Hg, Pb, and Bi.

One of main reason for the significant enrichment of the studied lichens in K, Mn, Ni, Cu, Zn, Se, Rb, Mo, Hg, and Pb is related to their biophility: the elements are accumulated due to biological concentration mechanisms [11].

The EF values of Zr, Th, Hf, REE, Y, Co, U, Nb, Ba, Sr, Cs, Ni, Ge, As, Ta, Bi, Cu, Pb, Zn, and Cd in the lichens sampled in the Lovozero tundra are higher by several times in comparison with those from other regions. Probably, the local rocks enriched in these elements are the source of the majority of them. The enrichment of lichens in Th, REE, Y, Ba, and Sr may be caused by dust transfer from the apatite–nepheline open pits and dispersing dumps [6]. The increased Cu, Ni, Co, Pb, and Cd contents in the lichens from the Lovozero tundra (Table 2) and their EF (Fig. 2) are probably the result of impact of the Monchegorsk Severonikel copper–nickel enterprise [4–6].

The median of the Hg EF of the lichens from the Lovozero tundra is slightly higher than in the majority of samples, and they are lower relative to other samples near the Kostomuksha ore dressing mill. No significant sources of Hg emission are known on the Kola Peninsula [6]. Coal burning is the main source of Hg for the atmosphere [12]. Elemental mercury (Hg^0) may be present in the atmosphere for a long time, which results in its global expansion.

Table 1. Dates of sampling of terricolous lichens and coordinates of sampling points

No.	Region	Date of sampling	Coordinates		Lichen species
			N	E	
1	Lovozero tundra	07.07.2004	67°54.1′	34°38.2′	*Alectoria ochrolleuca*
2	the same	the same	67°50′	34°41.2′	*Flavocetraria nivalis*
3	"	10.07.2004	67°46.4′	34°48.5′	the same
4	"	the same	67°43.1′	34°37.3′	*Cladonia stellaris*
5	Northwestern Karelia, Paanajarvi National Park	06.07.2006	66°15.8′	29°57.3′	the same
6	the same	09.07.2006	66°12.3′	30°33′	"
7	"	12.07.2006	66°12.2′	30°28.3′	"
8	Northwestern Karelia, Lake Kendo coast	10.07.2006	64°32.1′	30°5.4′	*Cladonia* sp.
9	Northwestern Karelia, outskirts of the town of Kostomuksha	21.07.2006	64°37.6′	30°43.1′	*Cladonia rangiferina*
10	the same	the same	64°42.6′	30°49.5′	the same
11	Northwestern Karelia, Muezer region	07.07.2006	63°56.8′	31°38.1′	*Cladonia* sp.
12	the same	the same	63°56.8′	31°38.1′	the same
13	"	"	63°57.1′	31°38.4′	"
14	"	"	63°57.1′	31°38.4′	"
15	"	"	63°56.4′	31°39.2′	"
16	Northwestern Karelia, Kurondarvi Lake coast	10.07.2006	63°52.1′	31°48.5′	*Cladonia stellaris*
17	Onega Peninsula, Unskii lighthouse	16.08.2006	64°50.6′	38°21.4′	*Cladonia* sp.
18	the same	the same	64°50.7′	38°21.4′	the same
19	"	"	64°50.5′	38°21′	"
20	Mouth of the Northern Dvina River, Kurtyaevo tract	31.05.2006	64°30.8′	39°14.8′	*Cladonia stellaris*
21	Delta of the Northern Dvina River, Kumbysh Island	21.05.2006	64°45.3′	39°57.1′	*Cladonia* sp.
22	the same	the same	64°45.3′	39°57.1′	the same
23	"	"	64°45.2′	39°58.2′	"
24	"	"	64°45.1′	39°58.6′	"
25	Arkhangelsk oblast, Primorskii region, right bank of the Laya River	19.05.2006	64°31.1′	40°16.2′	"
26	Arkhangelsk oblast, Primorskii region, Ilasskoe swamp	21.06.2006	64°19.4′	40°36.4′	"
27	the same	the same	64°19.6′	40°36.5′	"
28	Arkhangelsk oblast, Kepina River	14.08.2006	65°14.5′	41°15.1′	*Cladonia stellaris*
29	Arkhangelsk oblast, Soyana River	19.08.2006	65°13.6′	42°13′	the same
30	the same	21.08.2006	65°42.1′	42°54.4′	*Cladonia arbuscula*
31	Arkhangelsk oblast, Ambramovskii coast	24.08.2006	66°10.2′	43°39.9′	*Cladonia stellaris*

In the studied region, Pb, Bi, and Cd contribute mostly due to the long-range atmosphere transfer from remote industrial sources [13].

The lichens sampled near the Kostomuksha mining and concentrating combine (samples nos. 9 and 10) are characterized by a higher EF of Fe (36 and 14, respectively), which is explained by the proximity of the combine. These samples have decreased (relative to other samples) EF of Pb, Bi, and Cd (27 and 33 for Cd, 2.8 and 3.4 for Pb, and 3.8 and 3.8 for Bi). This is possibly related to the dilution of the aeolian substances near the combine by the local dust, contributing due to its dustfall. The Fe content in the lichens from the background regions of Northern Karelia (including sample no. 8 taken from Kostomuksha State Reserve) is close to its common content in the background regions of the Russian north [4, 5].

It was shown that the spectrum of the normalized average REE composition in three groups is similar to that of the average composition of the upper part of the continental crust [14] (Fig. 3). The lichens from the Lovozero tundra, however, are enriched in LREEs (especially La) in comparison with other samples. The lichens sampled near the Kostomuksha ore dressing

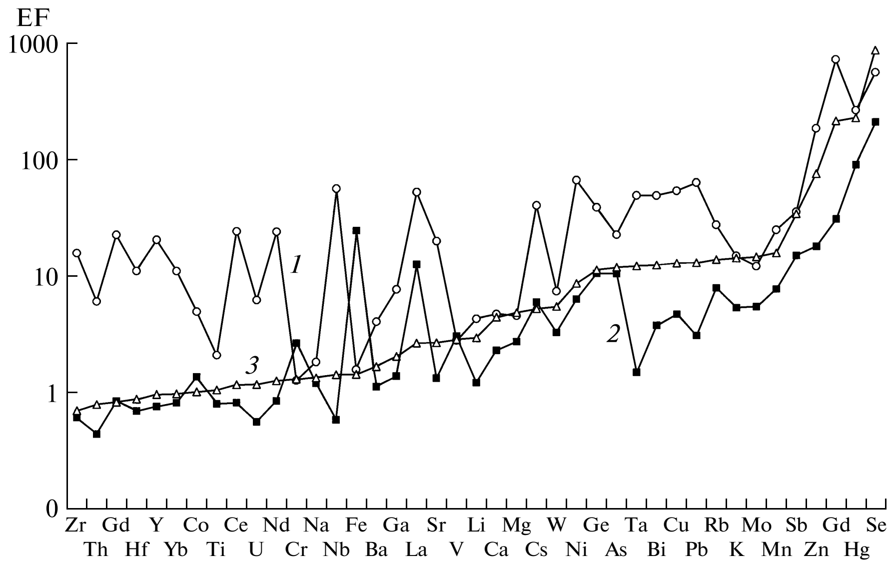

Fig. 2. Medians of enrichment factors of terricolous lichens by groups: (*1*) Lovozero tundra; (*2*) outskirts of the Kostomuksha ore dressing mill; (*3*) all other samples.

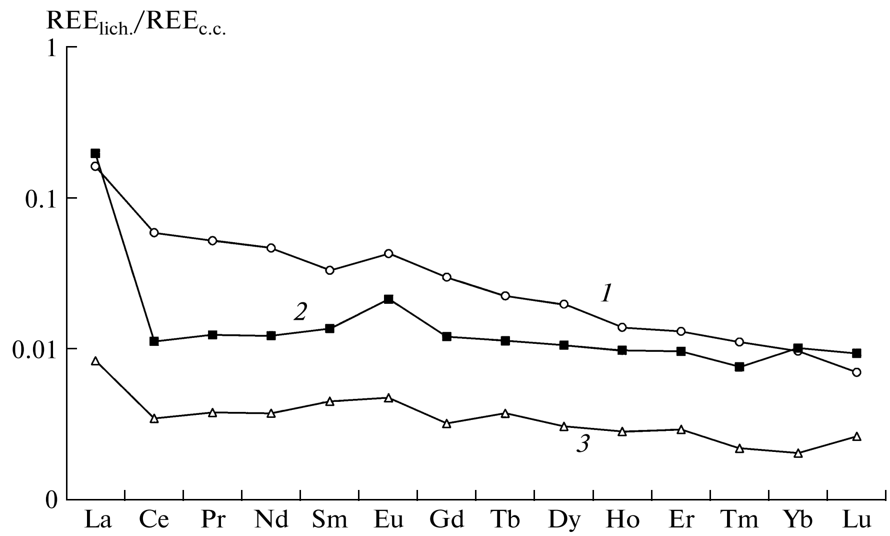

Fig. 3. Medians of REE contents in terricolous lichens (REE_{lich}) normalized on the REE contents in the upper part of the continental crust ($REE_{c.c.}$) [14]. *1*, *2*, and *3* see Fig. 2.

mill are notable for the significant (on one order) enrichment in La relative to other REEs. This reflects the significant pollution of these lichens by the mineral dust of the mill, which consists of dominant iron quartzites with the typical La anomaly [15].

The higher Na and Mg EF values (13–15) are characteristic of sample nos. 17–19 taken at the Letnii coast (near Unskii lighthouse). The enrichment in these elements is caused by marine influence. The Na/K ratio may serve as an indicator of marine influence because of its higher value in sea salts (components of marine aerosols) relative to lithogenic dust. The highest Na/K ratio is observed in the samples taken from Unskii lighthouse (0.40–0.55).

Generally, the chemical composition of the terricolous lichens varies widely and depends on many factors. The lithogenic dust plays a key role in the accumulation of Ti, Cr, Co, Ga, Fe, Zr, Nb, Ga, Th, U, and REEs. The long-range transport from remote pollution sources is significant for Pb, Zn, Cd, Bi, Hg, and Se. The Kostomuksha ore dressing mill provides the local enrichment of lichens in Fe, whereas the Monchegorsk copper–nickel enterprise has an influence over large distances and additionally enriches the lichens in Cu, Ni, Co, Pb, and Cd in comparison with

Table 2. Content of chemical elements in the terricolous lichens of the White Sea catchment area, μg/g

Element	Lovozero tundra ($n = 4$)				Outskirts of the Kostomuksha ore dressing mill ($n = 2$)				Other samples ($n = 25$)				Kirovsk, average
	min	max	average	st. dev.	min	max	average	st. dev.	min	max	average	st. dev.	
Li	0.06	0.60	0.23	0.25	0.35	0.45	0.40	0.07	0.039	0.52	0.21	0.12	
Na	24.9	232	115	96.6	336	486	411	106	38.2	456	151	125	40
Mg	85.8	200	153	48	566	574	570	6.1	127	377	241	84	150
Al	35.0	463	206	183	1030	1265	1148	166	92	620	260	147	277
K	628	1183	867	242	1701	1761	1731	42.3	570	1433	1000	248	2090
Ca	120	927	422	356	551	1163	857	433	194	1807	432	310	200
Ti	2.68	50.8	21.6	20.5	40.8	44.1	42.4	2.3	3.7	35.3	13.5	8.7	
V	0.36	1.10	0.63	0.33	3.03	5.51	4.27	1.75	0.22	4.28	1.12	1.09	1.7
Cr	0.17	0.58	0.31	0.19	3.38	3.41	3.40	0.02	0.086	0.93	0.35	0.219	0.65
Mn	21.1	42.6	34.7	9.8	63	110	87	33	7.8	109	42.8	27.5	21
Fe	37.8	361	149	145	6822	21723	14272	10537	73	366	167	80	170
Co	0.11	0.48	0.33	0.19	0.30	0.37	0.331	0.050	0.011	0.19	0.071	0.054	0.31
Ni	3.41	13.1	9.2	4.1	3.5	5.0	4.3	1.1	0.29	9.77	1.86	2.14	5.4
Cu	2.07	5.81	3.46	1.65	1.81	1.88	1.85	0.054	0.58	1.62	0.96	0.26	6
Zn	8.1	65.7	27.3	26.3	15.7	17.7	16.7	1.4	5.5	19.9	12.2	3.3	16
Ga	0.077	0.69	0.32	0.27	0.30	0.38	0.341	0.056	0.036	0.39	0.13	0.087	
Ge	0.029	0.28	0.13	0.11	0.14	0.29	0.216	0.106	0.006	0.253	0.054	0.049	
As	0.18	0.62	0.32	0.20	0.51	0.88	0.69	0.26	0.08	0.80	0.18	0.15	0.44
Se	0.065	0.36	0.15	0.14	0.25	0.26	0.26	0.002	0.01	1.16	0.29	0.27	
Rb	2.97	6.87	4.71	1.61	8.47	10	9.25	1.11	1.16	8.11	3.68	2.18	7.6
Sr	7.6	72.9	32.3	28.7	4.5	7.7	6.1	2.2	0.70	5.27	2.67	1.32	10
Y	0.21	4.16	1.24	1.95	0.20	0.24	0.219	0.023	0.021	0.152	0.065	0.039	0.5
Zr	0.86	27.3	9.27	12.27	1.45	1.86	1.66	0.29	0.084	1.97	0.45	0.39	
Nb	0.28	5.30	1.99	2.25	0.090	0.108	0.099	0.012	0.015	0.111	0.048	0.026	
Mo	0.02	0.057	0.04	0.016	0.063	0.110	0.086	0.033	0.025	0.11	0.05	0.026	0.06
Cd	0.041	0.246	0.136	0.084	0.032	0.047	0.039	0.011	0.017	0.146	0.054	0.025	<0.1

Table 2. (Contd.)

Element	Lovozero tundra ($n = 4$)				Outskirts of the Kostomuksha ore dressing mill ($n = 2$)				Other samples ($n = 25$)				Kirovsk, average*
	min	max	average	st. dev.	min	max	average	st. dev.	min	max	average	st. dev.	
Sb	0.024	0.081	0.048	0.026	0.071	0.1	0.086	0.021	0.016	0.112	0.04	0.021	
Cs	0.13	0.53	0.27	0.18	0.41	0.42	0.411	0.008	0.02	0.37	0.107	0.103	
Ba	2.31	8.75	5.29	2.78	8.9	10.9	9.9	1.43	0.60	8.99	3.08	1.94	4.2
La	0.59	8.53	4.67	3.28	2.81	8.81	5.81	4.24	0.06	1.12	0.3	0.25	
Ce	1.08	6.48	3.76	2.31	0.63	0.79	0.71	0.11	0.08	1.42	0.28	0.27	
Pr	0.11	1.19	0.51	0.47	0.078	0.097	0.087	0.013	0.01	0.175	0.033	0.033	
Nd	0.37	4.15	1.74	1.66	0.28	0.35	0.315	0.054	0.042	0.64	0.127	0.12	
Sm	0.063	0.68	0.26	0.28	0.057	0.065	0.061	0.005	0.006	0.089	0.023	0.017	
Eu	0.019	0.203	0.074	0.086	0.017	0.021	0.019	0.003	0.002	0.017	0.005	0.003	
Gd	0.043	0.76	0.26	0.33	0.036	0.055	0.046	0.014	0.002	0.048	0.013	0.01	
Tb	0.008	0.107	0.036	0.047	0.0064	0.0080	0.0072	0.0011	0.0005	0.0052	0.0025	0.0014	
Dy	0.04	0.55	0.18	0.25	0.035	0.039	0.037	0.003	0.001	0.021	0.01	0.006	
Ho	0.008	0.106	0.034	0.048	0.0068	0.0088	0.0078	0.0014	0.0006	0.0061	0.0028	0.0015	
Er	0.019	0.272	0.088	0.123	0.021	0.023	0.022	0.001	0.0017	0.0163	0.0076	0.0043	
Tm	0.002	0.031	0.01	0.014	0.0023	0.0027	0.0025	0.00033	0.00019	0.00188	0.00092	0.00058	
Yb	0.016	0.18	0.06	0.08	0.021	0.023	0.022	0.002	0.001	0.01	0.01	0.004	
Lu	0.002	0.02	0.01	0.01	0.003	0.003	0.003	0.00027	0.00008	0.00227	0.00103	0.00065	
Hf	0.02	0.51	0.17	0.23	0.051	0.052	0.051	0.001	0.004	0.057	0.015	0.011	
Ta	0.048	0.28	0.12	0.11	0.013	0.023	0.018	0.007	0.005	0.066	0.033	0.018	
W	0.019	0.054	0.032	0.015	0.057	0.124	0.091	0.047	0.012	0.082	0.035	0.02	
Hg	0.02	0.098	0.044	0.037	0.057	0.065	0.061	0.005	0.013	0.068	0.033	0.014	0.11
Pb	1.3	3.23	2.25	0.79	0.6	0.89	0.74	0.2	0.18	2.45	0.77	0.45	2.70
Bi	0.007	0.027	0.017	0.008	0.0076	0.0095	0.0085	0.0013	0.002	0.037	0.008	0.007	
Th	0.06	0.35	0.16	0.13	0.06	0.06	0.064	0.0004	0.008	0.068	0.026	0.015	
U	0.013	0.110	0.041	0.046	0.02	0.023	0.021	0.002	0.003	0.018	0.01	0.005	

background regions. The marine effect is reflected in the increased contents and EF of Na and Mg and the Na/K ratio. Thus, the terricolous lichens are an informative natural archive, which registers the gain of heavy metals (including toxic ones) from the atmosphere into the White Sea catchment area and adjacent water area giving the possibility of estimation of the relative contribution of lithogenic, biogenic, marine, and anthropogenic sources of these metals.

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