Effect of Corona Virus Pandemic Lockdown to Chemical Composition of Peat Mosses

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Abstract

Sphagnum mosses are used for biomonitoring of air pollution. In 2019, samples were taken from two peat bogs in Germany and two in Slovenia to determine differences in their levels of potentially toxic elements (PTE). The Corona Virus Disease (COVID-19) lockdown caused global decrease in air pollution. Therefore, we repeated the monitoring in 2020 to see if this was also reflected in moss composition. Despite the variability within bogs and the areas, it is possible to distinguish the degree of air pollution between the two countries. The Harz mosses have higher contents of almost all elements and Slovenian Cr and Hg in 2020. Comparison of the PTE contents, their ratios to Sc and the enrichment factors show that the COVID-19 lockdown led to a decrease in long-range pollutants bound to finest particles and increased the influence of local soil dusting. The effect prevailed over lower precipitation in 2020 compared to 2019. Transport and industry continued to contribute significantly to contamination. *Sphagnum* mosses proved to be good indicators of the spatial and temporal extent of pollution. Even relatively short periods of lower air pollution are reflected in moss PTE contents.

1. Introduction

Anthropogenic pollution increased during the Industrial Revolution and affected soil, water, and air. Rühling and Taylor (1968) suggested that atmospheric lead deposition could be tracked by chemical analysis of mosses. Mosses have no cuticle and roots and obtain their nutrients directly from atmospheric wet and dry deposition. In 1990, regular five-year moss surveys were started in Europe (Buse et al. 2003). Mosses were shown to be good indicators of temporal and spatial trends in heavy metal accumulation (Harmens et al. 2008; Schröder et al. 2008). Especially *Sphagnum* mosses have been found to be very suitable for monitoring air pollution because the shoots accumulate xenobiotics and their large surface area and unicellular thick leaf structure allows an abundance of cation exchange sites (Richardson 1981; Saxena 2006). In ombrotrophic bogs, nutrient supply is low and limited to atmospheric deposition (Rydin & Jeglum 2006). *Sphagnum* mosses are also used for active biomonitoring of trace elements using the "bag technique" (Aničić et al. 2009).

Towards the end of the 20th century, emissions to the atmosphere started to decrease due to pollution awareness, but were still high in Central Europe (Matschullat & Bozau 1996). Harmens et al. (2010, 2015) reported that the decrease in emissions led to a decrease in heavy metal concentrations in mosses for most metals, especially Pb, V, Cd, Cr, Zn, and Ni.

In December 2019, the first infections with Corona Virus Disease (COVID-19) were detected in Wuhan, China. The disease is very contagious and spreads very quickly to other parts of the world, and in March 2020 it was declared a global pandemic. It causes serious health problems and led to hospitals overload. As a result, the majority of countries opted for a lockdown, which resulted in a dramatic reduction of all types of transportation, industrial production, and trade worldwide (Safarian et al. 2020; Zhang et al. 2020). This led to a decrease in air pollution, e.g., concentrations of NO₂, CO₂, SO₂ and particulate matter (Zhang et al. 2020; Lian et al. 2020; Mohd Nadzir et al. 2020; Safarian et al. 2020; Zhang et al. 2020; Xu et al. 2020). *Sphagnum spp.* grow relatively fast (Foster, 1984), so they may be able to detect changes in air pollution through COVID-19 lockdown. For *Sphagnum magellanicum*, which also occurs on Pokljuka (Slovenia), the estimated annual growth rate is 5 cm (Kempter & Frenzel 2007). However, growth rates vary considerably between species and also for the same species at different sites in the bog.

In 2019, we sampled *Sphagnum* mosses in German and Slovenian ombrotrophic bogs to confirm their usefulness for biomonitoring of air pollution with potentially toxic elements (PTE). In 2020, we repeated the sampling at some sites.

The new contributions of the work are:

- determination of the regional and local variability in the chemical composition of *Sphagnum* mosses within a bog, between bogs in the same area, between areas and between Germany and Slovenia,
- identification of possible COVID-19 interception effect on the reduction of air pollution reflected in the *Sphagnum* moss PTE content.

2. Material And Methods

The study was conducted in Germany and Slovenia (Fig 1). In Germany, the sampling area were Harz Mountains, represented by two bogs – Acker (Ge-A) and Brocken (Ge-B). In Slovenia, two areas were considered - Pokljuka and Pohorje. In Pokljuka three bogs were sampled - Veliko Blejsko barje (SI-A), Šijec (SI-B) and Goreljek (SI-C), in Pohorje two - Črno jezero (SI-D) and Lovrenška jezera (SI-E).

The Harz Mountains are a highland area in northern Germany. The peat bogs of the Harz Mountains are found on the upper and mainly western parts of the mountain range. Sampling took place in the ombrotrophic bogs on the geological unit Acker-Bruchberg, developed on quartzite at an altitude of about 800 m and in the bogs around mount Brocken which is the highest peak of Harz Mountains consisting of granite at an altitude of 800 to 1120 m. Both areas receive about 1800 mm of annual precipitation.

Pokljuka is located in the northwestern part of Slovenia in Julian Alps and is part of the protected area Triglav National Park. It is a forested karst plateau at an altitude of about 1100 to 1400 m, which receives 2000 to 2500 mm of annual precipitation. The Pohorje massif is located in the northeast of Slovenia. The studied bogs formed on granodiorite at an altitude of 1200 to 1500 m. The annual precipitation is 1500 to 1600 mm.

A total of 48 *Sphagnum* moss samples were collected, 29 in 2019 (11 in Germany and 18 in Slovenia), 19 in 2020 (10 in Germany and 9 in Slovenia). Duplicate samples were collected at three sites in Germany and two sites in Slovenia. At each sampling site, one (Germany) to three liters (Slovenia) of the upper green parts of the living plant were collected.

In the laboratory, remnants of other plants were removed from the *Sphagnum* moss samples. The samples were washed three times with deionised water to remove dust and soil particles and dried at 40 °C. The ground samples were digested with aqua regia and analyzed by ICP-MS in Bureau Veritas (Acme) in Canada.

The contents of several elements were below the detection limit. In the case of less than 30% of such observations, the value "less than" was replaced by half of the detection limit. Since K and Mn concentrations in *Sphagnum* do not necessarily reflect atmospheric deposition (Kempter & Frenzel 2007), they were not considered in further analysis. The interpretation of the data therefore focused on Al, Ca, Fe, Ba, Cd, Co, Cr, Cu, Hg, La, Mo, Nd, Ni, Pb, Sc, Sr, Ti and Zn. The analytical quality was checked using 14 replicate samples and 2 standard materials (CDV-1 and V16). For all elements considered, the analytical error was less than 10%, except for Al at 20%.

Due to the small number of samples and the non-normal distribution of some elements, we used non-parametric statistics for statistical tests. Calculations were performed using the TIBCO Statistica programme (TIBCO Software Inc. 2017).

Distinguishing anthropogenic vs. geogenic trace metals in aerosols is possible by normalising to conservative lithogenic elements such as Al, Sc, and Ti. Normalisation to Sc as a measure of anthropogenic influence is proposed by Shoty et al. (2015). Soil-derived aerosols have values close to unity, industrial much larger (Peirson et al. 1974). Another advantage is that normalisation based on Me/Sc to crustal values generally reduces spatial variability

(Shotyk et al., 2015). Kempter & Frenzel (2007) noted that Ti concentrations in *Sphagnum* might be influenced by *Sphagnum* species productivity and Al might be depleted by air-crust fractionation (Rahn 1976). Nevertheless, because of the unexpectedly high increase in Sc content in 2020 compared to 2019, we calculated the enrichment factor (EF) for each element normalised to Ti and compared it to upper crustal content (UCC) values (Rudnick & Gao 2003) using the formula (Zoller et al. 1974; Weiss et al. 2002):

3. Results

In the *Sphagnum* mosses sampled in Germany and Slovenia in 2019 and 2020, the contents of the major elements are below 1%. They are highest for Ca with a mean value of 0.3%, followed by Al and Fe, both with similar ranges of values and mean values close to 0.05%. The contents of Ba, Pb, Sr, Ti and Zn range from a few mg/kg to over 100 mg/kg for Pb. On average, the contents of Ba, Sr and Ti are about 10 mg/kg, Pb is 20 mg/kg and Zn is 40 mg/kg. The contents of Cr and Cu average around 5 mg/kg, Ni around 2 mg/kg. The mean values of Cd, Co, La, Mo, Nd and Sc are less than 0.5 mg/kg. Average Hg content is around 30 µg/kg. Due to the generally low absolute values, relative comparisons of the contents may give the misleading impression of large differences, even if the absolute differences are only a few mg/kg.

4.1. Within bog variability

Sphagnum species generally behave similarly with respect to the uptake of atmospheric trace metal inputs, but measured contents are often highly variable due to the influence of various factors. The large variability within bogs can make it difficult to confirm statistically significant differences among bogs, areas, and regions. We first investigated the variability due to different moss species and visually checked the variability within peatlands using Box-Whisker diagrams (Fig. 2).

In Germany, we took two parallel samples of the same moss patches at two sites in Acker bog (Ge-A01-20 and Ge-A02-20). In Slovenia, at two sampling sites (SI-A01-19 and SI -A02-19) in Veliko Blejsko barje on Pokljuka, we sampled two *Sphagnum* species in close proximity, distinguished only by different colours - green and red.

Parallel samples from the same moss patches have similar chemical composition in terms of the contents of Al, Ca, Ba, Hg, Mo, Sc and Sr. In the case of sampling site Ge-A01-2020, Cd, Zn and Pb have quite different contents. Sampling site Ge-A02-20 is much more variable in terms of the list of elements and their degree of variability. The measured contents of Ba, Cd, Cr, Cu and Zn show less differences, but for Fe, La, Nd, Ni, Ti and Pb the variability is high.

Comparison of chemical composition of two different *Sphagnum* species shows quite low variability of Cr, Cu, Hg, Mo, Ni, Pb and Sr. For Al, Fe, Ba, Co and Ti the variability is low at the sampling site SI-A01-19 but higher at the other one. At the sampling site SI -A02-19, the variability is low for Ca, Cd and Zn and higher for other elements.

A comparison of the ranges of element contents (Fig. 2) shows that the variability within the bogs is basically larger in 2019 than in 2020. The elements reaching the maximum content ranges are also different. In general, larger ranges of element contents are observed in Germany. The variability for most elements is always highest in Broken (all elements except Ba, Hg and Sc in 2019 and Ca, Hg, Sc and Sr in 2020). In the bogs at Acker, variability was high only for Co, Pb and Zn in 2019, but in 2020 for most elements except Ca, Ba, Hg, La, Mo, Sc and Sr. In Slovenia, variability was high in 2019 for Cr in Veliko Blejsko barje, for Ca and Mo in Šijec, for Fe in Goreljek and for Sr in Črno jezero. In 2020, variability is high for Ca, Cu and Hg in Veliko Blejsko barje, for Fe, Co and Mo in Šijec, for Cr, Hg, Sr and Zn in Črno

jezero and for Fe, Cr, Cu, Mo and Ni in Lovrenška jezera. The variability of Sc is low, but greater in 2020, where, unlike the majority of other elements, the contents are also higher.

4.2 Spatial comparison

Comparison of peatlands using Kruskal-Wallis analysis of variance showed different results for 2019 and 2020. Statistically significant differences between bogs were found in both years for Ba and Zn contents, mainly due to high values of Ba in both German bogs and in 2020 also in Lovrenška jezera, and Zn in both German bogs. In 2019, the bogs also differed statistically significantly in the contents of Al, Cd, Co, Cr, Cu, La, Nd, Ni, Pb and Ti. Higher contents are observed in the two German bogs, especially in bogs around mount Brocken (Fig. 2). In 2020, differences were additionally confirmed only for Hg, which was low in the Acker and Brocken bogs and high in both Pohorje bogs. In contrast to 2019, in 2020 the levels of most elements were higher in Acker than in Brocken. In addition, although not statistically significant, the contents of Cr, Mo and Ni were highest in Pohorje bogs.

The Kruskal-Wallis analysis of variance comparing bogs within the three areas in 2019 and 2020 (Harz, Pokljuka, Pohorje) shows statistically different contents of certain elements only in Harz. In 2019, the contents of Al, Cr, La, Nd and Ti are significantly higher on the Brocken. In 2020, only Ba and Co show significantly higher contents in the Acker bogs.

The general comparison between German and Slovenian bogs performed with the Mann-Whitney test gives different results for the years considered. Again, the countries differ in many more elements in 2019 than in 2020. In both years, differences are indicated only for Ba, Cd, Cu, Nd and Zn, which are higher in German mosses. In 2019, German mosses also show significantly higher contents of Al, Co, La, Mo, Ni, Pb and Ti. In 2020, Slovenian mosses are significantly enriched in Hg compared to German mosses.

4.3 Effect of the COVID -19 lockdown on the chemical composition of mosses

Comparison of the chemical composition of *Sphagnum* mosses sampled in Germany and Slovenia in 2019 and 2020, performed with the Mann-Whitney test for the whole dataset, showed a statistically significant decrease in Cu (1.5-fold for the mean and 2.6-fold for the median) and an increase in the lithophilic elements, Ni (2-fold for the mean and 2.4-fold for the median) and Sc (2.8-fold for the mean, 2.3-fold for the median). Comparisons for some potentially highly toxic elements are shown in Fig. 3.

The results calculated separately for each country are different, except for Sc. In Harz decrease is confirmed for Cu (2.4-fold for the mean and 6.2-fold for the median), Hg (3-fold for the mean and 3.8-fold for the median) and Pb (about 7.7-fold for the mean and 11.5-fold for the median). In Slovenia, only Fe (about 1.6-fold for mean and median), Cr (2.8-fold for mean and 2-fold for median), Ni (3.1-fold for mean and 2.4-fold for median), Sc (about 2.85-fold for mean and median), and Ti (about 1.75-fold for mean and median) were found to increase. Although not statistically confirmed, the contents of all elements except Co, Ni, Sc and Ti also decreased at least slightly in Germany, and Ca, Ba, Cd, Pb, Sr and Zn in Slovenia. Despite lower median values for PTE in 2020, the variability and maximum contents of Co, Cr, Ni, Sc and Ti are higher in both countries, and additionally Cu, Hg, La, Mo and Nd in Slovenia.

Comparison of Sc-normalised contents of the most potentially hazardous elements for the whole data set (Fig. 4) and for each sampling site generally shows a decrease in the ratio for all elements, indicating a decrease in pollution, which is also confirmed by Mann-Whitney tests for the whole data set (except Cr/Sc and Ni/Sc), Germany (except Fe/Sc, Co/Sc, Cr/Sc, La/Sc, Nd/Sc, Ni/Sc and Ti/Sc) and Slovenia (except Cr/Sc and Ni/Sc). Although not statistically significant, the medians in 2020 are lower than in 2019 in all cases, but in particular for Cr and Ni the ranges and

maximum values are higher in 2020. The only elevated ratios in 2020 are Co, Cr and Pb in one sample from Acker and Cr and Ni in all four Pohorje samples.

From enrichment factors in Table 1 it can be seen that Al, Ca and Fe are strongly depleted in *Sphagnum* mosses compared to the upper continental crust (UCC); neglecting the maximum values, which are often due to some outliers, Ba, Co, La and Nd are only slightly enriched compared to the UCC, and Cr, Ni, Sc and Sr differ up to 30-fold. Extremely large deviations from the composition of the UCC are characteristic for Cd, Hg, Mo, Pb, and Zn, and to a lesser extent for Cu. In 2020, the mean, median, minimum, and maximum contents for most elements are lower than those observed in 2019. The exceptions are higher mean values of Co, Cr, Ni, Sc, and Sr. For Cr, Ni, and Sc, the median and maximum values are also higher in 2020. At the level of the whole dataset comparing only samples from the same sites, the decrease in EFs from 2019 to 2020 is statistically significant for Ba, Cd, Cu, La, Mo, Nd, Pb and Zn, and the increase for Sc. For the German mosses, EFs of all elements except Sc and Ti show a decrease, but it is not statistically significant. For the Slovenian mosses EF values of Ba, Cu, La, Nd and Zn are significantly lower and Sc higher in 2020 compared to 2020.

Table 1. Mean, median, minimum and maximum enrichment factors (EF) for German and Slovenian *Sphagnum* moss samples, sampled at the same locations in 2019 and 2020.

	Year	Average	Median	Min	Max		Year	Average	Median	Min	Max
Al	2019	0.00024	0.00034	0.00012	0.00235	La	2019	4	5	2	78
	2020	0.00021	0.00022	0.00004	0.00106		2020	4	4	1	39
Ca	2019	0.0052	0.0092	0.0007	0.0262	Mo	2019	198	249	39	453
	2020	0.0035	0.0048	0.0006	0.0154		2020	190	126	13	305
Fe	2019	0.0006	0.0007	0.0002	0.0012	Nd	2019	5	5	2	66
	2020	0.0006	0.0006	0.0001	0.0011		2020	4	4	1	31
Ba	2019	10	20	2	30	Ni	2019	12	22	6	39
	2020	7	7	1	19		2020	43	19	4	69
Cd	2019	3837	3368	365	40928	Pb	2019	155	599	66	6562
	2020	805	841	320	22063		2020	95	116	35	879
Co	2019	5	12	3	39	Sc	2019	14	14	2	41
	2020	7	8	4	20		2020	27	23	3	64
Cr	2019	24	25	6	54	Sr	2019	10	24	2	88
	2020	56	28	3	103		2020	13	11	1	53
Cu	2019	88	151	37	414	Zn	2019	312	511	105	888
	2020	7	24	4	289		2020	188	203	60	663
Hg	2019	460	549	54	1074						
	2020	375	351	11	742						

The decrease in the contents of PTE in 2020 is also evident by directly comparing the levels of EF from 2019 and 2020 at each sampling site (Fig. 5). In 2020, Cd shows an increase of EF in one sample from Veliko Blejsko barje, Cr shows a slight increase in one sample from Brocken and one from Goreljek and a huge increase in all Pohorje samples, Cu in one site Veliko Blejsko barje, Hg and Pb in one site in Veliko Blejsko barje and in one in Šijec. In Veliko Blejsko barje EF of Zn is also slightly elevated in one of the Veliko Blejsko barje replicate sites.

4. Discussion

5.1 Within bog variability

High variability even during a sampling event at neighbouring sites is quite common in biomonitoring (Kempter & Frenzel 2007). Moreover, it is usually not possible to sample only single *Sphagnum* species (Shotyk et al. 2015). Our comparison, although performed on only two samples and without knowledge of the *Sphagnum* species, confirmed a possible random variability of several elements, as already observed by Wojtuń et al. (2013).

High variability was also observed for the same species collected in parallel samples from the same moss patches. In fact, there are several other reasons for the variability in biomonitoring data besides *Sphagnum* moss species. One is the high variability of atmospheric deposition itself, caused by irregular deposition patterns, precipitation and wind (Matschullat & Bozau 1996). Moreover, it is not necessary that the chemical composition of mosses is directly correlated with atmospheric deposition, as some elements could be mobilised (e.g. Zn) or accumulated (e.g., Pb) in non-growing mosses (Kempter & Frenzel 2007; Kempter et al. 2010). In addition, the high variability could be due to different microsites (especially hummocks and hollows) where sampling took place (Wojtuń et al., 2013), annual height growth (Kempter & Frenzel 2007; Kempter et al. 2010) and tree canopy cover (Kempter et al. 2017).

Therefore, when comparing spatial and temporal trends, it is appropriate to consider mean values based on a sufficient number of observations to reduce variability. When the number of observations and/or the amount of material sampled is small, medians or comparisons of individual samples better reflect the characteristics of the population under the study.

5.2 Spatial comparison

The spatial distribution of the elements considered is different in 2019 and 2020. In relation to all four bogs, the highest mean and median values of all elements are observed on the Brocken in 2019, except for Mo and Pb on the Acker and Hg and Sr on the Črno jezero, as well as Ba median on the Lovrenška jezera. The maximum values of all elements are also reached on the Brocken. Exceptions are generally higher contents of Hg in Slovenia and high contents of Cr in Veliko Blejsko barje and Sr in Črno jezero. The situation is different in 2020, where highest mean, median and maximum contents for Al, Fe, Ba, Co, Cu, Pb, Ti and Zn are observed on Acker, where Cd also has the highest median value. On Brocken, highest mean, median and maximum contents are observed only for La and Nd. In Slovenia in 2020, besides Cr and Hg, Mo, Ni and Sc have the highest statistical parameters in Lovrenška jezera and Sr in Črno jezero.

Brocken and Acker show statistically significant differences only in the contents of Al, Cr, La, Nd and Ti in 2019, and Ba and Co in 2020. Variations in the chemical composition of mosses from three bogs within Pokljuka and two within Pohorje are not statistically significant in any of the observed years. Mann-Whitney test shows that the chemical composition of *Sphagnum* mosses from Pokljuka and Pohorje is very similar. In 2019 they differ only in Co (higher on Pokljuka) and Mo content (higher on Pohorje), and in 2020 in Cr, Mo and Ni content (higher on Pohorje).

In Harz Mountains, Brocken is on the highest elevation and receives the highest amount of precipitation (Table 2). This is consistent with the observation that increasing mountain elevation combined with increasing precipitation is reflected in the chemical composition of mosses (Zechmeister 1984; Thöni et al. 2011). However, in 2020, the measured contents of most elements are highest in Acker. In addition, the Pokljuka and Pohorje bogs are both at higher altitudes than Brocken and Pokljuka is also wetter, but the determined contents of elements are lower in Slovenia. We assume that the reason for the similarity of chemical composition of *Sphagnum* mosses from bogs on Pokljuka and Pohorje, and only for some elements between both massifs, is not only variability of data. The lack of influence of higher precipitation on elevated element contents in the mosses compared to the Brocken in the Harz Mountains could be due to less polluted air in Slovenia. There is much less industry and traffic, and the population density is lower in Slovenia than in Germany (Table 3). There are virtually no operating mines in Slovenia, and most electrical energy is generated by hydro and nuclear power. Elevated Hg levels in Slovenia could be due to the Idrija Hg mine, which is closed, but soils and sediments in the surrounding area are still contaminated with Hg (Gosar & Teršič 2015).

Table 2. Annual precipitation of the study areas (Source: <https://cdc.dwd.de/portal/>, <https://meteo.arso.gov.si/met/sl/archive/>)

	Year	Precipitation (mm)
Brocken	2019	1699
	2020	1809
Acker	2019	1228
	2020	1209
Pokljuka	2019	2440
	2020	2376
Pohorje	2019	1393
	2020	1125

Table 3. Population density, yearly per capita CO₂ emissions and energy consumption in Germany and Slovenia (Source: <https://www.worldometers.info/>)

	Population density	CO ₂ emissions	Energy
	p/km ²	t/y	BTU/y
Germany	240	9.44	170
Slovenia	103	7.10	137

5.3 Effect of COVID-19 lockdown to chemical composition of the mosses

The fact that the results of the statistical comparisons of the chemical composition of the mosses for 2019 and 2020 are different in all the statistical analyses carried out shows that the content of the elements are influenced by the level of air pollution in the years studied.

A general comparison based on the median values of the studied elements in all studied *Sphagnum* moss samples collected in Germany and Slovenia shows at least a slight decrease for the majority of potentially toxic elements and an increase of Sc and Ti, which could be explained by lower air pollution due to the COVID-19 lockdown. However, it should be taken into account that in 2020 weather conditions were different, with higher annual precipitation in 2019 in all bogs except Brocken (Table 2). However, in the Pohorje area, with almost half less precipitation than in Pokljuka, higher concentrations of several elements were observed in 2020 (Fig. 6). Although seven months were wetter in Harz Mountains in 2019 than in 2020, June, July, August, and October received more rain in 2020, and April, the month with the most intense lockdown in 2020, was the driest month in both years. Since the Brocken had the highest PTE levels in 2019, more rainfall in 2020 should have resulted in an increase in contamination, which was not the case. Similarly, in Slovenia, only April, May, July and November were significantly wetter in both areas in 2019, whereas in 2020, more precipitation fell in June and November (Fig. 6). Therefore, we assume that the effect of less pollution outweighs the amount of precipitation.

In Slovenia, the increase in Cr and Ni contents in the mosses sampled in 2020 is very striking in both Pohorje areas and slightly increased in one Pokljuka sample. This could be explained as a local geogenic input due to dusting of local roads. In fact, the Pohorje Masif also consist of serpentinite and eclogite, which are known for high Cr and Ni contents (Hinterlechner-Ravnik & Moine 1977). Another possibility is the influence of the Štore ironworks, located on the edge of Pohorje, and the Jesenice ironworks, located a little further from Pokljuka. Both produce steel with the addition of Cr, Mo and Ni. However, no increase in Fe based on EF is observed, and the Fe/Sc ratio and measured Fe contents are only slightly higher in 2020. Moreover, the Fe content in the serpentinite is also higher in comparison to UCC.

Also in Germany, opposite trend of elevated elemental contents in Acker and Brocken in 2019 and 2020 could be explained by higher input of local dust and less deposition of long-distance contaminants.

It is more difficult to explain the high Hg contents observed in Pohorje Masif in 2020, as there is no natural local source. In Slovenia Hg was mined in Idrija, and Hg is still present in soils and sediments, but Pokljuka is much closer to Idrija than Pohorje, so dusting cannot be a reason. The atmosphere is the main transport pathway for Hg emissions. The residence time of mercury in the air depends on the level and type of air pollutants, with a possible residence time of up to 18 months, and can be transported over long distances. (Gworek et al. 2018). Therefore, we assume that Hg levels in the atmosphere and its deposition on mosses do not always reflect the current situation.

Since soil-derived minerals are often the main or even only source of trace metals, it is important to include lithophilic elements (Al, Sc, Ti) in environmental monitoring to correct for contributions of soil dust to element inventories (Kemper et al., 2017). The Pb/Sc crustal ratio reported by Taylor & McLennan (1985) is 1.8, and for aerosols Shotyk et al. (2015) suggest a ratio of 5. Therefore, values above 5 in mosses indicate anthropogenic addition. All moss samples from 2019 were contaminated. Only in one sample from Črno jezero the ratio is 5.3. Four samples from the Harz and one from Pokljuka had Pb/Sc above 150 in 2019, one of them almost 600. In the 2020 samples the ratio is much lower, always below 30, and below 5 in three cases in Germany and five in Slovenia. Inspection of the ratios of other PTE with Sc confirms the lower contamination in Slovenia in both years, with similar Me/Sc values only for Hg and Cr in both countries. Me/Sc ratios in 2020 are much lower than in 2019 for all elements, indicating lower anthropogenic input for all elements and samples. The only exceptions are samples Ge-A02a and SI-E02 for Co/Sc and Cr/Sc, and Cu/Sc in SI -A01a,b. Ni/Sc and Cr/Sc are greater in 2020 than 2019 in all Pohorje samples, confirming geogenic input from local dust. One of the reasons for the drastic change in Me/Sc values is the increase in Sc content in all samples in 2020. It is not very likely that this increase is due to Sc contamination, as the use of Sc in the industry is quite new and has not yet been extracted in large quantities (Wang et al., 2020). Based on the

demonstrated good accuracy and precision of Sc analysis, it seems that this increase could be natural. Enrichment factors normalised to Ti and compared to the upper crust confirmed an overall decrease in pollution in 2020 for Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, and Zn, with only a few exceptions at individual sites.

The results are consistent with the reported decrease in air pollution from particulate matter (Chen et al. 2020; Lian et al. 2020; Mohd Nadzir et al. 2020; Safarian et al. 2020; Zhang et al. 2020; Xu et al., 2020). Typical geogenic aerosols measure 2 to 200 µm with a median around 20 µm, while anthropogenic ones are finer, measuring 0.1 to 1 µm (Whitby et al. 1974). Natural aerosols are composed of minerals, while anthropogenic aerosols are composed of glassy spherules produced by coal or municipal waste combustion, ore smelting, and the cement industry (Zdanowicz et al. 2006; Sanei et al. 2010). Dust particles larger than 10 µm are dense and settle rapidly in the air. They have similar properties to local soil and are mainly composed of lithogenic elements, e.g. Al, Hf, Sc, Ti, Th, Zr, while smaller particles travel longer distances, are anthropogenic in origin (Fennelly 1976) and are carriers of chalcophilic elements, e.g. As, Cd, Cu, Ni, Pb and Zn (Shotyk et al. 2015). Less traffic, not only during the March-April 2020 lockdown, but also due to significantly less tourism during the summer, resulted in less deposition of contaminating particulate matter. Indeed, an important source of anthropogenic Cd, Cu, Pb and Zn is traffic (Adamiec et al. 2016; Hjortenkrans et al. 2007).

Our results are similar to the observations of Yushin et al. (2020) for the Moscow region, who reported a decrease in Cd, Cu, Ni, and Pb in mosses from 2019 to 2020 at most sampling sites, except for the parts with extensive engineering and metal processing industries, and interpreted this as a decrease in traffic.

Despite the conclusion of Boquete et al. (2106) that it may be a misinterpretation to attribute high elemental concentrations in mosses to pollution, our data show that mosses are still sensitive enough to show spatial and temporal trends.

5. Conclusions

Our study confirmed that the measured contents of elements, including PTE, vary within a bog. Nevertheless, differences in Ba, Cd, Cr and Zn contents were found among the five studied bogs, mainly due to some extreme values at specific sites. Within one area, significant differences were found only for Harz Mountains, where the contents of most elements were highest on Brocken, which can be attributed to the higher location and thus more precipitation. In Slovenia, the chemical composition of mosses from Pokljuka and Pohorje is quite similar.

We found that the degree of variability is related to the degree of pollution. The observed ranges of elemental contents were larger in Germany and in 2019. Because of a number of factors that influence variability in the chemical composition of mosses, it is important to recognize that biomonitoring data are a rough estimate of conditions. Preferably, biomonitoring should be conducted at the same sites and, if possible, *Sphagnum* species and bog morphology should be considered. It is better to compare median rather than mean values when the number of observations is small.

The COVID -19 lockdown is found in the chemical composition of *Sphagnum* mosses. Comparisons between 2019 and 2020 show decreases in median contents, Me/Sc ratios, and enrichment factors for Cd, Cu, Ni, Pb, and Zn, and in the majority of cases for Cr and Hg. The results reflect reduced remote air pollution, which prevailed over lower precipitation in 2020, and therefore increased influence of dusting from local soils. However, the levels of PTEs still suggest an association with traffic and perhaps local industry.

Declarations

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Ethics approval and consent to participate

Not applicable

Consent for publication

Not applicable

Availability of data and materials

The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

Competing interests

The authors declare that they have no competing interests.

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Authors' contributions

Nina Zupančič: Conceptualization, Methodology, Investigation, Formal Analysis, Writing- Original draft preparation, and Editing

Elke Bozau: Conceptualization, Methodology, Investigation, Writing- Original draft preparation, and Editing

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Figures

Figure 1

Sketch of the Sphagnum moss sampling areas in Germany – Harz Mountains (Acker and Brocken) and in Slovenia – Pokljuka (Veliko Blejsko barje, Šijec and Goreljek) and Pohorje (Črno jezero and Lovrenška jezera).

Figure 2

Box-whisker diagrams of selected elements comparing studied bogs in Germany and Slovenia and sampling years 2019 (blue) and 2020 (orange). Legend: dash – median, box – interquartile range, whisker – max-min range.

Figure 3

Median, interquartile range, minimum and maximum contents of selected PTE in Germany and Slovenia, observed in 2019 and 2020. Legend is the same as in Fig. 2.

Figure 4

Mean and median values of Me/Sc ratios in 2019 and 2020 for German and Slovenian moss samples.

Figure 5

Comparison of enrichment factors calculated for each sampling site in 2019 and 2020.

Figure 6

Monthly precipitation in 2019 (blue) and 2020 (orange) in the studied areas. (Except for Brocken, there are no meteorological stations at the sampled bogs. For Acker we considered Braunlage, for Pokljuka Kredarica and for Pohorje Ribnica na Pohorju. For Brocken we used the annual mean due to missing data in December 2020).