Trace elements content of surface peat deposits in the Solovetsky Islands (White Sea)

K. Kozioł[1], J. Korzeniowska[2], D. Okupny[3], E. Bezak-Mazur[4], S. Żurek[5]

[1]Department of Analytical Chemistry, Gdansk University of Technology, Gdansk, Poland; [2]Institute of Geography, Pedagogical University, Cracow, Poland; [3]Institute of Marine and Environmental Sciences University of Szczecin, Szczecin, Poland; [4]Professor Emeritus, Faculty of Environmental, Geomatic and Energy Engineering, Kielce University of Technology, Kielce, Poland; [5]Professor Emeritus, Institute of Geography and Environmental Sciences, The Jan Kochanowski University in Kielce, Kielce, Poland

---

SUMMARY

Peatlands form environmental archives of trace element deposition. In this regard they are particularly valuable for areas such as the Arctic, where regular pollution monitoring is either impossible or extremely costly. The aim of this study was to assess pollution in the Solovetsky Islands (65° 05' N, 35° 53' E) by examining the spatial variability in trace element content of the uppermost layer of peat, immediately below the surface layer of green vegetation. We evaluated Cr, Cd, Ni and Pb contents in samples taken from ombrotrophic (raised bog) and mesotrophic (transitional) mires and in different microtopographical settings (hummock/hollow), and calculated the following pollution indices: geoaccumulation index (I_{geo}), contamination factor (C_f) and degree of contamination (C_{deg}). The contents of these elements were markedly lower in the Solovetsky Islands than reported from other parts of central and northern Europe. Depending on the pollution index considered, the studied peat samples could be classified as unpolluted to considerably polluted. The local spatial patterns showed the highest values of Cd in samples collected near the sea, while the highest contents of Cr and Ni were noted at sampling points located farther inland. Moreover, Cr and Pb concentrations were higher in raised bogs than in transitional mires, and this contrast was accentuated if raised bog was represented by hummocks alone. These patterns are consistent with the likely sources of Cr, Ni and Pb being atmospheric pollution; and with higher mobility of Cd in seawater, which periodically floods the transitional mires. Amongst the trace elements determined, the most consistent values across peat types and sampling locations were found for Ni, which could be successfully used for pollution monitoring even in transitional mires.

KEY WORDS: biogenic deposits, industrial pollution, mires, northern Europe, surface sediments

---

INTRODUCTION

The high organic matter content and anaerobic conditions of peat limit the mobility of metal pollutants within it, through adsorption and sulphide formation processes (Wilkin & Barnes 1997). For this reason, peatlands are important archives of environmental pollution by trace elements (Shotyk *et al.* 1990, Gorres & Frenzel 1997, Nieminen *et al.* 2002, Coggins *et al.* 2006, Silamikele *et al.* 2010, De Vleeschouwer *et al.* 2010, Veretennikova & Golovatskaya 2012, Allan *et al.* 2013), and the geochemistry of peat has become an increasingly interesting topic as human activity has increased over recent decades. Raised bogs have a unique role in this context because they are completely dependent on rainwater, which is collected by their living surface layers. Furthermore, we may expect significant differences between raised bogs and transitional mires in terms of the pollution found in their peat, due to different absorption mechanisms. Even hollows and hummocks within raised bogs may have different trace element contents and, thus, differ in their performance as pollution archives (cf. Shotyk 1996).

The Solovetsky Islands are located near the Arctic Circle, sparsely populated and distant from industrial areas. Like other parts of the Arctic, e.g. northern Norway (Steinnes 1987) and Svalbard (Pacyna 1995, AMAP 2005), they are an ideal monitoring location for regional pollution levels and the long-range transport of trace elements. Stations for direct monitoring of atmospheric pollution are extremely sparse in northern Russia, so indirect monitoring of trace element deposition in peat is a valuable tool for determining the regional spatial patterns.

In the research reported here, we studied the accumulation on the Solovetsky Islands of potentially toxic primary trace elements in transitional mires and raised bogs, and in hollows and hummocks within raised bogs. The objectives were: (i) to investigate the influence of local and regional pollution sources on the metal contents of these mesotrophic and oligotrophic mires; and (ii) to compare the usefulness of these different peatland types and microforms for pollution monitoring.

METHODS

Study area

The Solovetsky Islands (65° 05´ N, 35° 53´ E) make up the largest archipelago in the White Sea (Figure 1). The largest island in the group is Bolshoy Solovetsky Island, with an area of 246 km^2 (25 km long, 16 km wide). A short account of mires on Bolshoy Solovetsky Island by Kac (1971) describes a great raised bog in the northern part of the island, meso-oligotrophic forest mires, and quagmire mossy mires around lakes. The basins of the 560 lakes in the Solovetsky Islands were formed by erosion of glacier tongues or by meltwater. They terrestrialise from the shore towards the centre of the water body. The peat mosses growing on the lakeshore form floating mats, and separated fragments of *Sphagnum* lawn can form ‘floating islands’ (Żurek 2007). Most of the lakes and peatlands are located in the northern and central parts of Bolshoy Solovetsky Island (Figure 2).

Peatland biogeographical zones (Figure 1) take into account the zonal diversity of climate which, in turn, determines the character of vegetation, soil and biogenic accumulation environments (Tobolski 2005). Apart from the climatically determined zonal arrangement, intra/inter- and non-zonal peatlands can also be distinguished, mainly on the basis of factors other than climate, for example relief and surface lithology (Żurek 2012). The Solovetsky Islands lie on the border between the aapa mire and lowland raised bog peatland provinces (Eurola *et al.* 1984, Żurek 1984) (Figure 1). Aapa mires are usually extensive (not uncommonly covering thousands of hectares) with a characteristic surface structure of wide, flat, usually rather shallow depressions (‘flarks’) and long, narrow ridges (‘strings’). Raised bogs stretch south of the aapa peatland zone and cover a broad area. Their peat-forming surfaces are hummocks and (less frequently) string-like structures, separated by hollows, the hummocks (height 10–40 cm) generally occupying 70 % (and hollows 30 %) of the total area. Mesotrophic mires have mixed hydrological regimes, i.e. their water supplies include both groundwater and rainwater. The patches of vegetation in mesotrophic mire may form a mosaic of ombrotrophic components (e.g. hummocks or lens-like bulges) surrounded by fen (‘low-moor’) phytocenoses (Żurek 1971, Tobolski 2005, Żurek 2007).

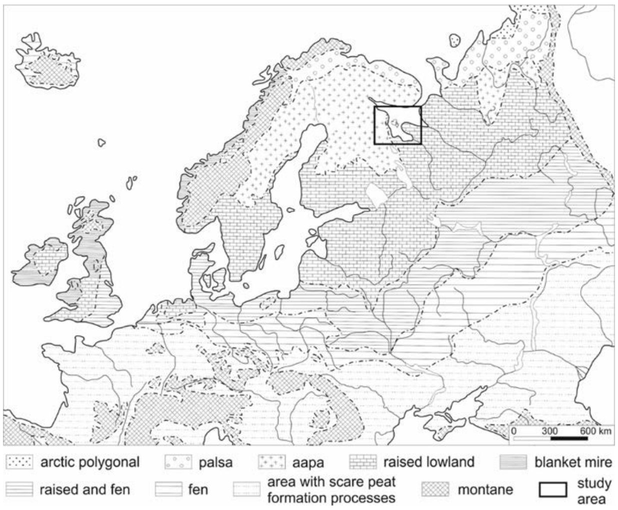

Figure 1. Map of the zonality of European mires (Żurek 1984), showing location of the study area.

Field survey and geochemical analysis

During an expedition to the Solovetsky Islands of the Institute of Botany, Russian Academy of Sciences (Saint Petersburg) in 1996, one of the authors (SZ) conducted surveys of contemporary peatland vegetation using the method of Braun-Blanquet (1964) and collected soil samples from the uppermost layer of peat, in transitional mires and raised bogs located in the central and southern parts of Bolshoy Solovetsky Island (Figure 2). The top 5 cm of peat was collected, starting immediately below the uppermost green part of the profile. The living green layer (of mosses) was, on average, 20 cm thick, and would contain the most recently accumulated trace elements. The sampled peat can be approximately associated with trace element deposition in the 1980s and before, spanning a period of 40–70 years (mean rate of peat layer growth in Russian Karelia is 0.7 mm yr^{-1} in the aapa province and 0.9–1.3 mm yr^{-1} in the raised bog province; Żurek 1987, Żurek 2009).

The investigated samples were collected from 42 sites in 26 peatlands. For the transitional mire type, nine peatlands were sampled (1–3 samples per peatland). An example of this mire type, near the sea coast, is shown in the upper part of Figure 3. For raised bogs, hollows were sampled at eight peatlands and hummocks were sampled at ten peatlands (1–2 samples per bog in both cases). The lower part of Figure 3 shows an example raised bog site at a lake.

For geochemical analysis, the peat samples (5–10 cm^3) were first dried to constant weight at 105 °C, then ashed in a muffle furnace at 550 °C for five hours, followed by testing at 900 °C to check the completeness of ignition. The organic matter content of each sample could then be calculated. The ashed

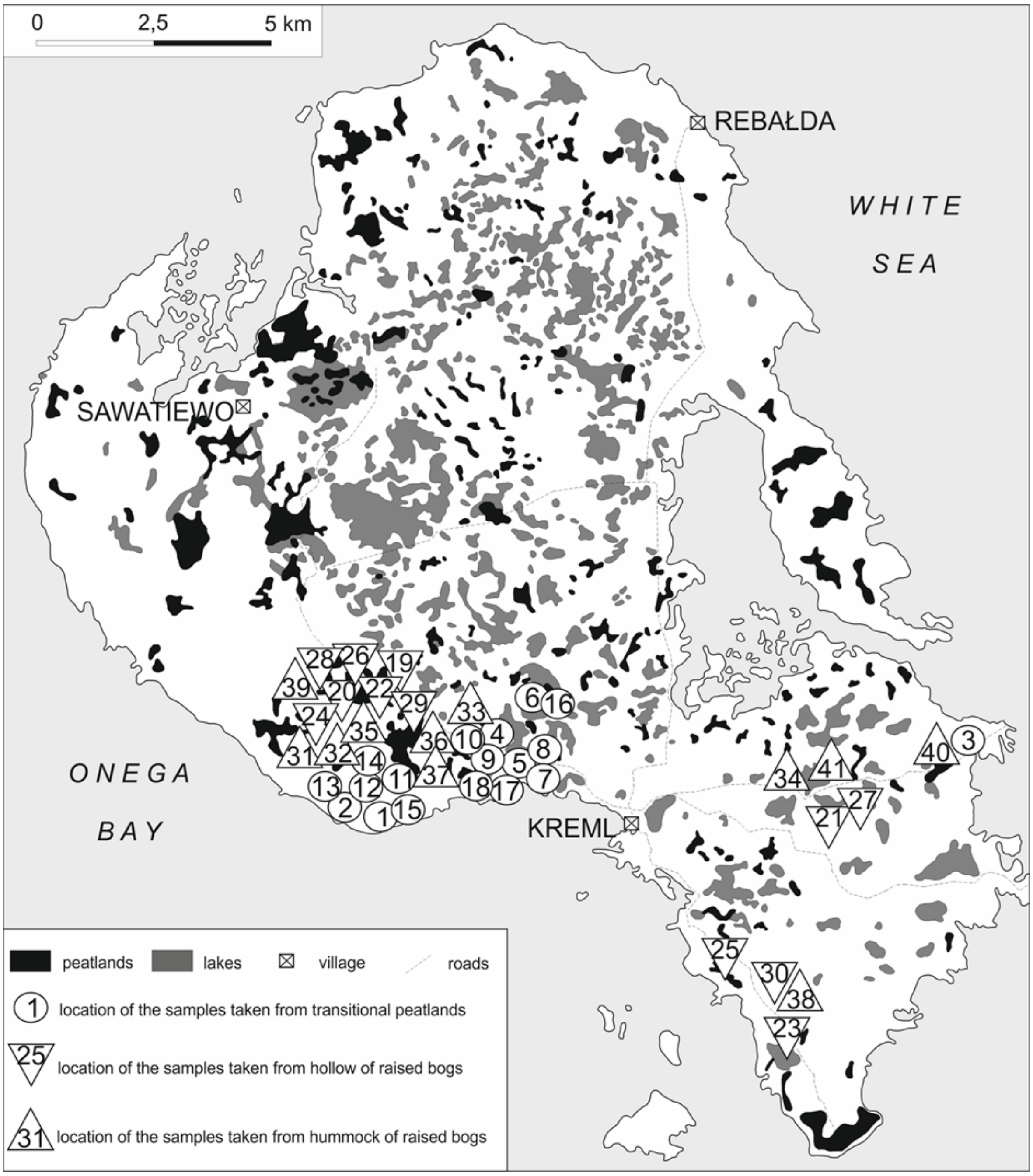

Figure 2. Map of Bolshoy Solovetsky Island showing the distribution of peatlands and lakes (Żurek 2007).

samples were dissolved in a 8:2:2 (by volume) mixture of concentrated nitric acid, 10 % hydrochloric acid and perhydrol, using a UniClever microwave mineraliser (Borówka 1992). The solution obtained was analysed by atomic absorption spectrometry (AAS PerkinElmer 3100) for concentrations of Cd, Cr, Ni and Pb (wavelengths 228.8 nm, 357.9 nm, 232.0 nm and 217.0 nm, respectively). Background level (blank sample read) was immediately subtracted from all readings. For pH measurements suspensions were prepared using dry peat with distilled water and 1M KCl at the ratio 1:2:5 (van Reeuwijk 2002). All of the laboratory analyses (for 41 samples) were conducted at Kielce University of Technology and Institute of Geography at The Jan Kochanowski University in Kielce.

Statistical analysis

Statistical analyses were performed using Statistica 13.1 (StatSoft Inc., Tulsa, Oklahoma, USA). To eliminate the influence of extreme values on the normal distribution of the results, we calculated quartiles (including median) and coefficients of variation (CV, calculated as the quotient of median trace element content and the difference between quartiles). Relationships between different characteristics were assessed using Spearman rank correlation coefficients. Kruskal-Wallis ANOVA was performed instead of parametric analysis of variance, in order to robustly identify significant differences between subsets of data without the assumption of their normal distribution.

Pollution indices

To assess the level of trace element pollution in the uppermost layer of peat, we calculated the following pollution indices: geoaccumulation index (I_{geo}), contamination factor (C_f) and degree of contamination (C_{deg}). The geoaccumulation index (I_{geo}) was calculated from the following relationship (Muller 1969):

$$I_{geo} = log_{10}\left(\frac{C_n}{1.5B_n}\right) \qquad [1]$$

where C_n is the content in the sample of a given metal and B_n is the geochemical background, in this case

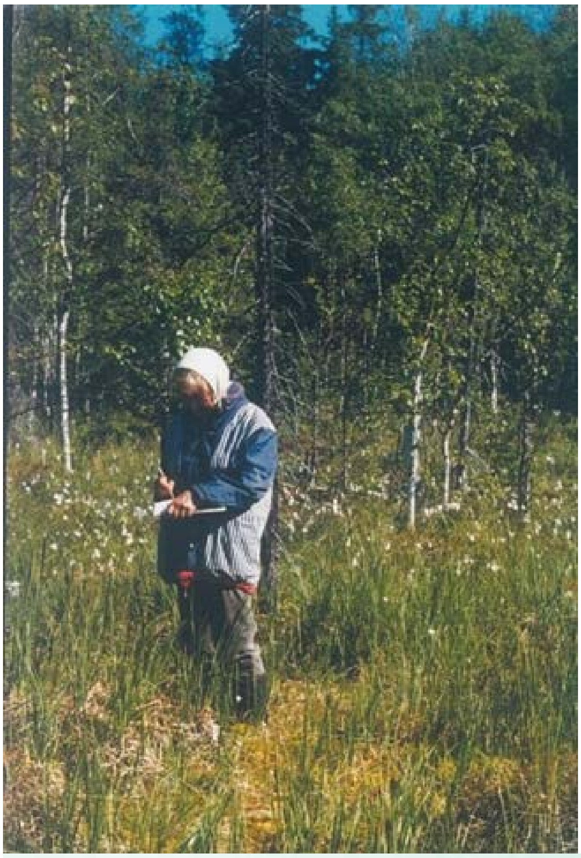

Figure 3. Above: Professor M. Botch working on a transitional mire with sparse forest (No. 9 in Figure 2) during the 1996 Solovetsky expedition. Below: floating vegetation mat at a raised bog site (No. 21 in Figure 2). A few herb species are visible among the (mainly *Sphagnum*) mosses. Photos: S. Żurek.

multiplied by 1.5 to reflect natural fluctuations in the content of a given metal in an environment with little human influence (all contents in ppm). Contamination factor (C_f) was calculated using the following equation (Hakanson 1980):

$$C_f = \frac{C_n}{B_n} \qquad [2]$$

where C_n is the metal content of the sample (ppm) and B_n is the metal content of the pre-industrial "baseline" sediment (ppm). The degree of contamination (C_{deg}) of a sample was expressed as the sum of individual values of C_f. The following contents of trace elements in the organic soil layer were assumed to constitute the geochemical background B_n (Salminen 2009): Cd = 0.32 ppm, Cr = 5.0 ppm, Ni = 6.47 ppm and Pb = 21.38 ppm.

RESULTS

Vegetation

Among the peatlands investigated, raised bogs predominated. These occurred mostly on the 'meadow terrace', 3–4 m above the seashore floodplain. Their hummocks were sparsely overgrown by trees (*Pinus sylvestris*, *Picea obovata*, *Betula tortuosa*) and frequently covered with dwarf shrubs (*Betula nana*, *Calluna vulgaris*, *Vaccinium uliginosum*, *V. myrtillus*, *V. vitis-idaea*, *Rubus chamaemorus*, *Ledum palustre*), other vascular plants (*Eriophorum vaginatum*, *Andromeda polifolia*, *Baeothyron caespitosum*, *Drosera rotundifolia*) and peat mosses (*Sphagnum fuscum*, *S. rubellum*, *S. tenellum*, *S. angustifolium*, *S. fallax* and *S. russowii*). Species occurring on the hummocks were dwarf shrubs (*Betula nana, Oxycoccus quadripetalus, O. microcarpus, Vaccinium uliginosum, Calluna vulgaris*), other vascular plants (*Andromeda polifolia, Baeothyron caespitosum, Drosera rotundifolia, D. anglica, Carex rostrata, C. pauciflora, C. nigra, C. rariflora*) and peat mosses (*S. fallax, S. cuspidatum, S. balticum*).

The transitional mires sampled were located within the seashore floodplain, in the terrestrialising zones of large lakes, or in areas fed by small rivers or groundwater discharge. These mires exhibited a mesotrophic character with a rich flora of vascular plants (*Carex chordorrhiza, C. aquatilis, C. nigra, C. lasiocarpa, C. limosa, C. rostrata*, *Juncus filiformis, Comarum palustre, Cornus suecica, Geranium pratense, Lathyrus paluster, Stellaria palustris, Pedicularis palustris, Bartsia alpina, Angelica sylvestris, Calamagrostis purpurea*), brown mosses (*Pleurozium schreberi, Drepanocladus vernicosus, Polytrichum commune, Calliergon stramineum, Selaginella selaginoides*), dwarf shrubs (*Salix pallonum, Rubus chamaemorus)* and, less frequently, peat mosses (*S. warnstorfii, S. rubellum*). An interesting biogeographical fact is that the dwarf shrub *Chamaedaphne calyculata*, which occurs frequently on raised bogs in the vicinity of the White Sea, is not present on Bolshoy Solovetsky Island (Żurek 2007).

Geochemical results

The organic matter content of peat samples collected from raised bogs exceeded 95 % (average value) and showed no variability connected to the sampling site (Table 1). The reaction of all samples was acidic (pH between 4.6 and 5.0) (Figure 4). The average organic matter content of samples from transitional mires was approximately 82 %, and their reaction was neutral or slightly alkaline (pH between 6.6 and 7.8) (Figure 4).

The median concentrations of Cd, Cr, Ni and Pb were 0.8, 1.27, 4.01 and 6.87 ppm, respectively

Table 1. The average concentrations of trace elements (ppm) and coefficients of variation (%) in samples from peatlands on Bolshoy Solovetsky Island and other countries in Europe.

Trace element	This study: median and CV (%)	Peat, Estonia (Orru & Orru 2006)	Peat, Finland (Nieminen *et al.* 2002)	Peat, Latvia (Silamikele *et al.* 2010)	Peat, Norway (Frontasyeva & Steinnes 2005)	Peat, Poland (Bojakowska & Lech 2008)
Cd	0.8 (144 %)	0.19	no data	0.14	no data	0.2
Cr	1.27 (106 %)	0.39	no data	1.17	12.5	< 3
Ni	4.01 (47 %)	0.71	25	1.38	4.30	3
Pb	6.87 (73 %)	9.62	18.1	4.77	no data	7

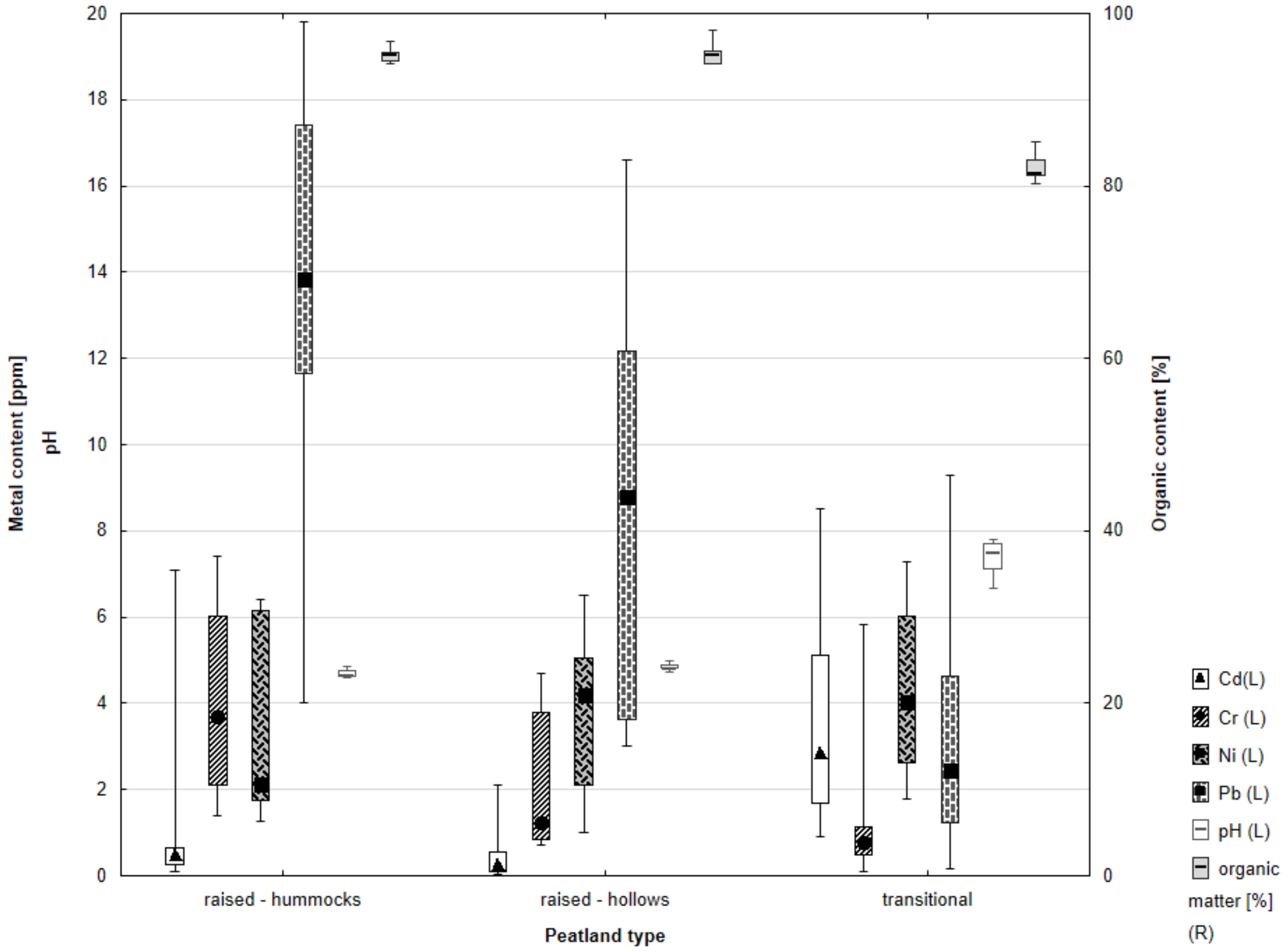

Figure 4. The range of values of the measured trace elements in the three peatland types. Each box indicates the quartiles (including median as a marker inside it), and the full range of values is shown by the whiskers.

(Table 1). The elements with the lowest median concentrations showed the highest coefficients of variance (CV), reaching 144 % for Cd, 106 % for Cr and 47 % for Ni. Among all samples collected in this study, statistically significant correlations were found for three element pairs, namely: Cr and Cd (-0.41, $p < 0.01$), Pb and Cd (-0.37, $p < 0.05$), and Pb and Cr (+0.33, $p < 0.05$) (Table 2). However, there were no statistically significant correlations specific to individual peatland types (data not shown), while the median concentrations of these elements differed between peatland types. The differences between the statistical distributions of these elements across peatland types were confirmed by the results of Kruskal-Wallis ANOVA, which were statistically significant in the case of Cd (KW-H (2;42) = 23.3; $p < 0.01$), Cr (KW-H (2;42) = 19.5; $p < 0.01$) and Pb (KW-H (2;42) = 23.7; $p < 0.01$). For Ni only, no statistical difference could be confirmed between peatland types. The highest content of Pb was determined in raised bog hummocks (19.8 ppm in Samples 33 and 34, see Figure 4), as was the top Cr content level (7.4 ppm, Sample 35). The other two elements considered, Ni and Cd, were most concentrated in transitional mire samples (Sample 17 at 7.3 ppm and Sample 12 at 8.5 ppm).

Table 2. Correlation coefficient matrix of trace element concentrations in peatlands (all samples) of Bolshoy Solovetsky Island, N = 42, ** $p < 0.01$, * $p < 0.05$, n.s. = not significant.

Cr	**-0.4093****		
Ni	0.2615 n.s.	-0.2984 n.s.	
Pb	**-0.3710***	**0.3292***	0.0423 n.s.
	Cd	Cr	Ni

Pollution indices

For all of the elements we studied except Cd, the geoaccumulation index (I_{geo}) was less than 0, which indicated that all peat samples were unpolluted with Cr, Ni and Pb. As regards Cd, I_{geo} exceeded 1.5 for Samples 12 and 37, and 1.4 for Samples 7, 10 and 17 (Tables 3–5), indicating moderate to high pollution with this element. Calculation of the contamination factor (C_f) made it possible to categorise samples into groups depending on how many times the actual values exceeded those characteristic of the geochemical background. In most samples, the C_f values for Cr, Ni and Pb were in the range 0–1, which indicates natural sources of these metals in the environment. The highest C_f values were found for Cd (Tables 3–5). Very high Cd contamination occurred in 38 % of all tested samples (i.e. in 16 out of 42 samples), and in 72 % (13 out of 18) of the transitional mire samples.

DISCUSSION

Pollution levels

Overall, the trace element pollution found in the uppermost layer of peat on the Solovetsky Islands is lower than reported from Estonia, Finland, Latvia, Norway and Poland (Table 1). On the other hand, the trace element concentrations show large variability, as indicated by the coefficient of variation, which even exceeded 100 % for Cd and Cr. In accordance with the criteria established by Hakanson (1980), 17 % of our samples showed a considerable degree of contamination ($16 < C_{deg} < 32$), 15 % had moderate ($8 < C_{deg} < 16$) and 68 % had low pollution levels ($C_{deg} < 8$). Most samples were significantly depleted relative to the geochemical background, and pollutant contamination was generally low for Cr, Ni and Pb (Tables 3–5). On the other hand, the contamination factor for Cd was substantial, and very

Table 3. Geoaccumulation index (I_{geo}) and contamination factor (C_f) for individual trace elements, and the degree of contamination (C_{deg}), in transitional mires on Bolshoy Solovetsky Island. Shading indicates certain levels of a each index, as follows: I_{geo}: not shaded = definitely unpolluted samples, light grey background = low to moderately polluted samples; C_f: white = $C_f < 1$ indicating low contamination, light grey corresponds to $1 \leq C_f < 3$ which is considered to indicate moderate contamination, dark grey indicates $3 \leq C_f < 6$ i.e. considerable contamination, shaded dark grey and printed in boldface means $C_f \geq 6$ which is a very high contamination factor; C_{deg}: no shading = a low pollution level, light grey = moderate, and dark grey = a considerable degree of contamination.

No.	I_{geo}				C_f				C_{deg}
	Cd	Cr	Ni	Pb	Cd	Cr	Ni	Pb	
1	1.102	-0.807	-0.356	-0.699	**8.4**	0.1	0.3	0.1	9.0
2	1.151	-0.642	0.057	-1.309	**9.4**	0.2	0.8	0.0	10.4
3	0.901	-0.437	0.066	-0.554	5.3	0.2	0.8	0.2	6.5
4	1.379	-0.588	-0.155	-0.437	**15.9**	0.2	0.5	0.2	16.8
5	0.972	-0.824	-0.158	-0.832	**6.3**	0.1	0.5	0.1	6.9
6	0.972	-0.569	-0.031	-0.489	**6.3**	0.2	0.6	0.2	7.3
7	1.415	-0.745	-0.156	-1.200	**17.3**	0.1	0.5	0.0	18.0
8	0.680	-1.523	0.212	-0.702	3.2	0.0	1.1	0.1	4.4
9	1.205	-0.620	0.145	-0.279	**10.7**	0.2	0.9	0.4	12.1
10	1.427	-1.222	0.198	-1.064	**17.8**	0.0	1.1	0.1	19.0
11	1.370	-1.143	0.211	-1.116	**15.6**	0.0	1.1	0.1	16.8
12	1.600	-1.523	-0.024	-1.033	**26.6**	0.0	0.6	0.1	27.3
13	0.680	-0.631	-0.217	-1.978	3.2	0.2	0.4	0.0	3.8
14	0.680	-0.807	-0.315	-1.064	3.2	0.1	0.3	0.1	3.7
15	1.033	0.244	-0.387	-0.689	**7.2**	1.2	0.3	0.1	8.8
16	1.151	-0.466	0.098	-0.185	**9.4**	0.2	0.8	0.4	10.9
17	1.451	-0.173	0.229	-0.964	**18.8**	0.4	1.1	0.1	20.5
18	0.625	-0.338	-0.315	-0.290	2.8	0.3	0.3	0.3	3.8

high in the case of Samples 4, 7, 10–12, 17 and 37.

In order to interpret these data, we compare them with trace element levels in biota and the abiotic environment of the neighbouring areas and with global averages from published sources. Kabata-Pendias & Pendias (2001) have given the following ranges (and means) of total contents of trace elements in organic soils calculated globally (ppm, dry weight (dw) basis): 0.19–2.2 (0.78) for Cd; 1–100 (12) for Cr; 0.2–119 (12) for Ni; 1.5–176 (44) for Pb. The same authors established typical ranges of trace element levels (ppm dw) for mature leaf tissue in vascular plants, as follows: 0.05–0.2 for Cd, 0.1–0.5 for Cr, 0.1–5.0 for Ni and 5–10 for Pb. Toxic contents (ppm dw) are: 5–30 for Cd, 5–30 for Cr, 10–100 for Ni and 30–300 for Pb.

Table 4. Geoaccumulation index (I_{geo}) and contamination factor (C_f) for individual trace elements, and the degree of contamination (C_{deg}), in hollows of raised bogs on Bolshoy Solovetsky Island. For key to shadings, see the caption of Table 3.

No.	I_{geo}				C_f				C_{deg}
	Cd	Cr	Ni	Pb	Cd	Cr	Ni	Pb	
19	0.510	0.150	-0.288	-0.315	2.2	0.9	0.3	0.3	3.8
20	0.387	-0.672	0.179	-0.209	1.6	0.1	1.0	0.4	3.2
21	-0.852	-0.474	-0.008	-0.014	0.1	0.2	0.7	0.6	1.6
22	-0.183	-0.583	-0.011	-0.558	0.4	0.2	0.7	0.2	1.4
23	-0.852	-0.489	0.040	-0.030	0.1	0.2	0.7	0.6	1.7
24	0.993	-0.620	0.065	-0.209	**6.6**	0.2	0.8	0.4	7.9
25	-0.028	0.033	-0.230	-0.635	0.6	0.7	0.4	0.2	1.9
26	-0.329	0.079	-0.329	-0.677	0.3	0.8	0.3	0.1	1.6
27	0.148	-0.620	-0.412	-0.137	0.9	0.2	0.3	0.5	1.8
28	-0.329	0.080	-0.626	-0.112	0.3	0.8	0.2	0.5	1.8
29	0.370	-0.399	0.073	-0.630	1.6	0.3	0.8	0.2	2.8
30	0.449	-0.178	0.165	0.066	1.9	0.4	1.0	0.8	4.1

Table 5. Geoaccumulation index (I_{geo}) and contamination factor (C_f) for individual trace elements, and the degree of contamination (C_{deg}), in hummocks of raised bogs of the Bolshoy Solovetsky Island. For key to shadings, see the caption of Table 3.

No.	I_{geo}				C_f				C_{deg}
	Cd	Cr	Ni	Pb	Cd	Cr	Ni	Pb	
31	0.273	-0.108	-0.531	-0.112	1.3	0.5	0.2	0.5	2.5
32	1.055	-0.085	-0.279	0.129	**7.6**	0.5	0.4	0.9	9.4
33	0.449	-0.383	0.165	0.143	1.9	0.3	1.0	0.9	4.1
34	0.449	-0.383	0.165	0.143	1.9	0.3	1.0	0.9	4.1
35	0.148	0.346	0.171	-0.005	0.9	1.5	1.0	0.7	4.1
36	-0.028	0.185	-0.394	0.025	0.6	1.0	0.3	0.7	2.6
37	1.522	-0.319	-0.032	-0.020	**22.2**	0.3	0.6	0.6	23.8
38	-0.329	0.257	-0.332	-0.550	0.3	1.2	0.3	0.2	2.0
39	0.516	0.258	-0.332	0.039	2.2	1.2	0.3	0.7	4.4
40	0.251	-0.025	-0.479	-0.064	1.2	0.6	0.2	0.6	2.6
41	0.449	0.107	-0.382	-0.319	1.9	0.9	0.3	0.3	3.3
42	-0.028	0.334	0.141	-0.037	0.6	1.4	0.9	0.6	3.6

The samples collected in this study originate from moss tissue, albeit altered by partial decomposition. Because mosses have been used in environmental studies for several decades, copious data on the metal contents of their tissues are available. Our data are compared with results from a Europe-wide survey of moss tissue by Harmens *et al*. (2010, 2013) in Table 6. Only Cr contents were similar, while the Cd, Ni and Pb contents determined for Solovetsky Islands peat were higher than moss tissue contents in Europe, Norway and Sweden (Tables 1 and 4). Grodzińska & Godzik (1991) undertook a study of trace element contents in the moss *Sanionia uncinata* near the Polish Polar Station in the well-studied remote arctic region of Svalbard. Their results were 0.41–0.82 ppm for Cd, 1.6–8.9 ppm for Ni and 2.4–16 ppm for Pb, and thus mostly comparable with ours, except that the Cd content of Solovetsky transitional mire peat was about four times that found in Svalbard moss.

In our study Ni and Pb contents were lower than the mean values for soils and below the toxic range for plants. We found values above the normal ranges for soils and plants only for Cd and Cr which, in a few samples, even reached the toxic levels quoted by Kabata-Pendias & Pendias (2001).

Table 6. Trace element concentrations (ppm) in moss tissue. The data for Solovetsky are median values for moss peat (only), obtained in this study. Mean values for Europe, Norway and Sweden in 2005, after Harmens *et al*. (2010, 2013), are shown for comparison.

Trace element	Solovetsky	Europe	Norway	Sweden
Cd	0.39	0.21	0.089	0.14
Cr	2.67	2.37	0.58	0.61
Ni	3.25	2.21	1.24	0.61
Pb	11.6	5.62	2.17	2.15

Possible sources of pollutants

Calculation of the enrichment factor (EF) (e.g. Zinkutė *et al*. 2017) might have enabled us to determine definitively the origin of the trace elements that we detected at Solovetsky. Unfortunately, we were not able to calculate EFs for samples from the 1996 expedition due to the small volume of material available, which meant it was not possible to perform a concentration analysis of normalising metals (e.g. Fe, Al, Si). A second sampling expedition obtaining comparative repeat samples from the same locations would allow a wider set of measurements including additional analyses to determine Fe and Al contents, as well as the clay fraction, thus enabling the calculation of enrichment factors. Meanwhile, we utilise other information to identify potential sources of the pollution that we observed.

The history of human influence on the territory of the Solovetsky Islands is characterised by comparatively low industrial activity; although there was a change in the late 19th and early 20th centuries, when channels were built between the lakes to enable transportation of goods such as wood, hay and fish by boat (Żurek 2007). Although the levels of trace elements found in the study sites are correspondingly low in general, correlations between them might be attributed to their originating from common sources, which may include distant industrial activity (Percy & Borland 1985). Some industries (as well as fossil fuel combustion) are significant sources of Ni, Cr and Pb, while the Cu-Ni industry is an important source of Ni and Pb. After emission into the atmosphere, these trace elements could propagate to the Solovetsky Islands through long-range transport (Pacyna 1995). In this case we would expect correlations between various metal contents to be especially clear in raised bogs, which obtain all of their water from precipitation.

The sampled uppermost layer of peat, interpreted with respect to the average peat growth rate in the area (Żurek 1987), could incorporate legacy atmospheric deposition from most of the 20th century (1910s to 1980s) and is very likely to include the deposition maximum from the second half of that century. Evidence of this maximum has been found as far away as the remote Svalbard archipelago; for example, in peat corresponding to the 1960s and 1970s for Pb. The subsequent drop in concentration and shift in isotopic composition indicated more natural sources later on (Liu *et al*. 2012); however, in more recent lake sediments the annual atmospheric deposition of Pb was still at a level of 120 mg m^{-2} in 1990 and 1995–2000, and only after that dropped to 40 mg m^{-2} yr^{-1} (Sun *et al*. 2006).

For the Solovetsky Islands, several potential sources of trace elements can be identified. The closest is the Kola Peninsula, where the industrial area of Monchegorsk, Apatity and Kirovsk is located at a distance of approximately 300 km from the islands. In 1979, Cu-Ni production in the Kola Peninsula emitted 535 t yr^{-1} of Ni and 412 t yr^{-1} of Pb, as well as 15 t yr^{-1} of Cd and 2 t yr^{-1} of Cr (Pacyna *et al*. 1985). In the Urals, the same industry was emitting 585, 1220, 70 and 5 t yr^{-1} of Ni, Pb, Cd and Cr, respectively. Emissions of Pb from gasoline combustion were equally high or higher at the time - estimated at 237 t yr^{-1} in the Kola Peninsula, 158 t yr^{-1} in the Pechora Basin and a striking 7630 t yr^{-1} in the Urals. Fossil fuel combustion and coal mining were also significant sources of, especially, Ni, Cr and Pb in the Kola Peninsula (40, 34 and 54 t yr^{-1}, respectively), the Pechora Basin (62, 60 and 27 t yr^{-1}) and the Urals (790, 150 and 173 t yr^{-1}). The iron and steel industry was an important source of Cr, emitting 47 t yr^{-1} in the Kola Peninsula and 1230 t yr^{-1} in the Urals. Among industrial sources of Cd, Cu-Ni production predominated; although phosphate fertiliser manufacturing in the Kola Peninsula should also be mentioned, with an emission of 10 t yr^{-1}.

Local conditions could also influence the trace elements content of the samples studied here. In Samples 32 and 37, which were collected close to the road, the concentrations of both Cd (2.42 and 7.1 ppm, respectively) and Pb (19.2 and 13.6 ppm) were high and similar to traffic pollution reported by other authors (Viard *et al.* 2004, Bakirdere & Yaman 2008, Korzeniowska *et al.* 2014). Proximity to the road is regarded as the main factor affecting roadside deposition; the metal contents of soils and plants normally decrease towards background level with increasing distance from the road (Zechmeister *et al.* 2005, 2006; Masoudi *et al.* 2012, Werkenthin *et al.* 2014, Kováčik *et al.* 2016, Giacomino *et al.* 2016).

Statistically significant correlations ($p \leq 0.05$) were found for three pairs of metals: Cr-Cd, Pb–Cd (negative), and Pb–Cr (positive). The negative correlations with cadmium may indicate its opposite chemical behaviour to the other two metals (dependent on the pH of the environment; see next section below). The other two elements (Pb, Cr) probably originate from medium- and/or long-range atmospheric transport of pollutants generated by common industrial sources. However, despite the likelihood of medium-range transport (over a distance of approximately 300 km) of trace elements from the Kola Peninsula mining industry, on the basis of our data we conclude that the Solovetsky Islands peatlands did not receive an intensive pollution load in the studied years.

Patterns related to the peatland type and microtopography

We found differences in the patterns of trace element contents across the three types of peatland environment studied, i.e. raised bog hummocks and hollows, and transitional mires. Hummocks had the highest average contents of Cr and Pb, while Cd was most abundant in transitional mires. Ni showed the smallest differences between these three environments.

Although the uppermost layer of peat was formed some time ago, either rainwater or surface water played an important role in its formation at that time. Thus, the loading of metals carried in such waters may originally have been the direct source of the pollution that we found in this study. To explore this angle of interpretation in the context of peatland type, we compare the general concentrations of Cd, Ni, Cr and Pb in rainwater and seawater, as a background for our data.

Comparison with average rainwater and seawater concentrations for each of the investigated metals shows connections to their environmental mobility features (Kabata-Pendias & Szteke 2012). In the case of Cd, the general concentrations in water are the smallest among the four elements considered here, and lower in rainwater (<0.01–0.05 μg L^{-1}) than in seawater (0.7–0.11 μg L^{-1}). Additionally, Kabata-Pendias & Szteke (2012) note that Cd is relatively mobile in seawater; whereas in freshwater it is quickly bound into organic complexes or carbonates, which facilitates uptake by plants. Cd also accumulates in marine fauna, especially fish, which were a local food source for the Solovetsky Islands. In combination, these factors could explain the different pattern of Cd content in peat, as compared to the other three metals; including the elevated Cd contents in transitional mires, some of which have contact with seawater during periodic flooding events. The change in pH at the seawater-peat boundary may additionally redirect Cd into plant tissue accumulation. An alternative mechanism to explain an inland decrease in the Cd content of peat may be the fast deposition of particulate Cd from marine aerosols through contact with fog droplets, as was suggested for Cd deposition in the Arctic by AMAP (2005).

For Cr, the situation is reversed; concentrations in rainwater are typically higher than in seawater (0.2–2.7 μg L^{-1} and 0.15–0.3 μg L^{-1}, respectively). This is consistent with the higher median Cr content for raised bog hummocks than for other locations in the peatlands (Figure 4). In aquatic environments, Cr is quickly bound by organic matter or precipitated as $Cr(OH)_3$, which limits its further transport.

The spatial patterns of Pb content in peatland were similar to those of Cr, but with higher values, whereas Pb concentrations in seawater are normally lower than for Cr (<0.03–0.27 μg L^{-1}). While we do not have worldwide data on Pb concentrations in rainwater, it is likely that in the Solovetsky Islands they reflect the high industrial emissions reported for this part of Europe by Pacyna (1995). Furthermore, Pb is more soluble in acidic environments (such as raised bogs, with a typical pH of about 4). Hence, Pb may be supplied to the raised bogs in rain, which scavenges atmospheric pollution, and distributed there. As plants easily take up Pb from rainwater and may even accumulate it beyond background levels in water, the high Pb contents noted here are not very surprising. Peat was even described by Kabata-Pendias & Szteke (2012) as an environment which accumulates Pb with a particularly high efficiency.

The small differences in Ni content between peatland types is consistent with the general range of Ni concentrations in rainwater and seawater being similar (0.3–0.7 μg L^{-1} for rainwater, average 0.65 μg L^{-1} for seawater; after Kabata-Pendias & Szteke 2012). Kabata-Pendias & Szteke (2012) claim that 50 % of Ni in surface waters originates from human activity, and the content of Ni in plants is usually proportional to its concentration in soil water. Thus, the lack of differences between various water media may have led to the relatively uniform Ni contents observed across the peatland types studied here.

Thus, the interpretation of trace metal contents in peat samples for atmospheric pollution monitoring must be considered alongside the possibility of enhancements due to various factors affecting the mobility of these elements, such as selective uptake by plants. Our results indicate that the utility of peat for monitoring pollution is subject to limitations arising from differences in uptake capacity between transitional mire and raised bog, as well as between hummocks and hollows within raised bog. The element with the least variable concentrations (nickel, Ni) may be used for calculating enrichment ratios to express the variation in uptake of other elements from seawater or precipitation. Such enrichment ratios could then be compared to the traditionally calculated enrichment factor (EF) based on the concentrations of Fe, Si or Al. Observed lead (Pb) and chromium (Cr) contents of raised bog peat may be significantly higher if measured on samples taken from hummocks rather than hollows. Therefore, we recommend that the origin of peat samples with respect to microtopography should always be noted when sampling for such studies in the future.

ACKNOWLEDGEMENTS

We are grateful to the Editor-in-Chief of the journal, Dr Olivia Bragg, for thorough editorial handling; and to the reviewers for their critical and helpful comments. The investigation of the Solovetsky Islands peatlands were conducted thanks to the help of Professor Marina Botch and Dr Viktor Smagin from the Department of Geobotany, Komarov Botanical Institute, Russian Academy of Sciences in St. Petersburg. The species identification of mosses was performed by Professor Kazimierz Karczmarz from Maria Curie-Sklodowska University in Lublin.

AUTHOR CONTRIBUTIONS

SZ participated in the expedition of the Institute of Botany of the Academy of Sciences in St. Petersburg, conducted the vegetation surveys and collected the soil samples. EB-M analysed the chemical composition of the peat samples. KK, JK and DO described the Methods and Results, and created the Figures and maps. All authors contributed to preparation of the concluding Discussion.

REFERENCES

Allan, M., Le Roux, G.S., Jeroen, E., Piotrowska, N., Streel, M., Fagel, N. (2013) Reconstructing historical atmospheric mercury deposition in Western Europe using Misten peat bog cores, Belgium. *Science of the Total Environment*, 442, 290–301.

AMAP (2005) *AMAP Assessment 2002: Heavy Metals in the Arctic*. Arctic Monitoring and Assessment Programme (AMAP), Oslo, Norway, xvi + 265 pp.

Bakirdere, S., Yaman, M. (2008) Determination of lead, cadmium and copper in roadside soil and plants in Elazig, Turkey. *Environmental Monitoring and Assessment*, 136, 401–410.

Bojakowska, I., Lech, D. (2008) Zróżnicowanie zawartości pierwiastków śladowych w torfach występujących na obszarze Polski (Variance of trace element content in peats occurring in Poland). *Zeszyty Naukowe Politechniki Śląskiej, Seria: Górnictwo*, 285, 31–41 (in Polish with English summary).

Borówka, R.K. (1992) *Przebieg i rozmiary denudacji w obrębie śródwysoczyznowych basenów sedymentacyjnych podczas późnego vistulianu i holocenu* (*The Pattern and Magnitude of Denudation in Interplateau Sedimentary Basins during the Late Vistulian and Holocene*). Wydawnictwo Naukowe Uniwersytetu im. Adama Mickiewicza w Poznaniu, Seria Geografia 54, 1–177 (in Polish with English summary).

Braun-Blanquet, J. (1964) *Pflanzensoziologie* (*Phytosociology*). Springer Verlag, Wien-New York, 865 pp. (in German).

Coggins, A.M., Jennings, S.G., Ebbinghaus, R. (2006) Accumulation rates of the trace elements lead, mercury and cadmium in ombrotrophic peatlands in the west of Ireland. *Atmospheric Environment*, 40, 260–278, doi: 10.1016/j.atmosenv.2005.09.049.

De Vleeschouwer, F., Le Roux, G., Shotyk, W. (2010) Peat as an archive of atmospheric pollution and environmental change: a case study of lead in Europe. *PAGES News*, 18(1), 20–22.

Eurola, S., Hicks, S., Kaakinen, E. (1984) Key to Finnish mire types. In: Moore, P.D. (ed.) *European Mires*, Academic Press, London, 11–17.

Frontasyeva, M.V., Steinnes, E. (2005) Distribution of 35 elements in peat cores from ombrotrophic bogs studied by epithermal neutron activation analysis. *Journal of Radioanalytical and Nuclear Chemistry*, 265(1), 11–15.

Giacomino, A., Malandrino, M., Colombo, M.L., Miaglia, S., Maimone, P., Blancato, S., Conca, E., Abollino, O. (2016) Metal content in dandelion (*Taraxacum officinale*) leaves: influence of vehicular traffic and safety upon consumption as food. *Journal of Chemistry*, Art ID 9842987, 9 pp.

Gorres, M., Frenzel B. (1997) Ash and metal concentrations in peat bogs as indicators of anthropogenic activity. *Water, Air, & Soil Pollution*, 100, 335–365.

Grodzińska, K., Godzik, B. (1991) Trace elements and sulphur in mosses from Southern Spitsbergen. *Polar Research*, 9, 133–140.

Hakanson, L. (1980) Ecological risk index for aquatic pollution control, a sedimentological approach. *Water Research*, 14, 975–1001.

Harmens, H., Norris, D.A., Steinnes, E., Kubin, E., Piispanen, J., Alber, R., Aleksiayenak, Y., Blum, O., Coşkun, M., Dam, M., De Temmerman, L., Fernández, J.A., Frolova, M., Frontasyeva, M., Gonzalez-Miqueo, L., Grodzińska, K., Jeran, Z., Korzekwa, S., Krmar, M., Kvietkus, K., Leblond, S., Liiv, S., Magnússon, S.H., Maňkovská, B., Pesch, R., Rühling, Å., Santamaria, J.M., Schröder, W., Spiric, Z., Suchara, I., Thöni, L., Urumov, V., Yurukova, L., Zechmeister, H.G. (2010) Mosses as biomonitors of atmospheric heavy metal deposition: spatial patterns and temporal trends in Europe. *Environmental Pollution*, 158(10), 3144–3156.

Harmens, H., Norris, D., Mills, G. and the participants of the moss survey (2013) *Heavy Metals and Nitrogen in Mosses: Spatial Patterns in 2010/2011 and Long-Term Temporal Trends in Europe*. ICP Vegetation Programme Coordination Centre, Centre for Ecology and Hydrology, Bangor, United Kingdom, 65 pp.

Kabata-Pendias, A., Pendias, H. (2001) *Trace Elements in Soils and Plants*. CRC Press, Boca Raton, 403 pp.

Kabata-Pendias, A., Szteke, B. (2012) *Pierwiastki Śladowe w Geo- i Biosferze* (*Trace Elements in the Geo- and Biosphere*). IUNG-PIP, Puławy, 269 pp. (in Polish).

Kac, N.J (1971) *Bagna kuli ziemskiej* (*Swamps of the Earth*). Państwowe Wydaw. Naukowe (PWN), Warszawa, 474 pp. (in Polish).

Korzeniowska, J., Panek, E., Baran, A. (2014) Testing of selected phytoindicators for assessment of trace metals (Cd, Cr, Cu, Ni, Pb and Zn) traffic pollution along the road Cracow – Zakopane. *Logistyka*, 4, 4486–4495.

Kováčik, J., Dudáš, M., Hedbavny, J., Mártonfi, P. (2016) Dandelion *Taraxacum linearisquameum* does not reflect soil metal content in urban localities. *Environmental Pollution*, 218, 160–167.

Liu, X., Jiang, S., Zhang, P., Xu, L. (2012) Effect of recent climate change on Arctic Pb pollution: A comparative study of historical records in lake and peat sediments. *Environmental Pollution*, 160, 161–168.

Masoudi, S.N., Ghajar Sepanlou, M., Bahmanyar, M.A. (2012) Distribution of lead, cadmium, copper and zinc in roadside soil of Sari-Ghaemshahr road, Iran. *African Journal of Agricultural Research*, 7(2), 198–204.

Muller, G. (1969) Index of geoaccumulation in the sediments of Rhine River. *Geojournal*, 2, 108–118.

Nieminen, T.M., Ukonmaanaho, L., Shotyk, W. (2002) Enrichment of Cu, Ni, Zn, Pb and As in a ombrotrophic peat bog near a Cu-Ni smelter in southwest Finland. *Science of The Total Environment*, 292(1–2), 81–89.

Orru, H., Orru, M. (2006) Sources and distribution of trace elements in Estonian peat. *Global and Planetary Change*, 53, 249–258.

Pacyna, J.M. (1995) The origin of Arctic air pollutants: lessons learned and future research. *Science of The Total Environment*, 160–161, 39–53.

Pacyna, J.M., Ottar, B., Tomza, U., Maenhaut, W. (1985) Long-range transport of trace elements to Ny Ålesund, Spitsbergen. *Atmospheric Environment* (1967), 19, 857–865.

Percy, K.E., Borland, S.A. (1985) A multivariate analysis of element concentrations in *Sphagnum magellanicum* Brid. in the maritime provinces, Canada. *Water, Air, & Soil Pollution*, 25, 331–338.

Salminen, R. (ed.) (2009) *Geochemical Atlas of Northern Europe*. Geological Survey of Finland, Espoo. Online at: http://weppi.gtk.fi/publ/negatlas/index.php, accessed 17 Aug 2014.

Shotyk, W. (1996) Peat bog archives of metal deposition: geochemical evaluation of peat profiles, natural variations in metal concentrations and metal enrichment factors. *Environmental Review*, 4, 149–183.

Shotyk, W., Nesbitt, W., Fyfe W. (1990) The behaviour of major and trace elements in complete vertical peat profiles from three *Sphagnum* bogs. *International Journal of Coal Geology*, 15(3), 163–190.

Silamikele, I., Nikodemus, O., Kalnina, L., Kuske, E., Rodinovs, V., Purmalis, O., Klavins M. (2010) Major and trace element accumulation in peat from bogs in Latvia. In: Klavins, M. (ed.) *Mires and Peat*, University of Latvia Press, Riga, 96–114.

Steinnes, E. (1987) Impact of long-range atmospheric transport of heavy metals to the terrestrial environment in Norway (Chapter 9). In: Hutchinson, T.C., Meema, K.M. (eds.) *Lead, Mercury, Cadmium and Arsenic in the Environment*, SCOPE 31, John Wiley & Sons Ltd., Chichester, 107–117.

Sun, Q., Chu, G., Liu, J., Gao, D. (2006) A 150-year record of trace elements in the varved sediments of Lake Bolterskardet, Svalbard. *Arctic, Antarctic, and Alpine Research*, 38, 436–445.

Tobolski, K. (2005) Peatland geography outline. In: Miotk-Szpiganowicz, G., Tobolski, K., Zachowicz, J. (eds.) *Deposits of the Biogenic Accumulation Reservoirs. Guide-book for Laboratory and Field Activity*. Polish Geological Institute, Gdańsk, 29–33.

van Reeuwijk, L. (2002) *Procedures for Soil Analysis*. Sixth Edition, International Soil Reference and Information Centre (ISRIC) and FAO, Wageningen. Online at: https://www.isric.org/sites/default/files/ISRIC_TechPap09.pdf, accessed 12 Feb 2020.

Veretennikova, E.E., Golovatskaya, E.A. (2012) Lead and mercury distribution in the peat deposits of West Siberia (Vasyuganye Peat Bogs). *Chemistry for Sustainable Development*, 20, 143–149.

Viard, B., Pihan, F., Promeyrat, S., Pihan, J-C. (2004) Integrated assessment of trace elements (Pb, Zn, Cd) highway pollution: bioaccumulation in soil, *Graminaceae* and land snails. *Chemosphere*, 55, 1349–1359.

Werkenthin, M., Kluge, B., Wessolek, G. (2014) Metals in European roadside soils and soil pollution – A review. *Environmental Pollution*, 189, 98–110.

Wilkin, R.T., Barnes, H.L. (1997) Formation processes of framboidal pyrite. *Geochimica et Cosmochimica Acta*, 61(2), 323–339.

Zechmeister, H., Hohenwallner, D., Riss, A., Hanus-Illnar, A. (2005) Estimation of element deposition derived from road traffic sources by using mosses. *Environmental Pollution*, 138, 238–249.

Zechmeister, H., Hagendorfer, H., Hohenwallner, D., Hanus-Illnar, A., Riss, A. (2006) Analyses of platinum group elements in mosses as indicators of road traffic emissions in Austria. *Atmospheric Environment*, 40, 7720–7732.

Zinkutė, R., Taraškevičius, R., Jankauskaitė, M., Stankevičius, Ž. (2017) Methodological alternatives for calculation of enrichment factors used for assessment of topsoil contamination. *Journal of Soils and Sediments*, 17, 440–452.

Żurek, S. (1971) Torfowiska aapa (Aapa peatlands). *Biuletyn Informacyjny Torf (Peat Information Bulletin)*, 31(4), 12–20 (in Polish).

Żurek, S. (1984) Verteilung und Charakter europäischer Moore (Distribution and character of European mires). *Telma*, 14, 113–125 (in German).

Żurek, S. (1987) *Złoża torfowe Polski na tle stref torfowych Europy (The Peat Deposits of Poland in the Context of the Peat Provinces in Europe)*. Dokumentacja Geograficzna (Geographical Documents) no. 4, Instytut Geografii i Przestrzennego Zagospodarowania PAN (Institute of Geography and Spatial Planning, Polish Academy of Sciences), Wrocław - Warszawa - Krakow - Gdańsk - Łodź, 84 pp. (in Polish).

Żurek, S. (2007) Przyroda i torfowiska Wysp Sołowieckich (Morze Białe) (Nature and peatbogs of the Solovetsky Islands (White Sea)). *Prace Instytutu Geografii AŚ w Kielcach* (*Proceedings of the Geography Institute, Świętokrzyska Academy in Kielce*), 16, 241–252 (in Polish).

Żurek, S. (2009) Badania zmian roślinności w holocenie na półwyspie Kola w oparciu o torfowiska palsa (Investigations of Holocene vegetation changes in the Kola Peninsula on the basis of palsa mires). *Prace i Studia Geograficzne*, 41, 261–271 (in Polish with English summary).

Żurek, S. (2012) Relief and lithology in relation to bog formation. In: Forysiak, J., Kucharski L., Ziułkiewicz, M. (eds.) *Peatlands in Semi-Natural Landscape - Their Transformation and the Possibility of Protection*. Bogucki Wydawnictwo Naukowe, Poznań, 73–84.

Submitted 09 Oct 2018, final revision 11 Feb 2020
Editors: Bartłomiej Glina and Olivia Bragg

Author for correspondence:
Dr Krystyna Kozioł, Department of Analytical Chemistry, Gdansk University of Technology, Narutowicza 11/12, 80-233 Gdansk, Poland. Tel: +48 58 347 21 10; E-mail: krystyna.koziol@pg.edu.pl