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A quarter century of biomonitoring atmospheric pollution in the Czech Republic

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Abstract The Czech Republic (CZ) had extremely high emissions and atmospheric deposition of pollutants in the second half of the 1980s. Since the beginning of the 1990s, moss, spruce bark and forest floor humus have been used as bioindicators of air quality. In the first half of the 1990s, seven larger areas were found to be affected by high atmospheric deposition loads. Six of these "hot spots" were caused by industrial pollution sources, mainly situated in coal basins in the NW and NE part of the country, and one large area in the SE was affected by increased deposition loads of eroded soil particles. After restructuring of industry in CZ, these hot spots were substantially reduced or even disappeared between 1995 and 2000. Since 2000, only two larger areas with slightly increased levels of industrial pollutant deposition and a larger area affected by soil dust have repeatedly been identified by biomonitoring. The distribution of lead isotope ratios in moss showed the main deposition zones around important emission sources. Very high SO_2 emissions led to extreme acidity of spruce bark extracts (pH of about 2.3) at the end of the 1980s. The rate of increasing bark pH was strikingly similar to the rate of recovery of acid wet deposition measured at forest stations in CZ. By about 2005, when the median pH value in bark increased to about 3.2, the re-colonisation of trees by several epiphyte lichen species was observed throughout CZ. An increase in the accumulation of Chernobyl-derived ^{137}Cs in bark was detected at about ten sites affected by precipitation during the time when radioactive plumes crossed CZ (1986). Accumulated deposition loads in forest floor humus corresponded to the position of the moss and bark hot spots.

Keywords Air pollution · Bioindicators · Moss · Spruce bark · Forest humus

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Introduction

In the second half of the twentieth century, environmental damage caused by air pollutants emitted from industrial sources, mainly SO_2 and particulate matter contents, became an international issue. Discussions about gradual reductions designed to prevent the negative health, economic and ecological effects of these pollution loads resulted in the UN Convention on Long-Range Transboundary Air Pollution (CLRTAP). This convention has been extended by eight protocols aimed to control not only major air pollutants but also heavy metals, acidification, reactive nitrogen, persistent organic pollutants, ground-level ozone, etc. The parties of these protocols have pledged to monitor atmospheric deposition loads, investigate the pollution effects on health and ecosystems, improve monitoring the deposition of pollutants and participate in reciprocal data exchange about air quality within Member States (e.g. EU 2008). Networks of measuring stations in the framework of the European Monitoring and Evaluation Programme (EMEP) and national networks of stations for measuring air pollution and atmospheric deposition rates of selected air pollutants were put in place. In addition, the effects of atmospheric deposition loads are biomonitored in the framework of the International Co-operative Programmes (ICPs) on the assessment and monitoring of air pollution effects using plant bioindicators (forest trees, mosses, crops, etc.) and humus, soil and water analyses.

The current Czech Republic (CZ), a part of the former Czechoslovakia, has been a party to the CLRTAP Protocols (1979). The country used to be considerably polluted due to the operation of abundant pollution sources (metallurgical, chemical and energy industries) and the extraction of coal and raw materials. Annual emissions data were adopted from the Register of Emissions and Air Pollution Sources, which is maintained by the Czech Hydrometeorological Institute (CHI 2013). Emissions of major air pollutants peaked in CZ in the second half of the 1980s (Fig. 1). The most industrialised coal basins in the country were among the most polluted areas in Central Europe, the so-called Black Triangles I and II (e.g. Černý and Pačes 1995; Markert et al. 1996). The first highly polluted area (Black Triangle I) was located in a brown coal basin in the NW part of CZ (50.55° N; 13.54° E) and the second area (Black Triangle II) in a black coal basin in the NE corner of CZ (49.83° N; 18.36° E). After political changes in 1989/1990, there was a restructuring of industry and introduction of new more environmentally-friendly technologies, causing a significant reduction in emitted amounts of industrial pollutants in CZ, mainly between 1990 and 2000 (Fig. 1). Due to substantial reductions in extracted amounts of local brown coal rich in As, Be, Cr, Cu, Mn, Pb, S, Sb, V and other elements (Bouška et al. 1999), the amount of these elements in the environment dramatically decreased. However, after 1990, the sale of cars sharply increased, with six times more cars registered in CZ in 1997 than in 1990. Desulphurisation equipment (scrubbers) was installed in coal power plants, and new technologies producing fewer emission amounts were introduced. At the end of the 1990s, the distribution of leaded petrol in CZ was reduced and completely halted in 2000. All these above-mentioned factors led to deep decreases in major emissions and atmospheric deposition between 1990 and 2000 (CHI 2013) followed by just small fluctuations with no significant trends in the subsequent decade from 2000 to 2010 (Fig. 1). There was a corresponding decrease in atmospheric deposition loads of acidifying compounds and heavy metals (e.g. Fottová 2003; Hůnová et al. 2004, 2014). However, very high or even increasing concentrations of fine particles (particulate matter (PM)) have persisted in the atmosphere around large cities and in former industrial areas in CZ as well as elsewhere in Central Europe (Houthuijs et al. 2001).

Besides instrumental measuring of air quality and atmospheric deposition rates at the limited number of EMEP or national measuring networks stations, chemical analyses of suitable plant biomonitors can provide a reliable estimation of local air quality (Markert et al. 2004). The Department of Biomonitoring of the Silva Tarouca Research Institute for Landscape and Ornamental Gardening has long monitored pollution in soil covers, plants, tree bark, etc. in both urban and agricultural landscapes.

At the beginning of the 1990s, the department was invited to participate in European programmes for the assessment of atmospheric deposition loads through analyses of suitable bioindicators, mainly pleurocarpous mosses. These programmes were initially coordinated by the Nordic Working Group on Monitoring and Data and, after 2000, by the ICP Vegetation Coordination Centre CEH, Bangor CEH (CEH 2015). Since then, several large-scale and fine-scale biomonitoring programmes have been carried out throughout CZ, most frequently using mosses, tree bark and forest floor humus.

Estimating atmospheric deposition rates by analysis of moss bioindicators was introduced and tested in the 1960s and 1970s (Rühling and Tyler 1971), and the moss method was soon adopted and introduced for territorial surveys of monitoring air quality (Smodis et al. 2004). Contents of heavy metals, total sulphur and nitrogen, isotopes of some elements, radionuclides, persistent organic pollutants (POPs), etc. have all been estimated using moss bioindicators. In spite of some objections to the reliability of the moss monitoring method (e.g. Aboal et al. 2010), element concentrations in moss indicators significantly and reproducibly correlate with long-term mean relative or

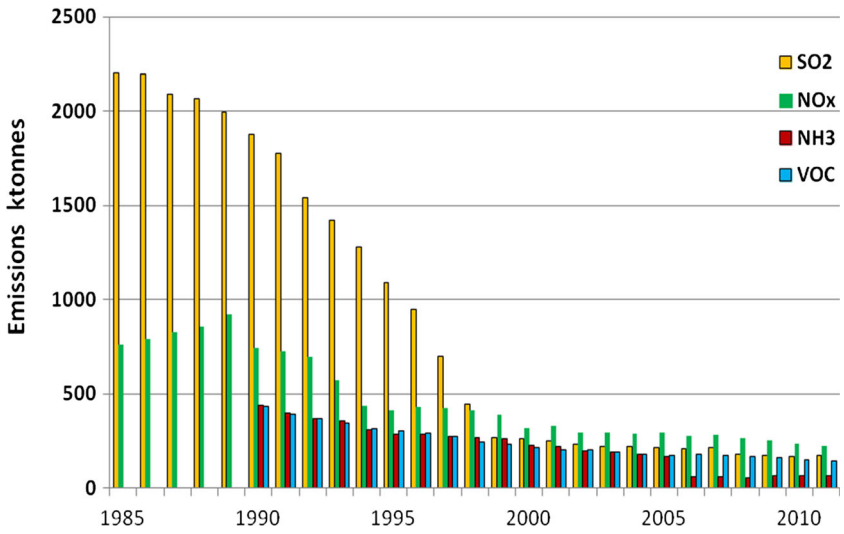

Fig. 1 Emission amounts of the main pollutants in CZ between 1989 and 2012 (CHI 2013). *VOC* volatile organic compounds

absolute atmospheric deposition levels found by independent methods at measuring stations (e.g. Ross 1990; Thöni et al. 1996; Zechmeister et al. 2004; Schröder et al. 2010; Harmens et al. 2011).

The outer bark of trees is composed of layers of the walls of predominantly dead cells (Schultze-Dewitz and Koch 2008). Tree bark has a high ability to effectively absorb and adsorb heavy metals, organic compounds and other pollutants (Vázquez et al. 1994; Ratola et al. 2003). In forest stands, tree bark traps pollutants from atmospheric and stemflow deposition. Some parameters of bark extracts (e.g. pH, electric conductivity, content of sulphates, etc.) have been used in the past as good indicators of acid rain loads (e.g. Berkman 1958; Härtel and Grill 1972; O' Hare 1974; Grodzińska 1977; Steindor et al. 2011). More recently, bark analyses have been used mainly for estimations of heavy metals, radionuclides, POPs and other airborne pollutant deposition rates (Poikolainen 1997; Böhm et al. 1998; Schulz et al. 1999; Rosamilia et al. 2004; Saarela et al. 2005).

Forest floor humus originates through the biological humification of litter. Biologically stable humic compounds (Stevenson 1994) in coniferous forests are accumulated in a well-defined H (Oh) horizon. Due to the considerable adsorption capacity of humic macromolecules, forest floor humus effectively and firmly adsorb positively charged metal cations, organic compounds and other pollutants (van Dijk 1971; Pichler et al. 1996; Lair et al. 2007). However, the ability of commonly available forest floor humus to accumulate deposition loads long-term or archive one-shot deposition episodes from the remote past has not been frequently utilised in biomonitoring campaigns and investigations (Melin et al. 1994; Reimann et al. 2000; Tamminen et al. 2004; Kirchner et al. 2009; Nygard et al. 2012). Instead, investigations of pollutant distribution along peat profiles have been more common.

Due to their various life spans, each of these three types of bioindicators interacts with the atmosphere at various timescales. The use of several bioindicators of air quality in biomonitoring surveys in parallel can extend or improve the particular time intervals for which the biomonitoring is being applied. However, international and large-scale biomonitoring campaigns use nearly exclusively only one bioindicator.

The aims of this paper are to provide information about important national biomonitoring programmes that have been carried out in CZ and introduce selected results and findings from both large-scale and fine-scale surveys.

Material and methods

Study area

National monitoring surveys have been carried out throughout the CZ (78,866 km^2; 10.5-m inhabitants) at about 195 basic "permanent" monitoring plots established in 1995, with minimum area 30×30 m and arranged in a network of about 15×15 km. If needed for specific objectives, the number of sampling plots was sometimes extended to 250–285. For fine-scale biomonitoring campaigns in the surroundings of pollution sources, other sampling designs were used, usually with a more dense sampling network (e.g. 2×2 km), locations of sampling plots along linear transects running radially in multiple directions from a pollution source, or were situated along altitudinal gradients at given elevation intervals.

Collecting and processing of samples

Collecting, treatment and analyses of moss specimens followed standard protocols used in European moss surveys, e.g. CEH (2015). In the Czech national moss monitoring campaigns, moss samples were collected in 1991/1992, 1995, 2000, 2005 and 2010. At each plot, seven to ten moss specimen subsamples, preferentially the species *Pleurozium schreberi* or *Scleropodium purum*, were collected within glades to obtain moss samples unaffected by throughfall and stemflow depositions. These subsamples were combined into one composite sample of about 8–10 l. For some fine-scale moss campaigns, *Hypnum cupressiforme* was used as an alternative bioindicator. The moss samples were hand-cleaned to remove adventitious material and dead decaying basal moss parts. The living parts of about 2.5–3 years old intended for analysis were air-dried. The dried samples were homogenised in a laboratory mill with a titanium rotor and a sieve. More details are available in the paper presenting results from the first moss surveys (Sucharová and Suchara 1998a). About 40 specimens of the moss *P. schreberi* from the herbaria of two CZ museums (PRM and BRNM) and two universities (PRC and BRNU) were analysed as well.

Bark from Norway spruce (*Picea abies*) trees was investigated in four large-scale surveys. Spruce bark was collected along one altitudinal gradient in the Krkonoše (Giant) Mts. and another in the Krušné (Ore) Mts. in parallel between 1987 and 2011. Chips of outer bark were lightly peeled from around the trunks at a height of 1.3±0.1 m and air-dried. For studies of urban and suburban parks in Prague and the surroundings, bark specimens from Norway spruce, Scots pine (*Pinus sylvestris*) and English oak (*Quercus robur*) were collected. From each sampling plot, individual samples from six trees, and since 1995 from ten trees, were analysed. The air-dried bark was milled and sieved to obtain a fine bark fraction (≤1.5 mm) and a coarser fraction (1.5–3.0 mm) for further extractions or for determining activities of ^{137}Cs. More details have been published, for example, in Suchara 1993 and Suchara 2012.

In two large-scale and several fine-scale monitoring campaigns, humus samples were collected to determine the distribution of long-term accumulated air pollutants or

estimate deposition rates from pollution leaks in the past. At the sampling plots, the surface L and F organic layers were removed from the forest floor. A core of the remaining humus material from the H (Oh) horizon was removed using a plastic cylinder with a 0.105-m diameter. Possible admixtures of mineral soil at a bottom of the humus core were scrapped off with a plastic ruler. From each sampling plot, seven to ten humus cores were taken and combined into one composite sample. If the mineral fraction exceeded 30 % in the composite sample, the sample was discarded and another humus sample was later collected. The air-dried humus samples were ground and sieved, and the proportion of organic matter was measured (loss on ignition). The protocol of humus surveys has been published in more details, for example, in Suchara and Sucharová (2000, 2002).

In order to extend the potential of the biomonitoring, recognise bedrock-type effects or check the results of a particular bioindicator, multiple bioindicators were collected in parallel during several national and fine-scale biomonitoring campaigns, for example, moss, bark, humus, some additional biological materials such as *Avenella flexuosa* grass, annual and biennial Norway spruce needles, forest topsoil and subsoil. Details are described in the relevant literature (e.g. Sucharová et al. 2011).

Analyses of samples

The plant and humus samples were subtotally digested in a mixture of HNO_3 + H_2O_2 in Teflon vessels using a closed microwave digestion system. Multi-element analyses were carried out by inductively coupled plasma mass spectrometry (ICP-AES JY 138 Ultrace, ICP-OES PE Optima 5300D, ICP-MS PE Elan 6000 and ICP-MS PE Elan DRC II). Before 1995, the element concentrations in samples were measured using atomic absorption spectrometry (Varian Spectra AA 300 with GTA-96). The total mercury concentrations were measured directly in powdered solid samples using an Hg single-channel atomic absorption spectrometer (AMA-254, Altec). Total nitrogen content in the samples was measured after combustion of the powdered specimens in a LECO TruSpec CN Determinator. Each sample was independently analysed at least three times using three different weights. In all analysed samples, the determined concentrations of elements were above the detection limits of the methods used. Simultaneous analyses of relevant commercial plant reference materials (mainly IAEA-336 Lichen, IAEA-V-10 Hay powder, NIST-1575a Pine Needles, NIST-1515 Apple Leaves, BCR-414 Plankton and BCR-279 Sea Lettuce) and inter-laboratory reference moss (M1, M2, M3) and humus (H1, H2, H3) materials (Steinnes et al. 1997) were performed for quality control of element content measurements in the samples. The quality of nitrogen content measurement was checked by analysis of Alfalfa Organic Analytical Standard 502-273. The relevant national moss surveys have presented data on the detection limits of the analytical methods used in individual moss monitoring campaigns, long-term determined element contents in the reference material and other details about the system of good laboratory practise used (e.g. Sucharová and Suchara 1998b; Sucharová and Suchara 2004a; Sucharová et al. 2008; Suchara et al. 2011a). The total activities of ^{137}Cs in bark and the humus samples were determined in the National Radiation Protection Institute in Prague by an accredited gamma spectrometry method in an HPGe detector for 24–72 h. The results were corrected for the radioactive decay of ^{137}Cs relative to the relevant sampling dates (Suchara et al. 2011b).

The coarser bark fraction was leached in fresh deionised water (4g/80 ml for 24 h), and total electric conductivity (EC) and dissolved sulphate content were measured. The total EC was measured using a WTW LF 191 conductometer with an LS 1/T-1.5 platinum electrode before 2000 and later with a WTW LF 597 conductometer and a TatraCon® electrode. The measuring system was calibrated by a standard KCl solution, and EC values were adjusted to a reference temperature of 25 °C.

The concentration of dissolved sulphates was measured turbidimetrically after precipitation of sulphates by $BaCl_2$ at a wavelength of 420 nm in a SPEKOL 10 spectrophotometer (Carl Zeiss Jena) with a TK turbidimetric attachment, calibrated by standard K_2SO_4 solutions (Kosmus and Grill 1986). Active reaction (pH-H_2O) was measured in extracts of the fine bark fraction and temperate boiled deionised water (4g/16 ml for 48 h) and in humus extracts (10 g/50 ml for 30 min). pH meters (Radelkis and Jenway) with a combination glass/pH electrode were used for measurements, calibrated with commercial buffer solutions. All presented pH values are adjusted to a reference temperature of 25 °C.

Statistical analysis

The StatSoft Statistica programme was used for statistical processing of the analytical results obtained in biomonitoring campaigns. Besides basic statistical processing, significant differences in temporal and spatial distribution of the detected bioindicator parameters and relationships between element concentrations detected in the investigated bioindicators were found. The effects of explanatory stand factors (elevation, precipitation sum, geology, land use, etc.) were mainly investigated for the element concentrations in moss. Results of correlation analysis, cluster analysis, factor analysis and other statistical evaluations have been presented and discussed in the relevant national moss surveys (e.g. Sucharová and Suchara 1998b; Sucharová and Suchara 2004a; Sucharová et al. 2008).

Map construction

Classed post maps and contour maps were constructed using PC Golden Software's Surfer® programme. For construction of the contour maps, a variogram procedure with the kriging gridding method was utilised. Element concentration classes for the moss element concentrations were adopted from the first European moss survey (Rühling 1994). For optionally determined elements and humus and bark samples, element concentration classes were defined in accordance with the element concentration ranges found in the first national monitoring surveys (1995–2000). In the contour maps, the CZ administrative regions were depicted. Maps of the ^{137}Cs activity distribution in bark and forest floor humus were constructed using the System for Automated Geostatistical Analyses. The pattern of ^{137}Cs activity distribution in spruce bark and forest floor humus was constructed using the Multilevel B-Spline Interpolation method (SAGA 2015).

Results and discussion

Element contents in mosses, air pollution and land use

Since 1990, European moss surveys have included an obligatory ten high-risk elements (As, Cd, Co, Cr, Cu, Fe, Ni, Pb, V and Zn), expanded in 1995 to include total contents of Hg, N and S. In addition to these obligatory elements, since 1995, CZ moss monitoring campaigns have included from 26 to 32 additional elements (Ag, Al, As, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Ge, Hg, In, K, La, Li, Mg, Mn, Mo, N, Na, Nd, Ni, Pb, Pr, Rb, S, Sb, Se, Sn, Sr, Th, Tl, U, V, Y, Zn). Some of these optionally investigated elements can have negative biological effects (e.g. Be, Li, Se, Tl, U) or can indicate a background level of moss contamination, for example, by soil particles due to wind erosion.

Some moss surveys (e.g. Thöni 1996) have found that there is a tight correlation between mean element concentrations in moss and the mean long-term (a year or longer) bulk deposition of many elements that are detected in atmospheric deposition at measuring stations. This allows element deposition loads to be approximately estimated from concentrations in moss. Most recently, regression analyses have demonstrated significant and tight spatial correlations between normalised element contents in mosses and normalised modelled EMEP deposition data for Cd, Pb, Hg and N between 1990 and 2010 in Scandinavia and in Central Europe, including CZ (e.g. Schröder et al. 2010; Harmens et al. 2011).

Our correlation analyses (e.g. Sucharová and Suchara 2004a; Sucharová et al. 2008) showed that the variability of element contents in moss samples is best explained by explanatory factors such as elevation, precipitation sum, forest, arable soil or urbanised area in a 5-km radius around sampling sites. Bedrock types and local relief had no significant effect on moss element contents. Despite the fact that all moss samples were taken at least 300 m from roads, there were significant and positive correlations repeatedly found for Cr, Cu, Fe, Mo, Sb and Zn contents in moss samples collected 300–2000 m away from roads and the annual average daily traffic at the closest road segments. We are not sure if the element contents in moss are actually influenced by traffic or if these correlations are accidental. The results of factor analyses have been presented in individual CZ national moss surveys (e.g. Sucharová and Suchara 2004a; Sucharová et al. 2008). Element contents in moss samples analysed in these surveys were mostly determined by the mean atmospheric deposition rates in the season before collecting samples.

The first two CZ national moss surveys both revealed seven (marked 1–7 in Figs. 2 and 3) large "hot spots," with the highest accumulations of the obligatorily investigated elements (Sucharová and Suchara 1998b). In the NW part of the country (the Black Triangle I area), there were four areas of relatively high or very high moss element contents, together forming one large hot spot covering 10.5 % of the CZ area. The first area (1), in the wider surroundings of the town Most (50.50° N; 13.63° E) and situated in a brown coal basin, was affected by the extraction of coal (and associated dust) and industrial burning of brown coal in local industrial furnaces (coal power plants, metallurgical and chemical industries). Similar pollution sources, i.e. extraction of brown coal and a coal power plant (Turów, Bogatynia) at the Polish border along with the domestic metallurgical and glass industries, also caused increased moss element contents in the surroundings of Liberec (50.77° N; 15.07° E) (2). High accumulations of elements in mosses were found in a large area (3) adjacent to the eastern margin of the previous hot spot (2). Steel metallurgical operations near Kladno (50.15° N; 14.11° E), engineering industry and battery production in Slaný (50.23° N; 14.09° E) and a brown coal power plant near Mělník (50.41° N; 14.42° E) were important sources of atmospheric pollution in this area. Operation of engineering and chemical industries and a coal power plant near Pardubice (50.05° N; 15.74° E) caused increased accumulation of elements in moss in this area (4). An area (5) of high and very high (covering 7.5 % of the CZ) accumulation of elements in mosses was situated in the Ostrava region (49.84° N; 18.42° E), highly affected by the extraction and processing of black coal and metallurgical industry operations. The remaining hot spots were identified around a secondary lead smelter (6) near Příbram (49.69° N; 13.99° E) and in the SE part of CZ (49.07° N; 17.45° E) in an area (7) of intensive agricultural land use. With the exception of this last hot spot, the area with the lowest contents of the elements in moss analysed was in the southern half of CZ, covering, for example, 37 % of the country in 1995. The northern half of CZ was influenced by the operation of numerous domestic and nearby Polish sources of air pollution

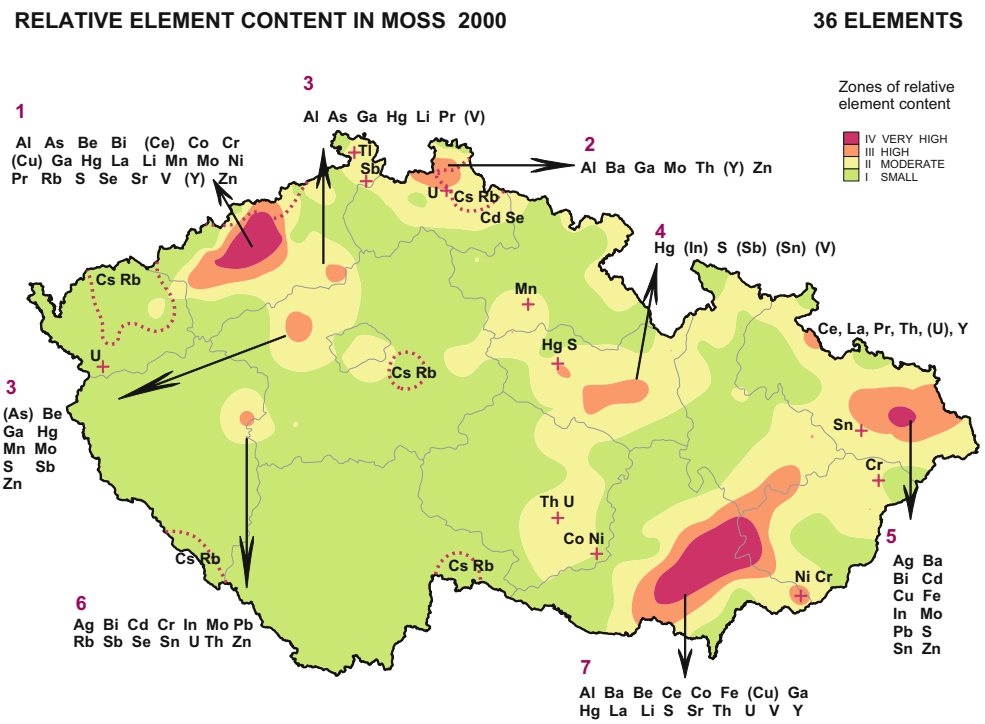

Fig. 2 Distribution of the mean accumulation (concentration class) of the investigated elements in moss and location of main hot spots throughout CZ in 2000 (Sucharová and Suchara 2004b; Suchara et al. 2007)

(metallurgical and engineering industries) resulting in significantly higher contents of As, Cd, Cr, Cu, Mo, Pb, V and Zn in moss. For example, the highest contents of S in mosses, exceeding 2400 mg kg^{-1}, were detected over an area of 348 km^2, and contents of Pb exceeding 75 mg kg^{-1} were detected over an area of 940 km^2 in 1995 (Sucharová and Suchara 1998a).

Steep reductions in moss element contents followed emission reductions between 1992 and 2000, mainly between 1995 and 2000, documented by contour maps of moss element distributions detected in the 1995 and 2000 monitoring campaigns (Sucharová and Suchara 2004a). Figure 2 depicts the distribution of mean element content class for all 36 elements

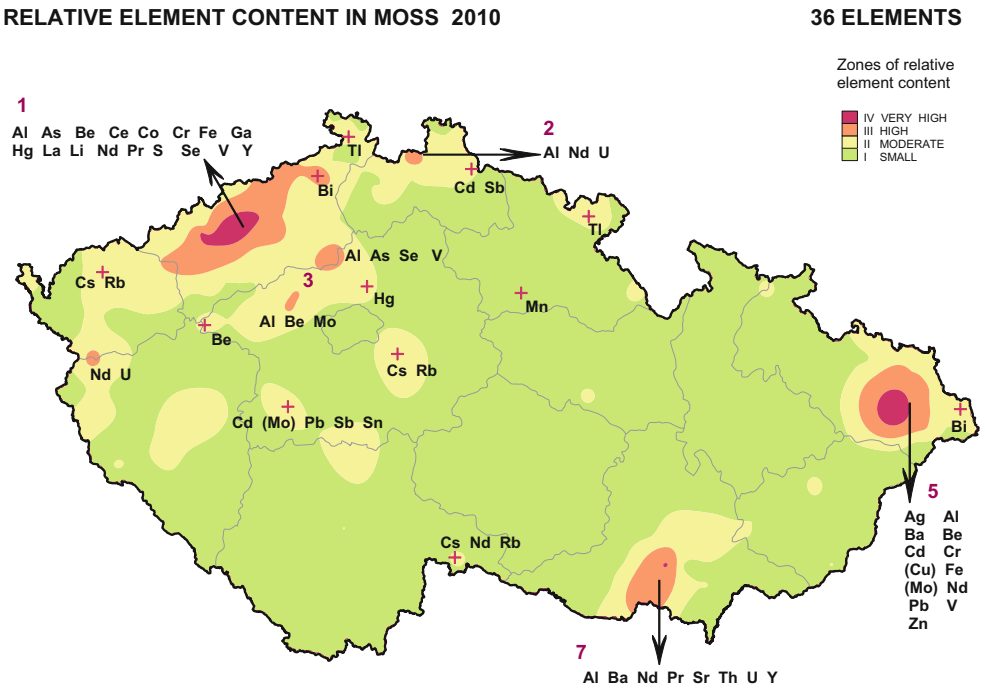

Fig. 3 Distribution of the mean accumulation (concentration class) of the investigated elements in moss and location of main hot spots throughout CZ in 2010 (STRILOG 2011)

investigated in moss throughout CZ after the crucial reduction of emission amounts in 2000. Arrows and symbols for chemical elements show the areas where the given elements were most accumulated in moss. Subsequent monitoring surveys carried out between 2000 and 2010 revealed only slow reduction in element contents in moss. The results of cluster analyses of moss element content variability (Sucharová and Suchara 2004a, Sucharová et al. 2008) did not show substantial differences in the element composition of the main clusters.

Compared to 2000, the element contents in moss decreased throughout the country in 2010. However, area and intensity of the former hot spots were moderately reduced in 2010 (Fig. 3). Significant reductions in the area of hot spots and in moss element contents were mainly found for those elements typically present in industrial emissions, e.g. As, Pb, S and V (Tab. 1). The CZ median content of elements in moss in 2010 compared to 1991/1992 decreased nearly six times for As, four times for V, three times for Pb and about 1.5 times for Cd, Cu, Fe, Hg, Ni, S and Zn. For elements that are present in both industrial emissions and re-suspended soil dust (e.g. Al, As, Co, Cr, Cu, Fe, Ni), the concentration decrease in mosses was lower and locally less regular. This is due to the variability of the element contents in soil and dust particle deposition, controlled by wind erosion and anthropogenic activities in the season before collecting moss samples (Sakalys et al. 2009). For example, due to high fluctuation in background Cr, the proportion of the median content of Cr in moss decreased irregularly between 1991 and 2005. However, the Cr content in moss slightly increased to 1.87 mg kg^{-1} between 2005 and 2010, which is only 10 % lower than the median content in 1991. Contents of typical lithogenic elements (e.g. lanthanides, Cs, Rb, Th, U), which are not significantly present in industrial pollution, indicated localities or samples (frequently in lowlands) affected by soil dust during a dry year or by local anthropogenic activities, for example, extraction of raw materials (large areas of brown coal basins), ploughing of large areas, building construction, etc. (Table 1). The reduced intensity of brown coal extraction and the reclamation of large abandoned pits have reduced large-scale dustiness mainly in the NW part of CZ. The distribution of Cs and Rb concentration variabilities in moss has repeatedly shown very similar patterns in the individual moss monitoring surveys (e.g. Suchara et al. 2007; Sucharová et al. 2008; STRILOG 2011, Figs. 2 and 3). Increased Cs and Rb contents in moss has mainly been found at sampling sites in areas with outcrops of granitic rocks rich in Cs and Rb. We suppose that the Cs and Rb contents in the moss samples do not come directly from wet deposition, throughfall or soils, but rather from the secondary contamination of moss plants by litter and humus debris transported over the forest floor surface by wind or bioturbation. The actual intensity of these factors in the period before collecting moss samples would thus determine the Rb and Cs contents in moss in these hot spots.

The most recent moss survey (STRILOG 2011) showed that the former hot spots of high element accumulation in moss were reduced in area (hot spots 2, 7) or even disappeared (4, 6) between 2000 and 2010 (Figs. 2 and 3). In the former two Black Triangle areas (1, 5) in the NE and NW corners of CZ, the moss element content was higher than in the remainder of the country. However, in comparison with the beginning of the 1990s, the content of elements in moss in these hot spots (1, 5) was substantially lower (e.g. about ten times for Pb, seven times for As, five times for V and about two times for S). The hot spot (2) in the NW near the Polish border has nearly disappeared due to desulphurisation of the coal power plant in Bogatynia. Moss has accumulated rather typical lithogenic elements in this hot spot recently. The former hot spot (3) between Kladno and Mělník has been reduced and split in two residual plots. The geogenic hot spot (7) of a variable area and intensity in the SE caused by deforestation and ploughing has been repeatedly detected in all moss monitoring surveys.

Since lead emitted by individual emission sources has a characteristic ratio of stable lead isotopes, the current deposition range of the main pollution sources in CZ was estimated using the distribution of lead isotope ratios in mosses (Sucharová et al. 2014). This distribution of Pb isotope ratios showed rather small areas and main deposition loads of Pb around industrial pollution sources in 2010 (Fig. 4).

Table 1 Median values of element contents in moss specimens (mg kg^{-1}, n=250–285) throughout CZ between 2000 and 2010

Element	Ag	Al	As	Ba	Be	Bi	Cd	Ce	Co	Cr	Cs	Cu	Fe	Ga	Hg	In	La	Li
2000	0.030	500	0.289	18.9	0.028	0.025	0.233	0.661	0.307	1.87	0.272	6.53	401	0.198	0.048	0.002	0.338	0.301
2005	0.032	477	0.292	18.7	0.027	0.032	0.233	0.715	0.275	1.15	0.262	5.23	409	0.184	0.045	0.002	0.353	0.314
2010	0.024	436	0.256	22.1	0.026	0.025	0.177	0.607	0.284	1.01	0.258	5.90	349	0.175	0.041	0.002	0.312	0.273

Element	Mn	Mo	N	Ni	Pb	Pr	Rb	S	Sb	Se	Sn	Sr	Th	Tl	U	V	Y	Zn
2000	470	0.152	11,806	1.95	5.66	0.076	20.8	1182	0.111	0.241	0.188	8.40	0.090	0.037	0.031	1.52	0.177	35.0
2005	367	0.179	11,127	1.42	4.94	0.080	17.2	1137	0.156	0.232	0.235	7.72	0.093	0.043	0.029	1.47	0.181	33.3
2010	449	0.141	11,822	1.15	2.85	0.066	18.5	997	0.095	0.186	0.213	8.21	0.078	0.037	0.025	1.18	0.174	33.9

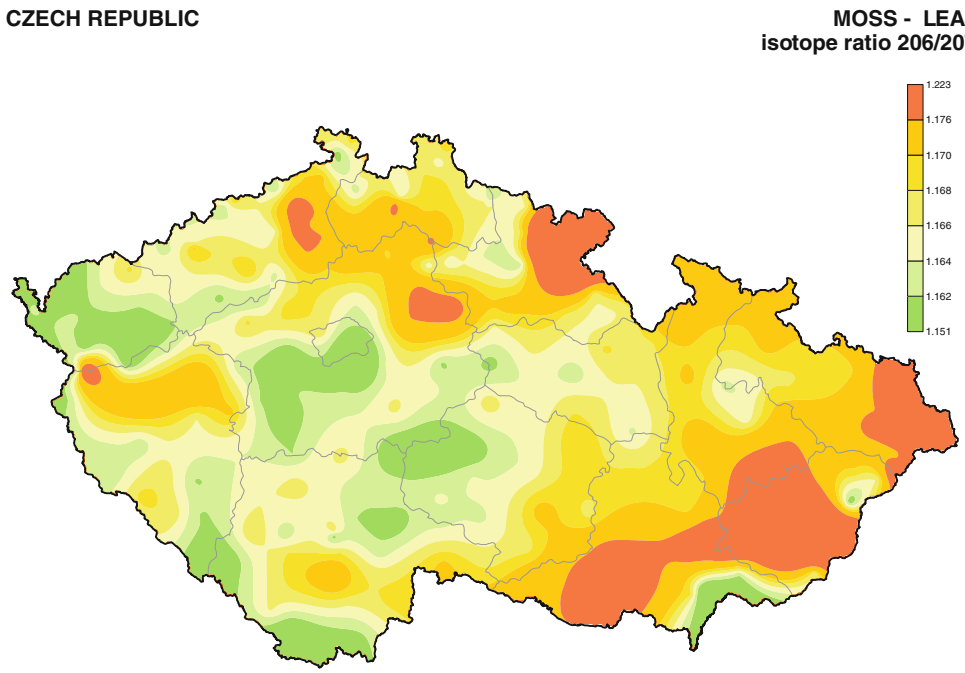

Fig. 4 Distribution of the lead isotope ratio $^{206}Pb/^{207}Pb$ in moss throughout CZ in 2010

In one of the fine-scale moss surveys, analyses were used to delimit new zones and atmospheric deposition gradients in a 14-km radius around the secondary lead smelter in Příbram after modernisation and installation of more environmentally-friendly technology (Sucharová and Suchara 2004b). The recent highest deposition zone of Ag, Cd, Cu, In, Pb, Sb, Zn, etc. around the smelter chimney was reduced from several tens of kilometres to 0.5–2 km. In addition, another local hot spot, of a diameter about 2 km, of increased accumulation of lithogenic elements (Al, Cr, Fe, La, Li, Nd, Pr, Sc, Th, U and Y) in moss was identified and delimited near Příbram. A mill for grinding stones from former uranium pits to be used for gravel was found in the centre of this local hot spot. Fine-scale moss analyses have also been used to delimit zones that were most affected by wind erosion in the SE part of CZ or for delimiting Hg contamination around a chlor-alkali plant after a flood. Integrated biomonitoring using moss, bark and humus analyses was also performed, and all bioindicators gave very similar results (Suchara and Sucharová 2006a). In addition, an important hot spot of Cd deposition was repeatedly detected near the Polish border in the north (50.76° N; 15.31° E), caused by the operation of a local glass and ceramic factory. Similarly, increased content of Be in moss has repeatedly been found near ceramic and brick works processing local clays in SW Bohemia (e.g. 50.11° N; 13.43° E). A larger area with only slightly increased accumulation of some elements typical for industrial emissions (e.g. Hg, N and Sb) was also repeatedly found in the SW part of the country near the German border (49.56° N; 12.63° E). The responsible source of pollution has not been found.

The CZ moss surveys demonstrate that the former crucial environmental problem in CZ, i.e. the massive atmospheric deposition rates of sulphur compounds, had ceased by about 2000. Between 2000 and 2010, sulphur emissions further decreased by 36 % (Fig. 1) and the median of total S contents in moss decreased by 16 % for the same period (Table 1). In parallel, while emissions of NO_x decreased about 25 % and emissions of NH_3 decreased about 70 % between 2000 and 2010 (Fig. 1), the median content of total nitrogen in moss did not change substantially between 2000 and 2010 except for a temporal reduction in total nitrogen by about 5 % in 2005 (Table 1). The likely reason is that the long-term and significant decrease in $N\text{-}NO_3$ wet deposition was only found at a few measuring stations usually situated at urban and industrial sites. In contrast, the wet $N\text{-}NH_4$ deposition loads have shown considerable temporal variability at rural stations and no significant trends have been found in wet $N\text{-}NH_4$ deposition after 2000 except at one rural station (Hůnová et al. 2014). Mosses may accommodate a linear uptake of nitrogen from atmospheric deposition up to a N deposition limit of about 20 kg ha^{-1} $year^{-1}$ to maintain an optimal nutrient content of N in moss plants (e.g. Solga and Frahm 2006; Harmens et al. 2011). Considerable spatial variation in mainly NH_4 atmospheric deposition rates and atmospheric deposition rates of total N approaching this saturation deposition limit may have led to the high spatiotemporal fluctuations in moss N content (Fig. 5) but the relative small changes in

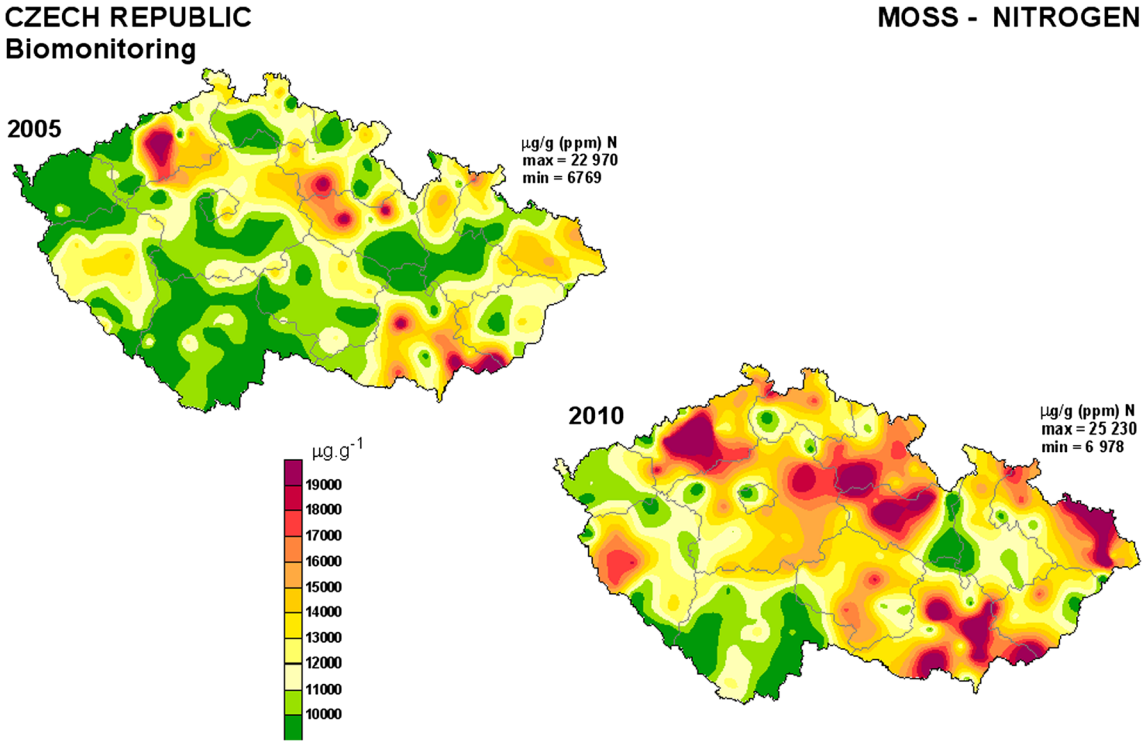

Fig. 5 Distribution of the total nitrogen content in moss throughout CZ in 2005 and 2010

median moss N content (Table 1). Recently, the highest increase of total moss N content was found in the former most industrial parts of CZ and in lowlands with both a high density of urbanisation and intensive agricultural production. A content of total N in CZ moss samples of 1 % corresponds to an N deposition rate of about 11–12 kg ha^{-1} $year^{-1}$, which is considered a critical load for temperate coniferous forests. The ratio of N/S content in atmospheric deposition and in moss has permanently increased since 1990, even though N and S are biogenic elements. For example, the N/S ratio in atmospheric deposition was about 1.0 in 2000 and about 1.4 in 2010, while in moss was 9.9 in 2000 and 11.9 in 2010.

Historic moss specimens collected in the past and archived in museum herbaria were investigated to provide information about past total nitrogen contents in moss (Harmens et al. 2006). Eight samples of the moss *P. schreberi* were contributed by CZ museums, collected between 1896 and 2005 in a mountain meadow above timberline, surely unaffected by throughfall, in the central part of the Krkonoše Mts., and 34 samples of *P. schreberi* were collected repeatedly at seven localities elsewhere in lowlands in CZ between 1883 and 2000. Figure 6 shows the temporal increase in N content in the specimens from the lowland sites and in the samples repeatedly collected at the locality above timberline. However, these samples were not collected using a standard protocol, indicating that herbaria specimens collected this way may not be reliable for retrospective reconstruction of past atmospheric element deposition rates.

Bark parameters and acid rain

Atmospheric deposition of acidifying compounds peaked in CZ in the mid-1980s. The negative impacts of strong acidification on soil cover, forest and water ecosystems, construction materials, etc. in CZ have been well documented in the literature (e.g. Hruška and Cienciala 2003). In the past, deposition rates of acidifying compounds were empirically estimated through the scarcity of epiphytic lichens and related parameters of tree bark extracts. However, no results from large-scale bark surveys had been compared with EMEP bulk atmospheric deposition data. Our long-term (1987–2010) data on spruce bark parameters (e.g. pH, EC, soluble sulphate content) from a monitoring plot situated close to the meteorological observatory CZ01 Košetice (49.5736° N; 15.0806° E) were correlated with the atmospheric deposition data measured at this station. For example, annual pH medians of spruce bark extracts (pH-H_2O) significantly correlated (r=0.95) with the annual mean precipitation pH measured at the station. Furthermore, the ongoing recovery of acidified spruce bark throughout CZ (n=190–250) has proceeded at nearly the same rate as the recovery of wet deposition found at CZ measuring stations. For example, from 1988 to 2010, the annual medians of spruce bark extract pH values increased according the following formula: $pH_{bark}=0.037\times year-72.21$; r=0.99. Similarly, the changes in annual pH means of wet deposition at the CZ stations situated in coniferous forest stands for the same period (Hůnová et al. 2014) are described by the following equation: $pH_{wet\ dep.}=0.027\times year-48.64$; r=0.93.

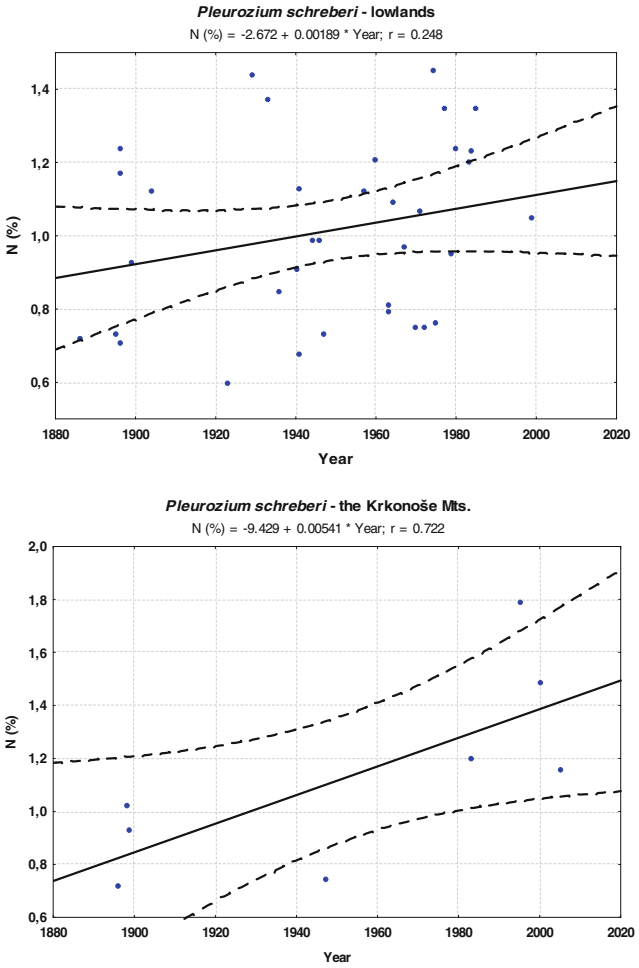

Fig. 6 Content of N (%) in herbarium moss samples as a function of time of collection at several sites in lowlands (*top*) and at a mountain locality (*bottom*). *Dashed lines* represent the 95 % confidence interval

The first spruce, pine and oak bark monitoring was carried out seasonally in urban and suburban parks in Prague between 1978 and 1988. It was found (Suchara 1993) that spruce bark parameters better detected stands that were variously affected by atmospheric deposition loads than oak bark or pine bark. At that time, spruce bark extracts collected in Prague and the surroundings had very low pH values (pH-H_2O=2.30–2.45). The bark acidity showed minor but significant seasonal fluctuations, with the maximum in spring and minimum in autumn. The mean EC of spruce bark was as high as 1524 μS cm^{-1}, and content of soluble sulphates frequently exceeded 8000 mg kg^{-1}.

At the beginning of the 1990s, the median spruce bark extract pH in CZ was 2.47, and very acid spruce bark (pH< 2.50) was found over about 80 % of the country. The acidification of bark at that time was so high that epiphytic lichens disappeared or occurred with just extremely low diversity. By 1995, the bark acidity had not decreased substantially. Large hot spots of highly acid bark persisted in the NW in the brown coal basin and in adjacent areas, in mountains in the north and in the central and northern part of the eastern half of CZ (Fig. 7). The least acid bark was found in mountains in the south and in the SE corner of CZ. Since EC and content of dissolved sulphates tightly correlate with pH, the distributions of EC and sulphate contents were similar. However, in dusty industrial and agricultural areas, the bark acidity was locally neutralised by dust. Surprisingly, in areas affected by high deposition loads of acidifying compounds, for example, in the mountains, spruce trees with more damaged crowns had less acid trunk bark than trees with larger crowns. This is because trees with intact crowns more effectively trap acidifying air pollutants for stemflow transport than trees with more defoliated crowns. The CZ median of spruce bark extract pH of 2.35 in 1989 increased 10–15 % by 1995 and 70 % by 2005 to a median pH of 3.25. For bark samples collected at the 185 identical permanent sampling plots, the medians of bark extract pH increased from 2.66 in 1995 to 3.23 in 2005. Widespread re-colonisation of tree bark by some acidophilous and nitrophilous epiphytic lichens was observed at the sampling plots in 2005. The most recent bark survey (2010) found respective medians for bark extract pH, EC and soluble sulphate content of 3.34, 213 μS cm^{-1} and 1400 mg kg^{-1}. At present, there are no large hot spots of acid bark and the whole CZ has been re-colonised by lichens. The recovery of bark throughout CZ has been described in more detail in Suchara (2012) and Suchara et al. (2014).

A long-term (1988–2012) seasonal investigation of spruce bark parameters was carried out in forests along altitudinal gradients in the Krkonoše (Giant) Mts. and the Krušné (Ore) Mts., both of which were substantially affected by acid rain in the past. Additional contributions of acidifying compounds in amounts from 20 to 80 % are expected in CZ mountains because of the frequent occurrence of occult (horizontal) precipitation (e.g. Hůnová et al. 2011). However, our measurements have consistently shown lower acidification, EC and sulphate content from the bark extracts of trees in these mountain ranges than from trees growing at lower elevations. Over time, bark recovery was observed at all stands; however, spruce bark in lowlands still contains more acidifying compounds than bark in the mountains (Fig. 8). Possible reasons for this discrepancy may be underestimations of the acidification effects of the polluted atmosphere during frequent lowland inversion episodes or the rather smaller absorption capacity of damaged mountain tree crowns to trap acidifying compounds from the atmosphere.

Spruce bark was used to retrospectively analyse the distribution of atmospheric deposition loads of Chernobyl-derived ^{137}Cs in CZ after the accident in spring 1986. In 1995, the ^{137}Cs activities in spruce bark exceeded 80 Bq kg^{-1} at about ten hot spots situated along a wide band running through the central part of CZ from the NE to SW. These hot spots correspond with sites where it was raining at the time when plumes crossed CZ. The repeated bark surveys in 2005 and 2010 found the same hot spots in the same positions (Rulík et al.

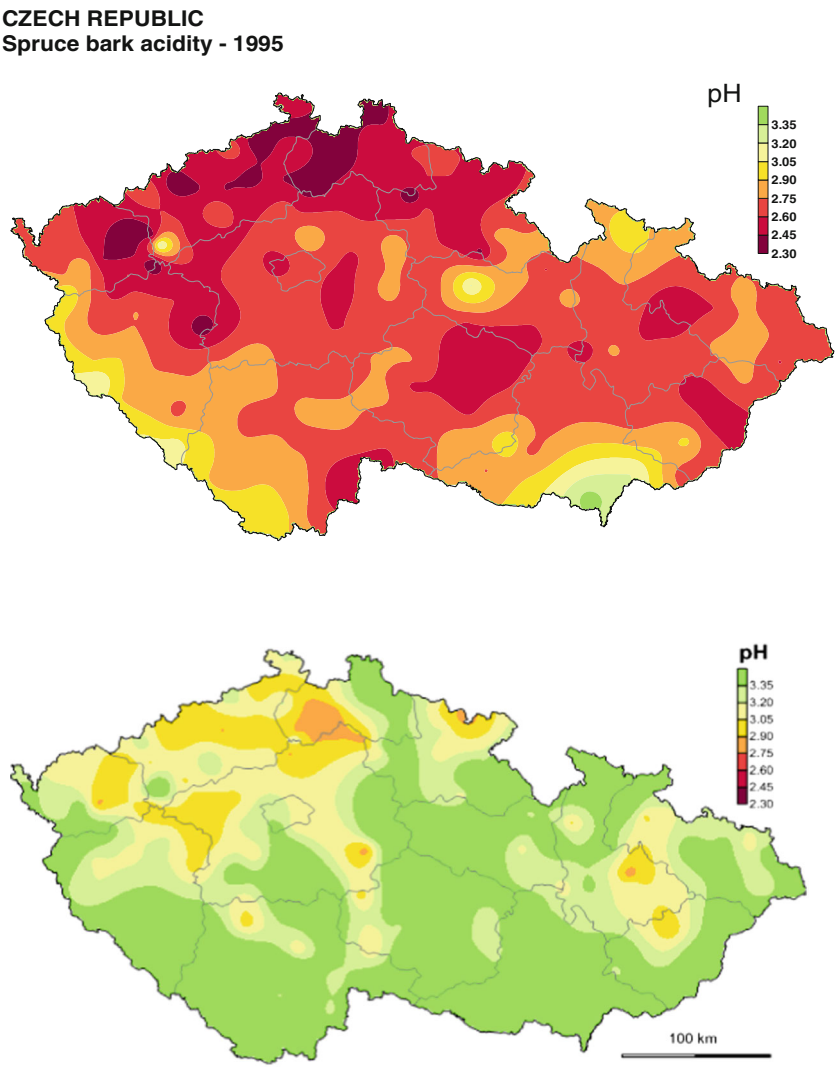

Fig. 7 Distribution of spruce bark extract acidity throughout CZ in 1995 and 2010

2014). The bark surveys also enabled an estimation of the contribution of global (pre-Chernobyl) ^{137}Cs fallout caused by nuclear tests in the 1960s, about 20 Bq kg^{-1} (Suchara et al. 2011b). Results also indicated that there is a long-term as-yet-unexplained mechanism governing the high ^{137}Cs activities in outer bark, which has a turnover time of about 15 years. Maps of the ^{137}Cs distribution in spruce bark throughout CZ are available at the following reports available on the Internet (Pilátová et al. 2011a; 2011b).

Long-term deposition loads archived in humus

The large-scale humus survey in 1995 mapped the distribution of 14 elements in forest floor humus throughout CZ (Suchara and Sucharová 2002). Hot spots of the highest long-term deposition loads of industrial emissions accumulated in forest humus were located in the same areas as the moss hot spots found the same year. However, an additional spot of high past forest humus contamination was found in the north near the Polish border in area of black coal basin (50.53° N; 16.05° E) where there were no industrial furnaces combusting local coal. This same hot spot was detected by the lead isotope ratio in moss. A second additional area of increased high-risk element contamination in humus was found in the SE around Třebíč (49.21° N; 15.88° E). In this case, the source is geogenic, with the local syenite (durbachite) bedrock type being rich in high-risk elements that easily get into the soil and humus through bioturbation and element cycling. In the 2010 humus survey, the CZ distribution of 39 elements in forest floor humus was analysed, with the same distribution of element hot spots found as in 1995. The factors controlling the distribution of these elements in forest humus are discussed in Sucharova et al. (2011b). Surprisingly, in many cases, current and former atmospheric deposition loads affected humus chemistry more than the local bedrock.

The large-scale humus surveys were also used in conjunction with the spruce bark surveys to locate hot spots of archived Chernobyl-derived ^{137}Cs activities in forest humus

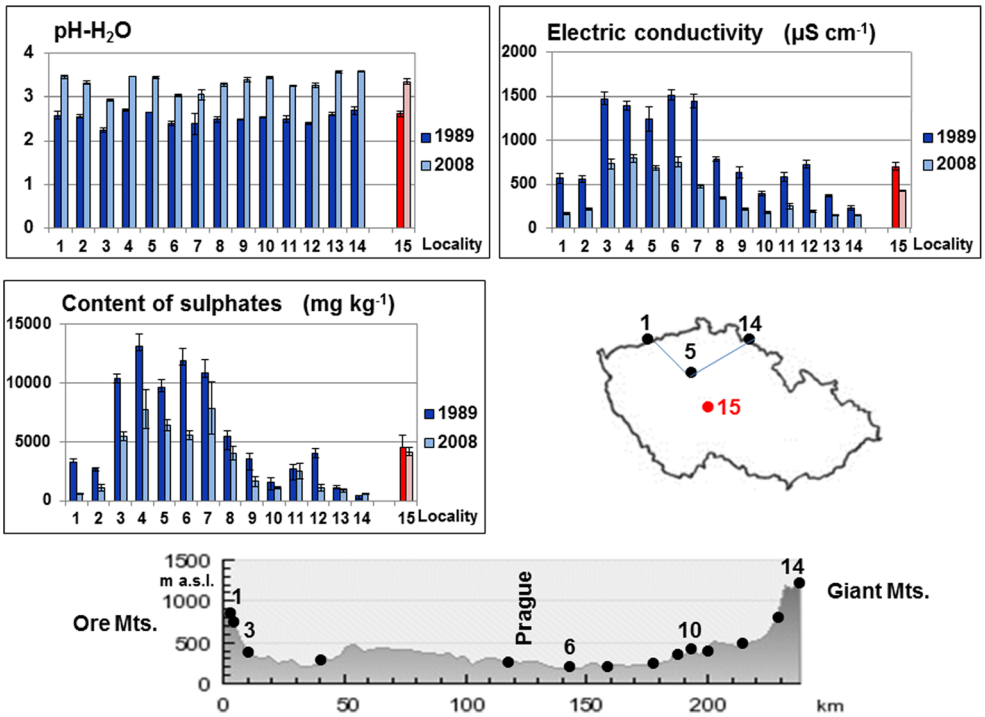

Fig. 8 The pH, EC and sulphate content in spruce bark extracts from altitudinal gradients in the mountains in 1989 and 2008. A reference locality 15 (in *red*), from a forest close to the CZ meteorological observatory Košetice, is given for comparison

throughout CZ. The distribution of ^{137}Cs activities in forest humus showed the same pattern as ^{137}Cs activities in spruce bark in both 1995 and 2010. These humus surveys demonstrate that humus can archive a historic deposition episode similarly as spruce bark and that ^{137}Cs remains in the forest humus layer due to being trapping in crystal structures of the clay minerals present. Maps of the distribution of ^{137}Cs activities in forest floor humus in CZ are available at the following reports available on the Internet (Pilátová et al. 2011c, 2011d).

The "long environmental memory" of forest humus was also used to determine the distribution of former deposition loads around industrial pollution sources that later reduced or halted emissions. For example, after the smelter in Příbram introduced new technology, the main deposition zone was reduced to 1–2 km around the smelter. However, humus analyses revealed hidden former deposition zones of chalcophilous elements reaching 5–10 km and in the case of Pb even about 30 km away from the smelter. Similarly, a hot spot of the long-term accumulation of e.g. Al, Be, Fe, Cr, Ga, Sc, Th and U was found near a mill that was used to grind stones from former uranium pits, and an accumulation of Mo was found in the wider surroundings of a factory producing piston rings (Suchara and Sucharová 2006b).

Conclusions

Atmospheric deposition rates obtained by biomonitoring campaigns in CZ were supported by independent measurements of air pollution by major pollutants at measuring stations. The positions of hot spots and patterns of element distributions were repeatedly confirmed using various bioindicators.

Moss bioindicators are suitable for determining current or short-term spatiotemporal changes in atmospheric deposition loads, since moss plants live for about 3 to 5 years. The turnover of outer spruce bark is about 15–20 years, during which the bark can interact with air-borne or stemflow pollutants. Bark is therefore suitable for detecting current and former deposition loads for a period of one to two decades. However, spruce bark was also able to archive the Chernobyl-derived ^{137}Cs deposition pulse for more than 24 years. Forest floor humus is recommended for analysing long-term accumulated deposition loads and particularly for revealing historic deposition loads around former pollution sources. Amidst the current seemingly clean environment, discovering distant or one-shot accidental pollutant leaks from the past archived in forest humus may contribute to protecting the health of local populations.

Biomonitoring is a very effective and inexpensive method for revealing current or historical atmospheric deposition loads. Biomonitoring surveys should continue to be supported even if emissions of major pollutants have been reduced and national emission ceilings fulfilled. Biomonitoring surveys can provide information about the distribution of high-risk elements in the environment that have not been measured at atmospheric deposition measuring stations, but which may have negative biological effects. In addition, some new pollutants (e.g. N, fine particles, persistent organic pollutants, new chemical compounds) can appear in atmospheric

deposition and again present ecological or health issues. Finally, biomonitoring can contribute to the knowledge of forest ecosystem recovery.

The results of our biomonitoring campaigns may serve as a reliable basis for planning and long-term landscape use in the country, and it is our hope that our biomonitoring database can be utilised in further environmental and ecological investigations.

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References

Aboal JR, Fernández JA, Boquete T, Carballeira A (2010) Is it possible to estimate atmospheric deposition of heavy metals by analysis of terrestrial mosses? Sci Total Environ 408:6291–6297

Berkman JJ (1958) Phytosociology and ecology of cryptogrammic epiphytes. Van Gorcum & Company N.V, Assen, p 681

Böhm P, Wolterbeek H, Verburg T, Musílek L (1998) The use of tree bark for environmental pollution monitoring in the Czech Republic. Environ Pollut 102(2–3):243–250

Bouška V, Pešek J, Kaigl J (1999) Distribution of trace elements in lignites based on statistical data. In: Nakoman E (ed) Proceedings of 3rd European Coal Conference, Izmir/Turkey, pp 57–63

CEH (2015) Manuals ICP vegetation, moss survey protocol. Centre for Ecology and Hydrology (CEH), Bangor. http://icpvegetation.ceh.ac.uk/manuals/moss_survey.html. Accessed May 2015

Černý J, Pačes T (1995) Acidification in the Black Triangle Region: field trip guide. Acid Rain '95, Czech Geological Survey, Prague, p 96

CHI (2013) Air pollution in the Czech Republic, maps, tables, graphs. Czech Hydrometeorological Institute (CHI), Prague. http://portal.chmi.cz/files/portal/docs/uoco/isko/grafroc/grafroc_EN.html. Accessed May 2015

EU (2008) Directive 2008/50/EC of the European Parliament and Council of 21 May 2008 on ambient air quality and cleaner air for Europe. Offic J Eur Union, 11.6.2008:L 152/1–152/44

Fottová D (2003) Trends in sulphur and nitrogen deposition fluxes in the GEOMON network, Czech Republic, between 1994 and 2000. Water Air Soil Pollut 150:73–87

Grodzińska K (1977) Acidity of tree bark as a bioindicator of forest pollution in southern Poland. Water Air Soil Pollut 8(1):3–7

Harmens H, Mills G, Hayes F, Jones L, Williams P, and the participants of the ICP Vegetation (2006) Nitrogen concentrations in historic moss samples. In: Air pollution and vegetation. ICP Vegetation Annual Report 2005/2006. Centre for Ecology and Hydrology, Bangor, p 16

Harmens H, Norris DA, Cooper DM, Mills G, Steinnes E, Kubin E, Thöni L, Aboal JR, Alber R, Carballeira A, Coşkun M, De Temmerman L, Frolova M, González-Miqueo L, Jeran Z, Leblond S, Liiv S, Maňkovská B, Pesch R, Poikolainen J, Rühling Å, Santamaria JM, Simonèiè P, Schröder W, Suchara I, Yurukova L, Zechmeister HG (2011) Nitrogen concentrations in mosses indicate the spatial distribution of atmospheric nitrogen deposition in Europe. Environ Pollut 159:2852–2860

Härtel O, Grill D (1972) Die Leitfähigkeit von Fichtenborken-Extrakten als Empfindlicher Indikator für Luftverunreinigungen. Eur J For Pathol 2:205–213

Houthuijs D, Breugelmans O, Hoek G, Vaskovi E, Mihalikova E, Pastuszka JS, Jirik V, Sachelarescu S, Lolova D, Meliefste K, Uzunova E, Mrinescu C, Volf J, de Leeuw F, van de Wiel H, Fletcher T, Lebret E, Brunekreef B (2001) PM10 and PM2.5 concentrations in Central and Eastern Europe: results from the Cesar study. Atm Environ 35(15):2757–2771

Hruška J, Cienciala E (2003) Long-term acidification and nutrient degradation of forest soils – limiting factors of forestry today. Ministry for the Environment, Praha, p 165

Hůnová I, Šantroch J, Ostatnická J (2004) Ambient air quality and deposition trends at rural stations in the Czech Republic during 1993–2001. Atm Environ 38(6):887–898

Hůnová I, Kurfürst P, Maznová J, Coňková M (2011) The contribution of occult precipitation to sulphur deposition in the Czech Republic. Erdkunde 65(3):247–259

Hůnová I, Maznová J, Kurfürst P (2014) Trends in atmospheric deposition fluxes of sulphur and nitrogen in Czech forests. Environ Pollut 184:668–675

Kirchner M, Faus-Kessler T, Jakobi G, Levy W, Henkelmann B, Bernhöft S, Kotalik J, Zsolny A, Bassan R, Belis C, Kräuchi N, Moche W, Simončič P, Uhl H, Weiss F, Schramm K-W (2009) Vertical distribution of organochlorine pesticides in humus along Alpine altitudinal profiles in relation to ambiental parameters. Environ Pollut 157(12):3238–3247

Kosmus W, Grill D (1986) Die Bedeutung verschiedener Parameter bei der Beurteilung von Immissionen anhand von Borkenanalysen am Beispiel des Stadtgebietes von Graz. Mitt naturwiss Ver Steiermark 116:161–172

Lair GJ, Gerzabek MH, Haberhauer G (2007) Sorption of heavy metals on organic and inorganic soil constituents. Environ Chem Lett 5(1):23–27

Markert B, Herpin U, Berlekamp J, Oehlmann J, Grodzinska K, Mankovska B, Suchara I, Siewers U, Weckert V, Lieth H (1996) A comparison of heavy metal deposition in selected Eastern European countries using the moss monitoring method, with special emphasis on the 'Black Triangle'. Sci Total Environ 193:85–100

Markert BA, Breure AM, Zechmeister HG (2004) Bioindicators and biomonitors. Principles, concepts and applications. Elsevier Science Ltd, Amsterdam, p 997

Melin J, Wallberg L, Suomela J (1994) Distribution and retention of cesium and strontium in Swedish boreal forest ecosystems. Sci Total Environ 157:93–105

Nygard T, Steinnes E, Royset O (2012) Distribution of 32 elements in organic surface soils: contribution from atmospheric transport of pollutants and natural sources. Water Air Soil Pollut 223(2):699–713

O' Hare GP (1974) Lichens and bark acidification as indicators of air pollution in west central Scotland. J Biogeogr 1(2):135–146

Pichler M, Guggenberger G, Hartmann R, Zech W (1996) Polycyclic aromatic hydrocarbons (PAH) in different forest humus types. Environ Sci Pollut Res 3(1):24–31

Pilátová H, Suchara I, Rulík P, Sucharová J, Helebrant J, Holá M (2011a) Maps of the content of ^{137}Cs in spruce bark in forests in the Czech Republic in 1995. Report SÚRO no. 27/2011(In Czech). National Protection Radiation Institute, Prague. https://www.suro.cz/cz/rms/monitorovani-slozek-zivotniho-prostredi/mapy-obsahu-137cs-ve-smrkovych-kurach-v-1995. Accessed May 2015

Pilátová H, Suchara I, Rulík P, Sucharová J, Helebrant J, Holá M (2011b) Maps of the content of ^{137}Cs in spruce bark in forests in the Czech Republic in 2010. Report SÚRO no. 28/2011(In Czech). National Protection Radiation Institute, Prague. https://www.suro.cz/cz/rms/monitorovani-slozek-zivotniho-prostredi/mapy-obsahu-137cs-ve-smrkovych-kurach-v-2010. Accessed May 2015

Pilátová H, Suchara I, Rulík P, Sucharová J, Helebrant J, Holá M (2011c) Maps of the content of ^{137}Cs in forest floor humus in the Czech Republic in 1995. Report SÚRO no. 25/2011(In Czech). National Protection Radiation Institute, Prague. https://www.suro.cz/cz/rms/monitorovani-slozek-zivotniho-prostredi/mapy-obsahu-cs137-v-humusu-v-1995. Accessed May 2015

Pilátová H, Suchara I, Rulík P, Sucharová J, Helebrant J, Holá M (2011d) Maps of the content of ^{137}Cs in forest floor humus in the Czech Republic in 2005. Report SÚRO no. 26/2011(In Czech). National Protection Radiation Institute, Prague. https://www.suro.cz/cz/rms/monitorovani-slozek-zivotniho-prostredi/mapy-obsahu-cs137-v-humusu-v-2005. Accessed May 2015

Poikolainen J (1997) Sulphur and heavy metal concentrations in Scots pine bark in northern Finland and the Kola Peninsula. Water Air Soil Pollut 93(1–4):395–408

Ratola N, Botelho C, Alves A (2003) The use of pine bark as a natural adsorbent of persistent organic pollutants—study of lindane and pentachlor adsorption. Chem Techol Biotechnol 78(2–3):347–351

Reimann C, Banks D, Kashulina G (2000) Processes influencing the chemical composition of the O-horizons of podzols along a 500-km north–south profile from the coast of the Barents Sea to the Arctic Circle. Geoderma 95(1–2):113–139

Rosamilia S, Gandino S, Sansone U, Melli M, Jeran Z, Ruisis S, Zucconi L (2004) Uranium isotope, metals and other elements in lichens and tree barks collected in Bosnia-Herzegovina. J Atm Chem 49(1–3): 447–460

Ross HB (1990) On the use of mosses (*Hylocomium splendens* and *Pleurozium schreberi*) for estimating atmospheric trace metal deposition. Water Air Soil Pollut 50(1–2):63–76

Rühling Å (1994) Atmospheric heavy metal deposition in Europe—estimation based on moss analysis. Nord 9(9):1–53

Rühling Å, Tyler G (1971) Regional differences in the deposition of heavy metals over Scandinavia. J Appl Ecol 8(2):497–507

Rulík P, Pilátová H, Suchara I, Sucharová J (2014) Long-term behavior of ^{137}Cs in spruce bark in coniferous forests in the Czech Republic. Environ Pollut 184:511–514

Saarela KE, Harju L, Rajander J, Lill JO, Heselius SJ, Lindroos A, Mattsson K (2005) Elemental analyses of pine bark and wood in an environmental study. Sci Total Environ 343(1–3):131–141

SAGA (2015) SAGA Software. System for Automated Geoscientific Analyses. Dept. of Physical Geography, Hamburg. http://www.saga-gis.org/en/index.html. Accessed August 2015

Sakalys J, Kvietkus K, Sucharová J, Suchara I, Valiulis D (2009) Changes in total concentrations of heavy metals in moss in Lithuania and the Czech Republic between 1995 and 2005. Chemosphere 76(1):91–97

Schröder W, Holy M, Pesch R, Harmens H, Ilyin I, Steinnes E, Alber R, Aleksiayenak Y, Blum O, Coşkun M, Dam M, De Temmerman L, Frolova M, Frontasyeva M, González Miqueo L, Grodzińska K, Jeran Z, Korzekwa S, Krmar M, Kubin E, Kvietkus K, Leblond S, Liiv S, Magnússon S, Maňkovská B, Piispanen J, Rühling Å, Santamaria JM, Spiric Z, Suchara I, Thöni L, Urumov V, Yurukova L, Zechmeister HG (2010) Are cadmium, lead and mercury concentrations in mosses across Europe primarily determined by atmospheric deposition of these metals? J Soil Sediments 10: 1572–1584

Schultze-Dewitz G, Koch G (2008) The anatomy of wood and bark of Scots Pine. A review of literature. Feddes Rep 119(7–8):655–668

Schulz H, Popp P, Huhn G, Stärk HJ, Schüürman G (1999) Biomonitoring of airborne inorganic and organic pollutants by means of pine tree barks. I. Temporal and spatial variations. Sci Total Environ 232(1–2):49–52

Smodis B, Pignata ML, Saiki M, Cortes E, Bangfa N, Markert B, Nyarko B, Arunachalam J, Garty J, Vutchkov M, Wolterbeek HT, Steinnes E, Freitas MC, Lucaciu A, Frontasyeva M (2004) Validation and application of plants as biomonitors of trace element atmospheric pollution—a co-ordinated effort in 14 countries. J Atm Chem 49(1–3):3–13

Solga A, Frahm J-P (2006) Nitrogen accumulation by six pleurocarpous moss species and their suitability for monitoring nitrogen deposition. J Bryol 28:46–52

Steindor K, Palowski B, Góras P, Nadgórska-Socha A (2011) Assessment of bark reaction of selected tree species as an indicator of acid gaseous pollution. Pol J Environ Stud 20(3):619–622

Steinnes E, Rühling Å, Lippo H, Mäkinen A (1997) Reference materials for large-scale metal deposition surveys. Accred Qual Assur 2(5): 243–249

Stevenson FJ (1994) Humus chemistry: genesis, composition, reactions, 2nd edn. J. Wiley, New York, p 512

STRILOG (2011) Biogeochemical exploration of forests as a basis for the long-term landscape exploitation in the Czech Republic, Project CZ0074. Project website, Silva Tarouca Research Institute for Landscape and Ornamental Gardening (STRILOG), Pruhonice. http://www.norwaygrantcz0074.eu/joomla/index.php?option=com_content&view=article&id=55&Itemid=70&lang=en. Accessed May 2015

Suchara I (1993) The use of some urban park woody species in an estimation of air pollution levels. Tree bark extract characteristics. Zahradnictví, Praha 20(4):241–260

Suchara I (2012) Temporal and spatial changes in spruce bark acidity at the scale of the Czech Republic in the last two decades, and the current abundance of epiphytic lichen *Hypogymnia physodes*. Water Air Soil Pollut 223(4):1685–1697

Suchara I, Sucharová J (2000) Distribution of long-term accumulated atmospheric deposition loads of metal and sulphur compounds in the Czech Republic determined through forest floor humus analyses. Acta Pruhoniciana 69:1–177

Suchara I, Sucharová J (2002) Distribution of sulphur and heavy metals in forest floor humus of the Czech Republic. Water Air Soil Pollut 136(1–4):289–316

Suchara I, Sucharová J (2006a) Distribution of 36 element deposition rates in a historic mining and smelting area as determined through fine-scale biomonitoring techniques. Part II: relative long-term accumulated atmospheric deposition levels. Water Air Soil Pollut 153(1–4):229–252

Suchara I, Sucharová J (2006b) Mercury distribution around the Spolana chlor-alkali plant (Central Bohemia, Czech Republic) after a catastrophic flood as revealed by bioindicators. Environ Pollut 151(2): 352–361

Suchara I, Sucharová J, Holá M (2007) Bio-monitoring of the atmospheric deposition of elements using moss analysis in the Czech Republic. Results of the international bio-monitoring programme UNECE ICP-Vegetation 2000. Part II: optional elements for the bio-monitoring programme. Acta Pruhoniciana 87:1–186

Suchara I, Sucharova J, Hola M, Reimann C, Boyd R, Filzmoser P, Engelmaier P (2011a) The performance of moss, grass, and 1- and 2-year old spruce needles as bioindicators of contamination: a comparative study at the scale of the Czech Republic. Sci Total Environ 409(11):2281–2297

Suchara I, Rulík P, Hůlka J, Pilátová H (2011b) Retrospective determination of ^{137}Cs specific activity distribution in spruce bark and bark aggregated transfer factor in forests on the scale of the Czech Republic ten years after the Chernobyl accident. Sci Total Environ 409(10):1927–1934

Suchara I, Sucharová J, Holá M (2014) The influence of contrasting ambient SO_2 concentrations in the Czech Republic in 1995 and in 2000 on the characteristics of spruce bark, used as an air quality indicator. Ecol Indic 39:144–152

Sucharová J, Suchara I (2004a) Bio-monitoring the atmospheric deposition of elements and their compounds using moss analysis in the Czech Republic. Results of the international bio-monitoring programme UNECE ICP-Vegetation (2000) Part I: elements required for the bio-monitoring programme. Acta Průhoniciana 77:1–135

Sucharová J, Suchara I (1998a) Atmospheric deposition levels of chosen elements in the Czech Republic determined in the framework of the International Bryomonitoring Program 1995. Sci Total Environ 223(1):37–52

Sucharová J, Suchara I (1998b) Biomonitoring of the atmospheric deposition of metals and sulphur compounds using moss analysis in the Czech Republic. Results of the international biomonitoring programme 1995. Research Institute of Ornamental Gardening, Průhonice, 183 pp

Sucharová J, Suchara I (2004b) Distribution of 36 element deposition rates in a historic mining and smelting area as determined through fine-scale biomonitoring techniques. Part I: relative and absolute current atmospheric deposition levels detected by moss analyses. Water Air Soil Pollut 153(1–4):205–228

Sucharová J, Suchara I, Holá M (2008) Contents of 37 elements in moss and their temporal and spatial trends in the Czech Republic during the last 15 years. Silva Tarouca Research Institute for Landscape and Ornamental Gardening, Průhonice, p 96

Sucharová J, Suchara I, Reimann C, Boyd R, Filzmoser P, Engelmaier P (2011) Spatial distribution of lead and lead isotopes in soil B-horizon, forest-floor humus, grass (*Avenella flexuosa*) and spruce (*Picea abies*) needles across the Czech Republic. Appl Geochem 26(7): 1205–1214

Sucharova J, Suchara I, Hola M, Reimann C, Boyd R, Filzmoser P, Engelmaier P (2011) Linking chemical elements in forest floor humus (Oh-horizon) in the Czech Republic to contamination sources. Environ Pollut 159:1205–1214

Sucharová J, Suchara I, Holá M, Reimann C (2014) Contemporary lead concentration and stable lead isotope ratio distribution in forest moss across the Czech Republic. Appl Geochem 40: 51–60

Tamminen P, Starr M, Kubin E (2004) Element concentrations in boreal, coniferous forest humus layers in relation to moss chemistry and soil factors. Plant Soil 259(1–2):51–58

Thöni L (1996) Vergleich von Elementkonzentrationen in drei Biomonitormoosen untereinander und mit Depositionsfrachten im Bulksammler nach Bergerhoff. Bundesamt für Umwelt, Wald und Lanschaft (BUWAL), Egg (Switzerland), p 879

Thöni L, Schnyder N, Krieg F (1996) Comparison of metal concentrations in three species of mosses and metal freights in bulk precipitations. Fresen J Anal Chem 354(5–6):703–708

van Dijk H (1971) Cation binding of humic acids. Geoderma 5(1):53–67

Vázquez G, Antorrena G, González J, Doval DM (1994) Adsorption of heavy metal ions by chemically modified *Pinus pinaster* bark. Biores Technol 48(3):251–255

Zechmeister HG, Grodzińska K, Szarek-Łukaszewska G (2004) Bryophytes. In: Markert B, Breure AM, Zechmeister HG (eds) Bioindicators and Biomonitors. Principles, concepts and applications. Elsevier Science Ltd, Amsterdam, pp 329–375