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REVIEW ARTICLE

Significance of the long-term biomonitoring studies for understanding the impact of pollutants on the environment based on a synthesis of 25-year biomonitoring in the Holy Cross Mountains, Poland

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Abstract

This review presents compiled results of complex biomonitoring studies that have been conducted in the Holy Cross Mountains, south-central part of Poland, since the 1990s. The significance of these studies results from several aspects: (i) a number and a variety of plant organisms used, e.g., mosses, lichens, coniferous and deciduous trees, and their tissues (wood, bark, needles, leaves, the aboveground parts of several vascular plants); (ii) applications of a broad scope of instrumental methods aiming at determining major and trace elements (including rare earth elements), organic compounds (PAHs, PCBs, phenols), and stable sulfur isotopes ($\delta^{34}S$); and (iii) different methodological and environmental issues addressed. The comparison and interpretation of results derived from seventeen sampling campaigns carried out between 1994 and 2017 are a valuable source of information on the following: (i) bioaccumulative properties of organisms used in air quality monitoring, (ii) identification and variations of local and regional pollution sources and geochemical landscape patterns and processes over years, and (iii) establishing environmental factors that variously affected chemical composition of plants growing under physiological stress, including roadside vegetation and plants from acid mine drainage areas.

Keywords Biomonitoring · Plants · Holy Cross Mountains · Major and trace elements · Organic compounds · Stable sulfur isotopes

Introduction—plants as bioindicators

Biomonitoring with plants has been one of the most common methods of air quality assessment since the 1960s (Rühling and Tyler 1968, 1973). Analysis of both vascular and non-vascular plants or their selected organs provides information on the spatial and temporal distribution of major and trace elements, organic compounds, or stable isotopes in the atmosphere (Agnan et al. 2014; Foan et al. 2014; Solga et al. 2005; Xiao et al. 2010). It also allows us to indicate the origin of pollutants and understand several aspects that affect the process of accumulation (Boquete et al. 2014; Pérez-Llamazares et al. 2010).

The use of different plants in biomonitoring studies reflects their ability to accumulate pollutants according to specific mechanisms and paths. Identification of pollution sources is more reliable when we know more on how plants accumulate pollutants from the environment. Lower plants and fungi, like mosses and lichens, do not have roots, and take up elements directly from the atmosphere, which is the main source of bioessential elements for them. They do not have protective layers (epidermis and cuticle), so their tissues can be easily penetrated by pollutants which are accumulated by the whole plant surface (Augusto et al. 2010; Grodzińska and Szarek-Łukaszewska 2001). In case of higher plants, e.g., trees, the process of accumulation is more complex. They take up substances not only from the atmosphere but also from soil, bedrock, and surface- and groundwaters. Due to several accumulation paths, their use in biomonitoring studies is usually limited to analysis of external parts, like bark, needles, or leaves (De Nicola et al. 2016; Ratola et al. 2003).

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In plants, the process of accumulation runs according to two main mechanisms. The first one includes the presence of substances that enhance the process of accumulation and/or places where it occurs. It refers to living organisms, like mosses and lichens, or parts of vascular plants, like needles and leaves. The second one is based on mechanical surface deposition and occurs in dead tissues, such as tree bark. Moreover, the individual features of plants may increase or reduce the accumulation of selected substances leading to between-species differences (Boltersdorf et al. 2014; Boquete et al. 2015; Poikolainen 2004). The environmental factors have a significant impact on the chemical composition of plant bioindicators. These encompass geologic setting of a sampling area and its topography, altitude, temperature, amount of precipitation, wind rose, phenology, hydrology, etc. These can lead to within-species differences between samples taken from the same area, but from variously located sampling sites (Dołęgowska and Migaszewski 2015; Fernández et al. 2015; Migaszewski et al. 2009). Understanding all these environmental variables and acquiring detailed knowledge of the sampling area combined with localization and identification of pollution sources are crucial to obtain reliable and comparable results of biomonitoring studies. Despite several requirements that have to be met, this approach is still popular. Besides, biomonitoring is cheaper than classic, direct methods, and easier to perform. It can be conducted on a small scale (Capozzi et al. 2017; Foan et al. 2015; Kłos et al. 2018) or on a large scale (Agnan et al. 2014; Lazo et al. 2019; Likus-Cieślik et al. 2020). Plants give the possibility to follow both seasonal changes and long-term trends. They can be used in their natural habitats (passive samplers) (Gałuszka 2007; Lehndorff and Schwark 2004) or in places where they do not occur naturally (active samplers) (Giordano et al. 2013, Milićević et al. 2017).

In the Holy Cross Mountains (HCM), biomonitoring studies with plants have been conducted since 1994. The first 3-year study (1994–1996) under the guidance of Z.M. Migaszewski was aimed at the determination of concentration baselines, and spatial and temporal distribution of major and trace elements, organic compounds, and variations in stable sulfur isotope ratios (Migaszewski 1998, 1999; Migaszewski et al. 1996). These issues were developed during 2007–2008 by the subsequent international comparative moss study on polycyclic aromatic hydrocarbons (PAHs) and trace elements (Migaszewski et al. 2009, 2010b, 2011). The 1994–1996 project included a broad range of analytical methods (geochemical, isotopic, mineralogical) and the novel calculation of the geochemical baselines utilizing a "barbell" unbalanced, nested ANOVA design, starting long-term biomonitoring studies, which have been performed in the HCM region until now (Dołęgowska and Migaszewski 2020). These and other complementary studies were carried out using various naturally growing vascular and non-vascular plants and topsoil. The uniqueness of this research in the HCM is closely linked to a number and a variety of plant species used and to a broad range and objectives of the sampling campaigns. The scope of these case studies also encompassed methodological issues, connected with sample preservation and preparation, and determination of uncertainty arising from sampling, preparation, and analysis (Dołęgowska et al. 2017; Dołęgowska and Migaszewski 2019, 2020; Pasławski and Migaszewski 2006). Except for plant bioindicators, soil and wherever possible rock and water samples were collected and analyzed. This approach provided the best snapshot of the state of natural ecosystems and enabled us to better understand various geochemical interactions.

This review is a compilation of the biomonitoring studies conducted in the HCM region by the scientific group of Z.M. Migaszewski during the last 25 years. Comparison of results derived from different bioindicators, over many years, can be a valuable source of information on the (i) differences in bioaccumulative properties of various bioindicators, (ii) changes in pollution patterns, and (iii) methodological aspects to be considered in the planning of biomonitoring studies. For the sake of brevity, the other media (soils, rocks, waters), being an integral part of these complementary studies, have not been discussed in more detail.

The Holy Cross Mountains—geology, soils, vegetation, and pollution sources

The Holy Cross Mountains (HCM) are located in the south-central part of Poland. This region is geologically bipartite consisting of the Paleozoic block and the Permo-Mesozoic cover. The Paleozoic block is composed of two geologic-tectonic units (terranes), i.e., the northern (Łysogóry) and the southern (Kielce), separated by the Holy Cross Fault (Thrust). The first one is made of Middle/Upper Cambrian quartzites, quartzitic sandstones, and silty-clayey shales; Ordovician-Silurian clayey sandstone with subordinate carbonate sediments; Lower Devonian quartzitic sandstones; Middle–Upper Devonian dolomites and limestones; and Lower Carboniferous clayey sandstone siliceous deposits. In contrast, the Kielce unit contains nearly the same Lower Cambrian to Lower Carboniferous sequence of rock formations, but is characterized by distinctly shallower facies (Fig. 1). The Permo-Mesozoic cover occurs at the southern and northern margins of the region and is built of terrigenous-carbonate (Upper Permian, Triassic, and Lower Jurassic) and carbonate (Upper Jurassic) deposits. Toward the southwest and south, the HCM border on the Nida Trough (Cretaceous carbonates) and the Carpathian Foredeep (Paleogene-Neogene claystones, sandstones, limestones, and gypsum).

Cambrian and Devonian rock series form nearly parallel mountain ranges, whereas Ordovician, Silurian, and

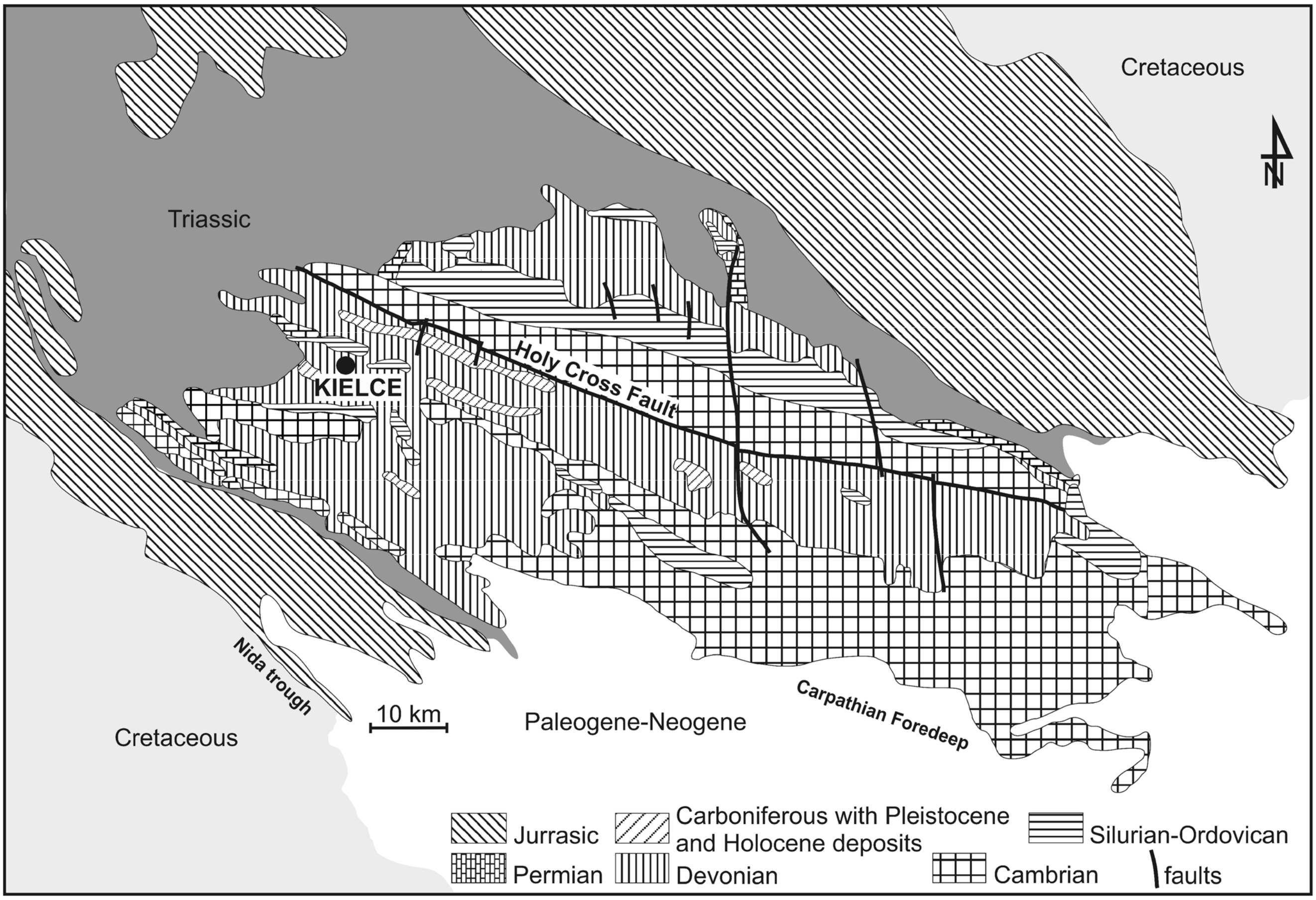

Fig. 1 Geologic sketch map of the Holy Cross Mountains (modified from Czarnocki, 1938)

Carboniferous rock series build broad depressions. The last mentioned are typically covered with Pleistocene and Holocene deposits (tills, sands, muds, loess). Different soil taxonomies are closely linked to this diverse lithology of bedrock; for example, rankers and cambisols are developed on sandstones and siltstones; rendzinas on carbonate rocks; arenosols, podzols, and fluvisols on various fluvioglacial deposits; and chernozems on loess deposits. The pH of soils ranges from acidic (4.0–5.0) through circumneutral (6.7–7.0) to somewhat alkaline (up to 7.4) (Migaszewski and Pasławski 1996; Migaszewski et al. 2001).

Considering biomonitoring studies in the HCM, it should be stressed that about 28% of the Świętokrzyskie province is wooded. More than 7000 ha of forests take up the Holy Cross Mountains National Park (HCMNP) and numerous nature reserves. Two major natural coniferous habitats can be distinguished in the region: (i) dry coniferous forest (*Cladonio-Pinetum*) and (ii) continental coniferous forest (*Querco roboris-Pinetum*), and less common habitats like degraded continental coniferous forest, substitutional community for poor species, mixed lime-oak-hornbeam forest, degraded pine monoculture, and lowland acid beech wood. European beech (*Fagus sylvatica* L.) and European silver fir (*Abies alba* Mill.) are predominant species among coniferous and deciduous trees, especially in the northern part, whereas pine is represented only by the species *Pinus sylvestris* L. Lichen flora is diverse, but *Hypogymnia physodes* (L.) Nyl. and *Xanthoria parietina* (L.) Th. Fr. are most widespread. The moss species are, in turn, dominated by *Hylocomium splendens* (Hedw.) Schimp. and *Pleurozium schreberi* (Brid.) Mitt. (Fig. 2; Gałuszka 2007; Migaszewski et al. 2009, 2010a).

When it comes to discussing the pollution sources of the region, both natural and anthropogenic sources should be taken into account. The HCM are characterized by a slightly risen geochemical background of Pb highlighted by higher levels of this element (linked to galena PbS) in Upper Paleozoic (Devonian, Upper Permian) and lowermost Triassic rock series. Moreover, the occurrences of veined and scattered metal(loid) sulfide and barite mineralization, particularly in Devonian carbonates, may cause higher concentrations of some elements (e.g., As, Cu, Fe, Mn, Sb) in different environmental compartments, including plants (Migaszewski and Pasławski 1996; Migaszewski et al. 2001).

The contribution of anthropogenic pollution sources to the total pollution budget of the region has changed over the years. In the 1990s, when the first sampling campaigns were performed, the principal pollution sources included cement and lime plants located south of Kielce, Kielce and Ostrowiec heat

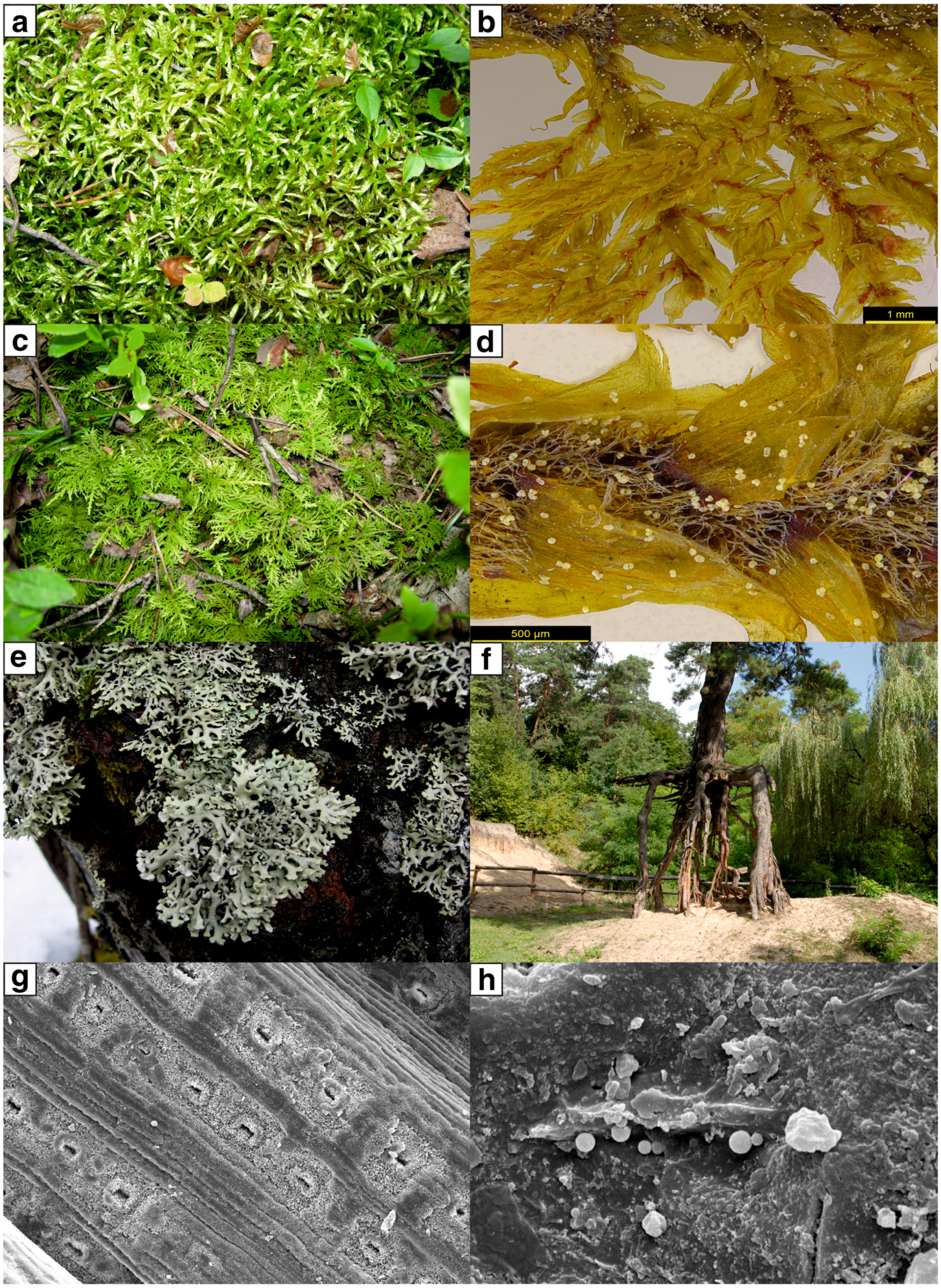

Fig. 2 **a**, **b** Moss *P. schreberi* with pine pollens (right microphotograph). **c**, **d** Moss *H. splendens* with pine pollens (right microphotograph). **e** Lichen *H. physodes*. **f** Scots pine tree (*P. sylvestris*). **g**, **h** SEM images: Scots pine needle with stomata (left microphotograph) and spherical technogenic particulates (right microphotograph)

generating plants, Ostrowiec Steelworks, "Mesko" metal facility in Skarżysko-Kamienna, from the west Konin lignite-fired power-generating plant, from the southwest neighboring highly industrialized Upper Silesian-Cracovian region, and from the south Sendzimir Steelworks in Cracow, to mention only the most significant examples. All these industrial facilities were the source of stack and lime dusts (cement and lime plants); coal dusts (power- and heat generating plants); and ore, cyclone, and extractor dusts (steelworks). The other pollution sources encompassed residential combustion of coal, road traffic, and waste incineration. Changes in Poland's heavy industry, which were initiated in the 1990s, have resulted in a reduction in coal extraction and consumption, and also in a decrease of domestic metallurgical production (Andonova 2007). The development of transport infrastructure and the expansion of urbanized areas have added more to the pollution budget of the region. The current major pollution sources include cement and lime plants, residential and industrial combustion of bituminous (hard) coal, and gasoline- and diesel-powered vehicles. All these activities are a source of both organic and inorganic pollutants which can deteriorate the air quality and negatively affect conditions of biotic and abiotic environmental compartments.

Sampling campaigns—location of sampling areas and type of bioindicators collected

The detailed characteristics of the individual sampling campaigns are presented in Tables 1 and 2, which comprise information on the following: years of sampling, sampling area, type of bioindicators used, compounds/elements determined, and issues investigated. Locations of sampling areas/points are presented in Fig. 3.

Organic compounds—PAHs, PCBs, phenols—in plant bioindicators of the Holy Cross Mountains

Persistent organic compounds (POPs), e.g., polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and phenols, are a group of chemicals of global concern mainly due to their persistence in the environment and lipophilic properties which lead to their accumulation in living organisms. The most frequent representatives of POPs in the environment are PAHs, which include more than one hundred compounds with two or more fused aromatic rings. They are formed as a result of pyrolysis and pyrosynthesis during incomplete combustion of organic materials (Harmens et al. 2013; Ravindra et al. 2008; Sienra et al. 2005). Of the sixteen PAHs, which have been classified by the US Environmental Protection Agency as the priority pollutants, eight (benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, chrysene, fluoranthene, and indeno(1,2,3-c,d)pyrene) have potential human mutagenic and cancerogenic properties.

The presence of PAHs in the environment is directly related to the molecular weight of individual compounds and their ability to long-range atmospheric transport. Low molecular weight PAHs occur mainly in gaseous form. They are transported over long distances, hence their presence in remote pristine environments. In turn, high molecular PAHs are connected with particulate matter and predominate in samples collected near pollution sources (Augusto et al. 2010; Xia et al. 2010).

Except for organic soil horizon (especially fermentative-humic subhorizon Ofh), vegetation is one of the most important sinks of PAHs in the environment (Migaszewski and Gałuszka 2008). Plants can accumulate even 44% of the total PAHs emitted to the atmosphere, and their use as bioindicators in the HCM region dates back to the 1990s (Migaszewski and Pasławski 1996). Chemical analysis of different plant bioindicators, including (i) 1-, 2-, and 3-year-old pine needles (*P. sylvestris*); (ii) pine, oak (*Quercus robur* L.), and birch (*Betula pendula* Roth) bark; (iii) pine wood; (iv) *H. physodes* lichen thalli; and (v) *H. splendens* moss tissues, was carried out in the years 1993–1996 and in 2000 and included the determination of selected PAHs and other POPs, like PCBs, pesticides, and phenols (Migaszewski 1999; Migaszewski et al. 2002). These were the first studies which included several groups of organic compounds in more than one plant bioindicator (Table 1).

The upshots showed that, in all bioindicators examined, PAHs were the most prevalent compounds. Enrichment in phenol, observed only in pine samples (needles, wood, and bark), was related to its probable production by pine. It is worth mentioning that the youngest needles had the highest phenol contents due to their intensive metabolic processes (Migaszewski et al. 2002). An interesting relation was also observed between the age of needles and the PAH content. The oldest needles had the highest concentrations of total PAHs resulting from their successive accumulation during a needle growth, whereas the youngest were enriched in high molecular weight hydrocarbons (e.g., dibenzo[a,h]anthracene and indeno[1,2,3-c,d]pyrene). This suggested that the number of heavy PAHs accumulated by pine needles may decrease over time as a result of wind and rainfall removal of particles that are the main carriers of these compounds. These findings were confirmed by studies from different parts of the world (Luo et al. 2020; Piccardo et al. 2005). Regardless of the research area (Tibetan Plateau, Italy), these authors noticed that older needles compared to younger ones had lower concentrations of heavier PAHs and higher concentrations of lighter PAHs. Concentrations of total PAHs in needles were much lower than in other plant bioindicators from the HCM. Although pine needles are recommended for biomonitoring of organic compounds (De Nicola et al. 2016; Navarro-Ortega et al. 2012), it should be stressed that the presence of lipid-rich cuticle on their surface may significantly reduce their permeability, resulting in lower PAH content (Lehndorff and Schwark 2004).

The use of higher plants as bioindicators of organic compounds, including PAHs, is based on fact that their uptake through the roots and translocation inside the plant are hampered. Determination of PAHs in samples representing different morphologic parts (tissues) of a single pine tree (1- and 2-year needles, 1-year shoots, bark, outer and inner wood, and root), collected in 2000 (Fig. 3), showed comparable concentrations in the root and inner and outer wood (Migaszewski et al. 2002). They varied from 57 (root) to 72 μg kg^{-1} (outer wood) and were about three times lower than in needles (216 μg kg^{-1}) and six times lower than in bark (383 μg kg^{-1}). The order of PAH content in pine tissues was as follows: bark > 2-year needles > 1-year shoots > 1-year needles > outer wood > inner wood > roots, which clearly pointed to aerial pollution and limited translocation between plant tissues. Much higher concentrations in bark than in other parts of pine trees are caused by physical properties of this tissue. Bark is a porous, outermost part of trees, which accumulates pollutants in a passive way. On one hand, the rough

Table 1 Detailed characteristics of sampling campaigns conducted in the Holy Cross Mountains over 25 years

Time of sampling	Sampling area	Plant species[1]	Determined elements and organic compounds/investigated issue	Instrumental method used	References
Biomonitoring studies					
1994	Holy Cross Mountains National Park (HCMNP), southern part of the Holy Cross Mountains (HCM)	1. Lichen *H. physodes* 2. Mosses *P. schreberi*, *H. splendens*, *H. cupressiforme* 3. 1- and 2-year-old Scots pine (*P. sylvestris*) needles	1. Major and trace elements 2. Stable sulfur isotopes ($\delta^{34}S$)	1. FAAS, HGAAS, CVAAS, ICP-OES, LF 2. IRMS 3. GC-MS, GC-ECD	Migaszewski and Pasławski (1996)
1995		1. Lichen *H. physodes* 2. Scots pine, birch (*B. pendula*) bark, larch (*L. decidua*) bark 3. 1-, 2-, and 3-year-old pine needles	1. Major and trace elements 2. Stable sulfur isotopes 3. Organic compounds (PAHs, PCBs, pesticides, phenols)		Migaszewski et al. (1996)
1996		1. Lichen *H. physodes* 2. Scots pine, birch, and larch bark 3. 1-, 2-, and 3-year-old Scots pine needles	1. Major and trace elements 2. Stable sulfur isotopes, 3. Organic compounds (PAHs, PCBs, pesticides, phenols)		Migaszewski (1998, 1999)
1998	Five habitats located in the northern, southern, and southwestern parts of the region	1. Lichen *H. physodes* 2. Scots pine bark (external, internal bark, pulp, root), oak (*Q. robur*) and birch bark 3. 1-, 2-, and 3-year-old Scots pine needles	1. Major and trace elements	1. FAAS, HGAAS, CVAAS, ICP-OES	Migaszewski et al. (2001)
2000	Three representative habitats located in the southern and northern parts of the HCM	1. Lichen *H. physodes* 2. Mosses: *H. splendens*, *P. schreberi*, *H. cupressiforme* 2. Scots pine, oak, birch, and aspen (*P. tremula*) bark 3. 2-year-old Scots pine needles 4. Different Scots pine morphologic parts (tissues): root, inner, outer wood, bark, 1-year shoots	1. Major and trace elements 1. Stable sulfur isotopes 2. Organic compounds (PAHs)	1. FAAS, HGAAS, CVAAS, ICP-MS, ICP-OES 1. IRMS 2. GC-MSD 3. SSME	Gałuszka (2003, 2005), Migaszewski et al. (2002)
2002	HCMNP vs. Magurski Natl. Park (SE Poland) and Wigierski Natl. Park (N Poland)	1. Lichen *H. physodes* 2. 1- and 2-year-old Scots pine needles 3. Scots pine bark	1. Major and trace elements	1. FAAS, HGAAS, direct mercury analysis (AAS-AMA), ICP-OES 2. SSEM	Migaszewski et al. (2004, 2006)
2005	Southern part of the HCM	1. Mosses: *H. splendens*, *P. schreberi*	1. Major and trace elements 2. Organic compounds (PAHs)	1. ICP-MS, ICP-OES 2. GC-MSD	Gałuszka (2007)
2007–2008	Ten habitats in the HCM (vs. two Alaskan Natl. parks)		1. Trace elements 2. PAHs	1. ICP-MS, direct mercury analysis (AAS-AMA) 2. GC-MS	Migaszewski et al. (2009, 2010b, 2011)
2008	Twenty-four habitats in the vicinity of Kielce		1. Trace elements (including REEs) 2. Organic compounds (PAHs)	1. ICP-MS 2. GC-MS	Dołęgowska and Migaszewski (2011), Dołęgowska et al.

Table 1 (continued)

Time of sampling	Sampling area	Plant species[1]	Determined elements and organic compounds/investigated issue	Instrumental method used	References
			3. Stable sulfur isotopes	3. IRMS	(2013), Migaszewski et al. (2010a)
2010	Kielce	1. Leaves and barks of several trees: ash *F. excelsior*, linden *T. cordata*, *T. platyphyllos*, pine *P. sylvestris*, maple *A. pseudoplatanus*	2. Elemental composition of roadside trees affected by different chloride de-icers	1. ICP-OES, FIA, spectrophotometric method (Cl-), potentiometric method with ion-selective electrode (ISE)	Gałuszka et al. (2011)
2011	Two habitats in the vicinity of Kielce	1. Moss *P. schreberi*	1. Rare earth elements	1. ICP-MS	Dołęgowska and Migaszewski (2013)
2014	Three habitats in the HCM	1. Roots and aboveground parts and of *J. effusus*	1. Trace element (including REEs)	1. ICP-MS	Krzciuk and Gałuszka (2019, 2020)
2016, 2017	Western part of the HCM (Wiśniówka massif)	1. Aboveground parts of several vascular plants 2. Mosses: *P. schreberi*, *H. splendens*, *D. aduncus*	1. Trace element (including REEs) 2. Stable sulfur isotopes	1. ICP-MS, XRF 2. IRMS	Gałuszka et al. (2020)

[1] Soils are not included

FAAS, flame atomic adsorption spectrometry; *GFAAS*, graphite furnace atomic absorption spectrometry; *HGAAS*, hydride generation atomic absorption spectrometry; *CVAAS*, cold vapor atomic absorption spectrometry; *AAS-AMA*, atomic adsorption spectrometry–advanced mercury analyzer; *ICP-MS*, inductively coupled plasma-mass spectrometry; *ICP-OES*, inductively coupled plasma-optical emission spectroscopy; *LF*, laser fluorometry; *SSEM*, surface scanning electron microscopy; *GC-MS*, gas chromatography-mass spectrometry; *GC-ECD*, gas chromatography with electron capture detection; *XRF*, X-ray fluorescence; *FIA*, flow injection analysis; *IRMS*, isotope ratio mass spectrometry

Table 2 Detailed characteristics of research concerning methodological aspect of biomonitoring studies

Sampling area and time of sampling	Plant species	Investigated issue	Sampling details	Sample storage and preparation	Instrumental methods used	References
Holy Cross Mountains National Park (HCMNP), southern part of the Holy Cross Mountains (HCM); 1994–1996	*1. H. physodes* *2. P. schreberi*, *H. splendens*, *H. cupressiforme* 3. Scots pine needles (*P. sylvestris*)	Quality of element determinations in plant materials	Sampling duration: 3–4 days at each year Sampling strategy: 1. Lichens: collected within an area ranging from 10 × 10 m to 100 × 100 m, on several trees at a height of 0.25 to 2.0 m 2. Mosses: composite samples consisting of 5 to 10 subsamples collected within an area of 10 × 10 m 3. Needles: pine trees of the same age occurring at sampling sites	Storage: at an ambient temperature Preparation: washing with deionized water and drying at an ambient temperature (this procedure was repeated three times)	ICP-OES, ICP-MS, FAAS, CVAAS	Pasławski and Migaszewski (2006)
Ten habitats in the HCM; 2007	*H. splendens*, *P. schreberi*	Sample preparation vs. trace element concentration variability	Sampling duration: 6–8 days Sampling strategy: 1. Apical green parts of mosses 2. Composite samples (~ 50 g) consisting of 5 to 10 subsamples, collected within an area of 10 × 10 m	Storage: at an ambient temperature Preparation: triple rinsing with deionized water	ICP-MS	Migaszewski et al. (2010b)
Three habitats in the vicinity of Kielce; 2014–2017	*P. schreberi*	Estimation of sampling, sample storage, and sample preparation uncertainties	Sampling duration: 3 days at each year Sampling strategy: 1. Apical green parts 2. Composite samples (~ 50 g) consisting of 8 to 10 subsamples, collected within an area of 10 × 10 m	Storage: 1. At an ambient temperature 2. At 4 °C 3. At − 20 °C Preparation: 1. Triple rinsing with deionized water 2. Manual, mechanical cleaning	FAAS, GFAAS, ICP-MS	Dołęgowska (2016, 2017), Dołęgowska et al. (2017), Dołęgowska and Migaszewski (2019, 2020)

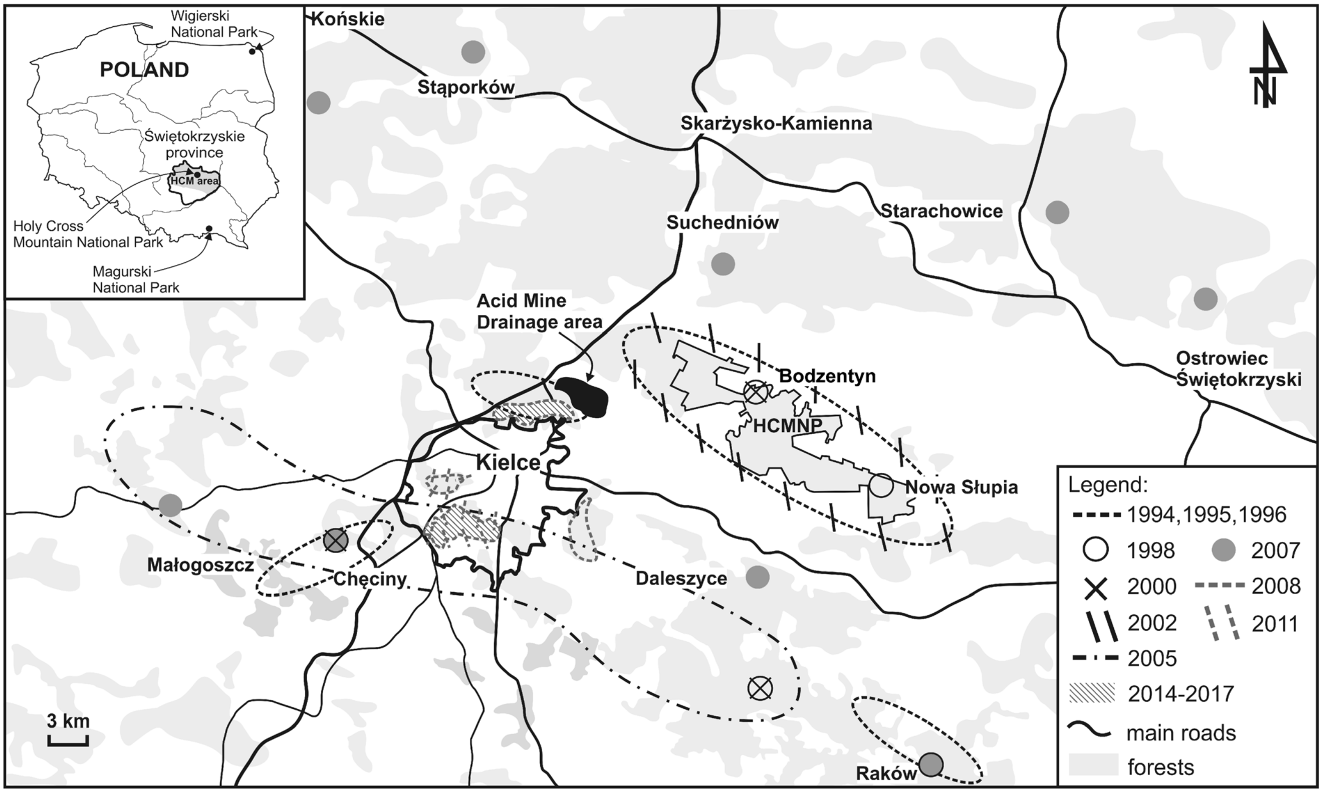

Fig. 3 Boundaries of sampling areas and sampling points located within HCM area and selected in individual sampling campaigns

surface favors the process of accumulation, but on the other hand, precipitation that drains the bark removes particles and compounds deposited on its surface. A comparison of results obtained for bark, as substratum, and lichens taken from the same tree showed that, regardless of tree species, lichens accumulate up to 10 times more PAHs than bark. These differences result from different accumulation processes. As previously mentioned, pollutants are deposited on the surface of bark or adsorbed in its outer parts. Lichens accumulate pollutants actively, they do not have protective barriers, and therefore, substances absorbed by the whole surface can easily penetrate the thalli inside. Studies carried out in 1995, 1996, and 2000 confirmed that the best bioindicators of organic compounds, including PAHs, were lichens, followed by mosses, bark, and needles of different ages (Migaszewski 1996, 1999; Migaszewski et al. 2002). Results of other studies also indicated lichens as better bioindicators of PAHs compared to pine needles and mosses (Augusto et al. 2010; Capozzi et al. 2020; Yang et al. 2013). This is due to their ability to entrap PAHs and preserve them from degradation during lichen exposure.

Mosses also have no protective barriers. They contain only a single cell layer that makes the pollutants pass through their tissues as easily as in the case of lichens (Capozzi et al. 2020). In the HCM region, biomonitoring studies with mosses as indicators of PAHs started in 2000 and were continued for the next 8 years (Dołęgowska and Migaszewski 2011; Migaszewski et al. 2002). During four sampling campaigns (Table 1; Fig. 3), 90 samples of *H. splendens* and *P. schreberi* were collected and analyzed for selected PAHs. The studies confirmed that mosses are useful bioindicators of these compounds. However, their accumulative capabilities are influenced by their morphology, which should be taken into account in comparative studies with different species.

Biomonitoring studies conducted in the HCM region concerned not only the comparison of bioaccumulation of organic compounds in various plants but also their use for the identification of possible pollution sources. Because each emission source has a specific PAH signature (fingerprint), the PAH profiles and individual diagnostic ratios are successfully used for this purpose (Tobiszewski and Namieśnik 2012 and reference therein). Results of studies performed over a 12-year period showed a predominance of 3- and 4-ring hydrocarbons (phenanthrene, fluoranthene, pyrene, and chrysene) in all the bioindicators examined (Fig. 4). This can be explained by the fact that lighter hydrocarbons occur mainly in gaseous form and are more accessible to plants (Ratola et al. 2003). The same relationship was also found by other authors (Shukla and Upreti 2009; Yang et al. 2013). However, the enrichment in individual PAHs was dependent on the location of sampling site and the vicinity of pollution sources. The presence of significant amounts of light PAHs in samples collected from higher elevations, located in the HCMNP, away from local pollution sources, was a clear evidence on their ability to

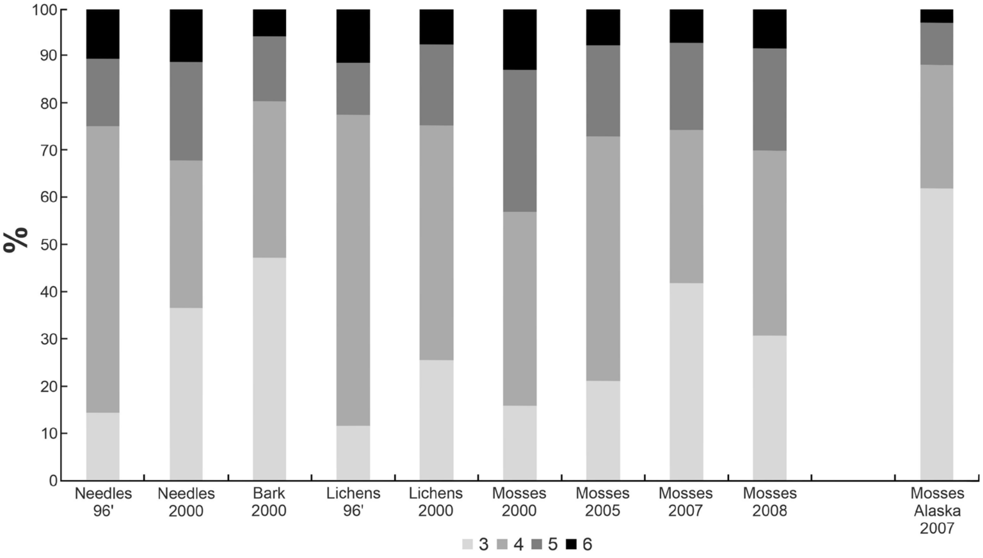

Fig. 4 Contribution of 3-, 4-, 5-, and 6-ring hydrocarbons to total PAHs in different plant bioindicators over a 12-year period in the HCM compared to 2017 Alaskan mosses (Wrangell-Saint Elias National Park and Preserve and Denali National Park and Preserve) (data from Dołęgowska and Migaszewski 2011; Gałuszka 2007; Migaszewski 1999; Migaszewski et al. 1996, 2002, 2009)

long-distance atmospheric transport (Migaszewski et al. 2002). It was the first time when the relationship between the volatile PAHs and the altitude was noticed. An increasing trend in light PAH concentrations (2-, 3-, and 4-rings) with increasing altitude was also found in pine needles collected from Tibetan Plateau (Luo et al. 2020), but only up to an altitude of 3354 m a.s.l. At higher altitudes, the concentrations of lighter PAHs decreased mainly due to their susceptibility to photolysis (Yang et al. 2013).

In most cases, the comparison of compounds with different numbers of rings showed a gradual decrease in the total of 4-, 5-, and 6-ring hydrocarbons in favor of 3-ring compounds (Fig. 4). The observed increasing contribution of light hydrocarbons was related to changes in energy and transport sectors in Poland. Bituminous (hard) coals were, and still are, principal fuels of different industries, but their extraction and consumption dropped almost twofold in the early 2000 compared to the 1990s. Polish hard coals are enriched in 5- and 6-ring hydrocarbons and in benzo(a) anthracene and chrysene (Bojakowska and Sokołowska 2001a,b), hence their significant contents in 1996 samples (Fig. 4). The gradual reduction in consumption of solid fossil fuels and an increase in the use of liquid and gaseous equivalents explain an enrichment in 3-ring hydrocarbons in 2000 needles and lichens in comparison to the 1996 samples. It is worth mentioning that the concentrations of 3-ring hydrocarbons found in bark from 2000 were the highest in comparison to other bioindicators. Moss samples collected in the following years also show this trend. In 2007 mosses, more than 40% of total PAHs were 3-ring compounds (Fig. 4). A slight decrease in the contribution of lighter PAHs observed in the samples collected in 2008 is not surprising given the specificities of the sampling areas. In 2007, mosses were collected from forest areas located mostly away from cities and residential estates, while in 2008 the sampling survey was conducted mainly within administrative boundaries of the provincial capital city of Kielce, in the vicinity of housing estates (Table 1; Fig. 3).

Changes in the PAH profiles were reflected by the calculated PAH individual ratios. Of several ratios applied for the identification of PAH sources, the Flu/Flu+Py, BaA/BaA+Chr, and IcdP/IcdP+BghiP seem to be the most suitable due to their relative stability in the environment. As shown in Fig. 5, the average BaA/BaA+Chr ratio of 1996 lichens was about 0.21 and had not changed until 2000 (~0.20). In all the samples collected in 2000 (lichens, bark, mosses), the average values were also close to 0.20. An interesting change was observed for mosses during 2000–2008 when this ratio increased to 0.48. This change indicates a higher contribution of hydrocarbons from vehicular emissions (phenanthrene, fluoranthene, and pyrene). The decrease in the Flu/Flu+Py and Ind/Ind+BghiPe ratios, observed mainly in mosses, also points to a higher contribution of compounds derived from combustion of liquid fossil fuels (Tobiszewski and Namieśnik 2012).

Interesting information about the PAH sources was also provided by a comparison of the same two moss species (*H. splendens* and *P. schreberi*), collected in the same year (2007), but from two remote areas—the HCM region (Poland) and two national parks in Alaska (USA) (Migaszewski et al. 2009). Alaskan mosses had much higher concentrations of 3-ring hydrocarbons (more that 60% of total PAHs) than their Polish equivalents (Fig. 4). The computed 3+4-ring/total PAH ratio was about 0.91, which clearly pointed to wood combustion sources in Alaska. However, the Flu/Flu+Py and BaA/BaA+Chr ratios indicated the mixed petrogenic and pyrogenic origin of hydrocarbons, such as wood combustion and oil and coal products (Yunker et al. 2002). In Polish mosses, the 3+4-ring/total PAH ratio changed over the years from 0.57 to 0.80, confirming the predominance of coal combustion sources, but also a noticeable shift toward other PAH sources connected with combustion of liquid fuels (Schauer et al. 2001). At that time, similar sources

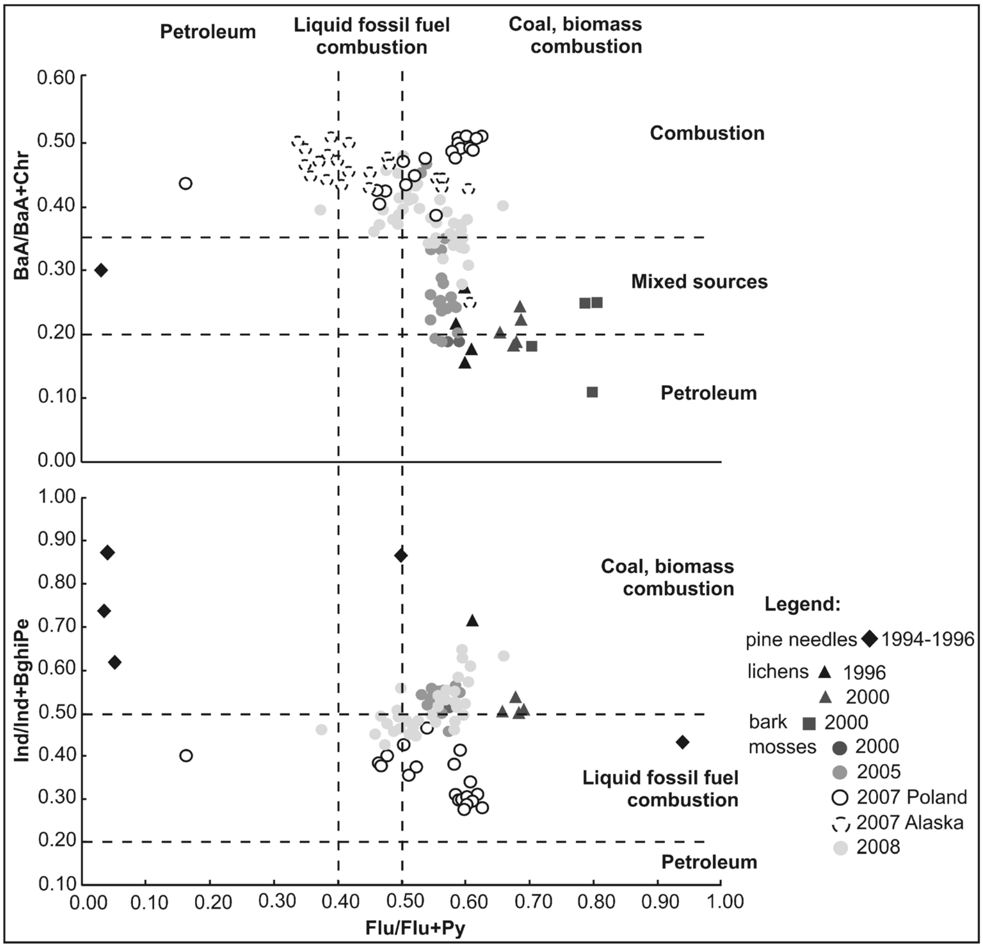

Fig. 5 Variations of selected PAH ratios in bioindicators from the HCM (data from Dołęgowska and Migaszewski 2011; Gałuszka 2007; Migaszewski 1999; Migaszewski et al. 1996, 2002, 2009)

of PAHs were identified in other European countries, including Italy (Gerdol et al. 2002), Hungary (Ötvös et al. 2004), or Czech Republic (Holoubek et al. 2000).

Considering this, the biomonitoring studies of organic compounds from the HCM showed that plants can be successfully used for identification of pollution sources and for tracking changes in the contribution of individual sources to the total pollution budget over the years. However, the selection of appropriate bioindicators showing different bioaccumulative capabilities and the knowledge on the interspecies differences are the most important issues, which should be taken into account, especially in comparative, interregional studies. Among several plants used, mosses and lichens seem to be the best bioindicators of organics, including PAHs. Their morphological structure favors the accumulation of gaseous pollutants and those connected with particulate matter.

Major, trace, and rare earth elements in plant bioindicators of the Holy Cross Mountains

Plants have been successfully used as bioindicators of trace and major elements since the 1960s (Rühling and Tyler 1968, 1973). Many species including trees, mosses, and lichens have become popular in air quality biomonitoring due to several technical and economic aspects (Dołęgowska and Migaszewski 2015). They are widespread, which gives possibility to conduct studies on a large scale, and moreover accumulate pollutants in quantities that allow them to be determined by different analytical techniques (Pasławski and Migaszewski 2006).

The first biomonitoring studies of major and trace elements in the HCM were carried out between 1994 and 1996 (Table 1; Fig. 3). The scope of the study included the chemical analysis of different plants and parts of plants widely used in biomonitoring studies, like (i) *H. physodes* lichen thalli growing on deciduous and coniferous trees; (ii) *H. splendens*, *P. schreberi*, and *Hypnum cupressiforme* Hedw. moss species; (iii) Scots pine needles of different age classes; and (iv) bark of different trees (Scots pine (*P. sylvestris*), birch (*B. pendula*), larch (*Larix decidua* Mill.), aspen (*Populus tremula* L.), and rowan (*Sorbus aucuparia* L.)). This research was continued until 2002 and included analysis of different tissues of single Scots pine tree (bark, wood, shoots, needles) (Gałuszka 2003, 2005). This was a part of a large bioindication study that covered 3 national parks of Poland:

HCMNP (north-central part of the region), Magurski Natl. Park (SE Poland), and Wigierski Natl. Park (N Poland) of different anthropogenic impacts (Fig. 3). Aside from trace element determinations in *H. physodes* lichen thalli, 1- and 2-year old Scots pine needles and bark, and topsoil, SEM-EDS microanalysis of airborne particulates was initiated (Migaszewski et al. 2004, 2006). This technique was applied in subsequent studies and became one of the complementary microanalytical techniques used worldwide in biomonitoring of air pollution by particulate matter (Table 1) (Aboal et al. 2011; Di Palma et al. 2017; Spagnuolo et al. 2013). Of the plant bioindicators, the pine needles turned out to be the best natural traps of particulate deposition, fingerprinting geogenic, and anthropogenic pollution sources.

Over a period of 8 years, 151 pine needles, 78 lichens, 86 tree barks, 15 mosses, and 11 wood samples were collected in two areas: the HCMNP and the vicinity of Kielce city (southern, central, and north-eastern parts of the region) (Fig. 3). Samples were analyzed for major (Al, Ca, K, Mg, Na, P, S), trace (As, Ba, Cd, Cr, Cu, Fe, Hg, Li, Mn, Ni, Pb, Sr, Ti, V, Zn), and rare earth (La, Yb + Y) elements. The results were used to assess a possible impact of local and off-regional industrial facilities on the environment and to compare bioaccumulative properties of several species.

The broad-based studies showed that the comparison and interpretation of results derived from chemical analysis of different bioindicators can be challenging because of diverse individual plant responses. Despite these difficulties, the use of different plants is the only way to know and identify the interspecies differences. The results of studies conducted during 1994–2002 showed that lichens were the best bioindicators of most major and trace elements. Poikolainen (2004) also noted that lichens may accumulate trace elements more efficiently; however, other studies have shown that this is not a common rule (Kłos et al. 2018; Loppi and Bonini 2000). Lichen tolerance, especially to trace metal(loid)s, is closely linked to an active mechanism of detoxification and production of metal-binding peptides (Spagnuolo et al. 2011). The process of accumulation is also facilitated by the presence of metal chelating agents in lichen thallus (usnic and atranorin), that is, compounds that belong to lichen metabolites and show a number of biological activities (Studzińska-Sroka et al. 2017). Production of usnic and atranorin acids is affected by environmental factors, including temperature, humidity, and altitude, hence higher concentrations of metals in samples from remote, but elevated regions. Lichens collected from the highest parts of the HCMNP also had the highest concentrations of most elements examined, which can be explained not only by the abovementioned relationship but also by local environmental factors (e.g., exposure to sunlight, topsoil chemistry, precipitation) and by exposure to airborne pollution transport (Migaszewski 1998, 1999; Migaszewski and Pasławski 1996; Migaszewski et al. 1996, 2004). It is noteworthy that this relationship was later found in lichens collected from other European mountainous areas, within an altitude range of 200 to 1300 m (Doucet and Carignan 2001), and from the high-altitude Tibetan Plateau (3000–7000 m a.s.l.) (Shao et al. 2016).

The use of lichens as bioindicators of air quality is possible because these organisms take up substances directly from the atmosphere and the exchange of elements between lichen and its substratum (bark) is inhibited. However, higher natural concentrations of elements in bark of deciduous trees compared to bark of coniferous trees corresponded to their higher concentrations in lichens growing on these trees. The comparison of *H. physodes* lichen thalli collected from selected deciduous (rowan, oak, aspen, birch) and coniferous (pine, fir, larch) trees during 1994–2002 (Table 1) showed that lichens growing on coniferous trees had lower concentrations of most elements determined, excluding Al, Cu, Fe, and Hg. In the case of lichens growing on pine and birch trees, differences in Pb and Mn concentrations reached even up to 70% (Fig. 6a).

It is noteworthy that the diversity in element composition of lichens was observed between samples from the same group of trees (coniferous and deciduous) and between samples from the same tree species (Scots pine). In coniferous trees, statistically significant differences ($p < 0.05$) were found for Al, Ba, Cd, Mn, and Pb, whereas in deciduous trees for Al, Ba, Cu, Mn, and Pb. Lichens from Scots pine showed a significant difference for Ba, Ca, and Cr, but only in some places. Among lichens growing on deciduous trees, those from oak revealed the highest contents of most elements. This is not surprising, considering that the oak bark was also enriched in most elements compared to the bark of other tree species. Chemical analysis of lichens collected from Scots pine trees several meters apart showed that differences in element composition of lichens increased with a distance between the trees. This also indicates that accumulation and translocation of elements from substrate to lichen thalli depend on several environmental and biological factors, including different topographies of tree locations, and morphological and physiological features of lichen species. Going further, the comparison of chemical composition of bark and accompanying lichen thalli showed that, regardless of tree species, bark had always higher concentrations of Ba, Ca, and Pb relative to lichen. These results were consistent with those obtained by De Bruin and Hackenitz (1986), but the review of the literature revealed differences in the reported data. For example, Lippo et al. (1995) noted higher concentrations of Al, Cu, and Fe in *H. physodes* thalli than in pine bark, while Loppi et al. (1997) found lower concentrations of the same metals in *Parmelia caperata* L. thalli in comparison to oak bark (Loppi et al. 1997). Moreover, the characteristic enrichment in Ba of samples from the HCM was not observed in the bark samples collected from the two other Polish national parks mentioned above. The only explanation seems to be the

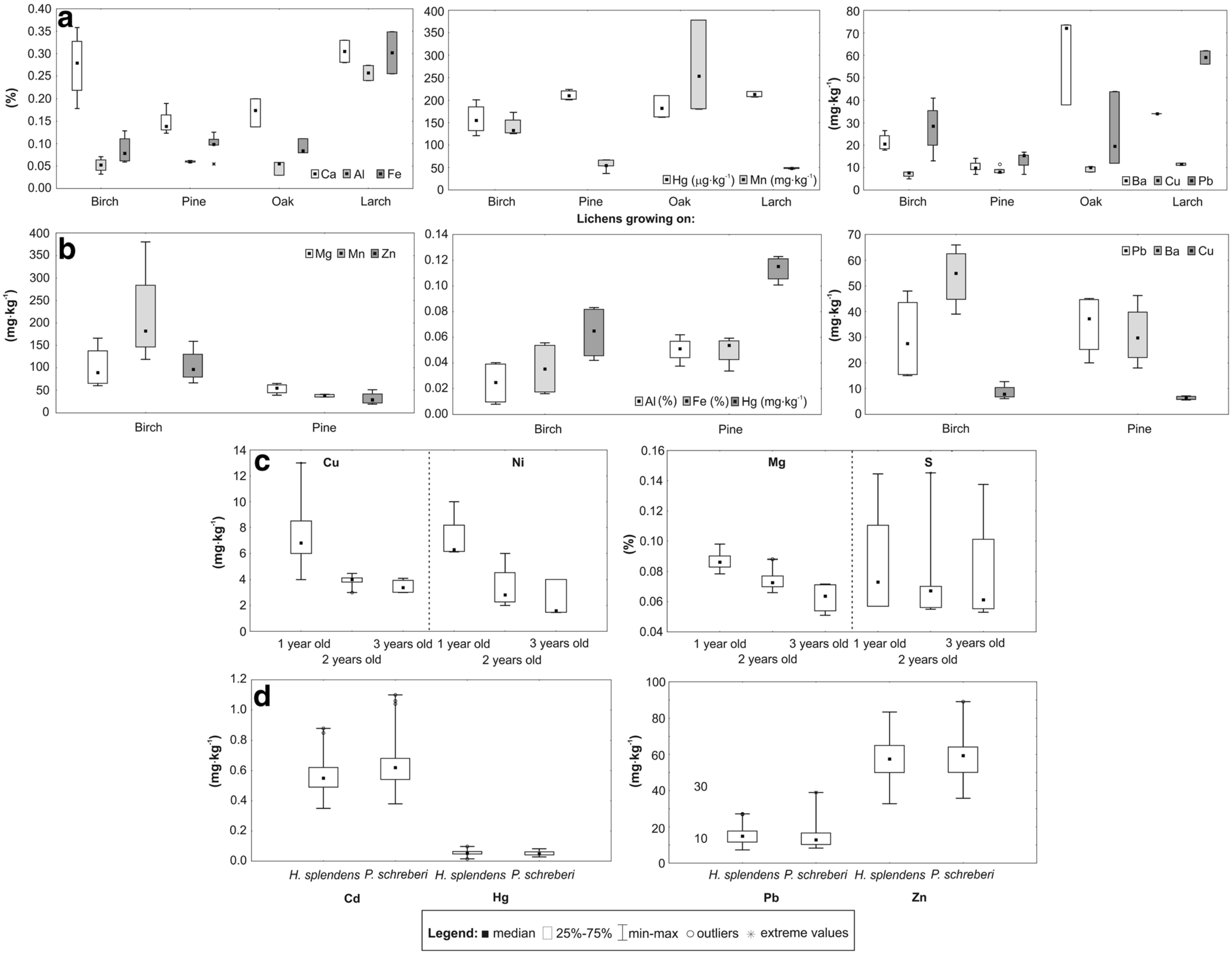

Fig. 6 Concentrations of selected elements in **a** lichens growing on different trees, **b** bark of deciduous and coniferous trees, **c** Scots pine needles of different age classes, **d** *H. splendens* and *P. schreberi* moss species (data from Dołęgowska et al. 2013; Gałuszka 2005, 2007; Migaszewski 1998; Migaszewski and Pasławski 1996; Migaszewski et al. 2001, 2004, 2009)

presence of barite mineralization in local limestones (Migaszewski et al. 2004).

Different chemistry of lichens and bark may result from several factors including diverse accumulation processes. Tree bark, as a dead tissue, accumulates pollutants in a passive way. This is rich in waxy substances that protect it from water loss and reduce element translocation into wood, but also make deposited particulates and adsorbed pollutants easy to remove by stemflow or downward running water (Poikolainen 2004). Both in lichens and mosses, a mechanism of accumulation depends on the presence of chelating acids or ion exchange sites which bind metals in the cell walls and plasma membrane or inside the cells (Hájek et al. 2014).

The process of accumulation in bark depends also on its surface structure. In general, the porous tree bark accumulates pollutants more efficiently than the smooth one. The first mention of differences in chemical composition of deciduous and coniferous tree bark appeared in 1978 (Rasmussen 1978). Results of 1995–2002 studies of bark derived from different trees (birch, oak, aspen, Scots pine, larch) confirmed that the bark of deciduous trees was significantly enriched in elements, like Mg, K, P, Zn, and Cu, but also Mn and Ni, as opposed to the bark of coniferous trees. The comparison of birch and pine bark collected during four of five sampling campaigns (1995, 1996, 1998, 2000) (Table 1) revealed that the birch bark preferred K, Mg, P, Cu, Mn, Zn, and B, whereas the Scots pine took up more Al, Cd, Cr, Fe, and Hg (Fig. 6b; Gałuszka 2003, 2005; Migaszewski 1998; Migaszewski and Pasławski 1996; Migaszewski et al. 2001, 2002). It is noteworthy that, regardless of the sampling time and site, the pine bark had the highest concentrations of Hg (Fig. 6b). The chemical analyses of bark of deciduous (*Platanus orientalis* L.) and coniferous (*Pinus nigra* Arn.) trees collected in three European cities showed that the rough bark of *P. nigra* had better accumulative properties than the plane bark of *P. orientalis*. Like in the HCM studies, the pine bark displayed higher contents of Cr, whereas the platanus bark was abundant in Cu (Sawidis et al. 2011).

Differences in the chemical composition of different types of tree bark resulted not only from the structure but also from the composition of phellem and thickness of outer and inner bark layers. In bark, accumulation takes place on the surface of dead bark cells. Passive and active translocation inside the wood is limited; however, it depends on the size of particulates and the chemical element species. The first studies of outer and inner bark, wood, and roots of Scots pine trees were conducted in the HCM in 1998 showing variability in chemistry of samples collected from different sites (unpublished data). There was no clear relationship between the type of tissue and the element content. Higher element concentrations were noted in inner bark in relation to its outer part, but only in some cases, which was probably connected with the influence of stemflow. Further analysis of bark and outer and inner wood as well as 1-year shoots, roots, and needles of individual Scots pine tree showed that higher Hg and Pb contents in bark and roots did not correspond to higher contents of these elements in other tissues (Gałuszka 2005; Migaszewski et al. 2002). This indicates that a transfer of non-essential elements is inhibited (Walkenhorst et al. 1993).

In 1-year shoots, concentrations of toxic elements, like Cd and Pb, were below the limit of quantification (Cd and Pb < 0.5 mg kg^{-1}), whereas the Hg contents were at the same level as in outer and inner wood (~ 7 μg kg^{-1}). Both S and Zn showed an opposite trend; 1-year shoots (S 0.094%, Zn 51 mg kg^{-1}) had much higher concentrations than outer (0.010%, 18 mg kg^{-1}) and inner (0.011%, 13 mg kg^{-1}) wood, but similar to those found in bark (0.064%, 75 mg kg^{-1}) and in 1-year pine needles (0.110%, 48 mg kg^{-1}) (Gałuszka 2001; Migaszewski et al. 2002). This suggests that essential elements are actively accumulated in the youngest tissues, whereas the passive accumulation takes place in the outermost dead tissues. In most cases, needles had the highest sulfur content of all the pine tissues; however, it depended on the pine needle age class (Manninen and Huttunen 2011). In the HCM, biomonitoring studies of air quality with pine needles began in 1994 (Table 1). During the first sampling campaign, 1- and 2-year-old pine needles were collected from fourteen sites located in different parts of the region (Fig. 3). The studies were continued in 1995, 1996, 1998, 2000, and 2002. The results showed a relationship between the age classes of pine needles and their chemical composition, but only concentrations of some elements increased with needle age. In all cases, older pine needles were depleted in Cu, K, Mg, and P and in some cases also for Ni and S (Fig. 6c). Higher concentrations of these elements in the youngest needles (1 year old) pointed to their intensive accumulation during their rapid growth. According to the literature, Cu plays a major role in plant metabolism that is why the youngest tissues, including young needles, may accumulate this metal more intensively (Price et al. 1972). Ni is also known as a plant micronutrient with many biological functions. For example, it induces a growth of shoots and its deficiency in young tissues may cause chlorosis (Ahmad and Ashraf 2011; Cindrić et al. 2018). Needle samples collected along a 350-km-long transect, from the Kola Peninsula to the Finnish-Swedish border, showed the same age-related correlation for Cu and Ni (Rautio and Huttunen 2003), whereas 1- and 2-year-old needles from the Słupsk City (Poland) had comparable concentrations of these two metals (Parzych and Jonczak 2014). This means that the lack of correlation may result from the fact that samples were taken in residential and industrial areas directly exposed to urban pollution. As mentioned before, older needles had higher concentrations of most elements, like Ba, Fe, Hg, Mn, Sr, and Zn (Gałuszka 2005; Migaszewski 1998; Migaszewski and Pasławski 1996; Migaszewski et al. 1996, 2001, 2004). These elements are not so active in biogeochemical processes as K or Cu; therefore, they undergo accumulation in older pine needles (Gałuszka 2005). The enrichment in Ba, observed in almost all needle and bark samples, is probably connected with the specificity of the sampling area. Studies by Cindrić et al. (2018) showed that different pine species from the same region can accumulate diverse amounts of this metal, and there are no similarities between the species.

After 2002, biomonitoring studies in the HCM focused on the analysis of two commonly used moss species, namely *P. schreberi* and *H. splendens* (Table 1). Mosses were analyzed for major, trace, and rare earth elements (REEs) that were applied to assess their bioaccumulative properties and to identify pollution sources. Some studies also addressed methodological issues (Table 1). The environmental factors that may affect chemical composition of mosses are the same as for lichens. Mosses belong to lower, non-vascular plants without roots and protective layers. Accumulation in these organisms is enhanced by the high surface to volume ratio and high cation exchange capacity (Zechmeister et al. 2003). In the HCM, the first moss species (*P. schreberi*, *H. splendens*, and *H. cupressiforme*) were collected in 1994, but a larger-scale survey began in 2005 (Gałuszka 2007). In 1994, the authors did not find a relationship between the species and the element contents. Somewhat higher concentrations were noted in *H. cupressiforme*, but the number of samples was too small to draw clear conclusions. Interestingly, in contrast to *H. physodes* thalli, moss tissues revealed higher concentrations of Al, Ca, K, Mg, and P.

Analysis of twenty samples of *H. splendens* and *P. schreberi*, collected from the same sampling sites, in the northern part of the HCM in 2005, showed that each species tends to accumulate different elements. In general, *H. splendens* was enriched in most of the elements examined, but statistically significant differences ($p < 0.05$) were obtained only for As. Higher concentrations of Cd, Ca, K, and S were recorded in *P. schreberi* (Gałuszka 2007). The subsequent comparative study from the HCM and Alaska (Wrangell-Saint Elias National Park and Preserve and Denali National Park and Preserve) showed that in the HCM anthropogenic airborne particulates supplied most of trace metal(-loid)s, whereas in Alaska geogenic sources of metal(loid)s played a more significant role (Migaszewski et al. 2009). The study by Dołęgowska et al. (2013) confirmed a better capability of *P. schreberi* to accumulate Cd, but also Mn, Sr, and Zn (Fig. 6d). This ability was not observed for other toxic elements, like Pb or Hg, for which both species showed similar bioaccumulative properties. The ability of *P. schreberi* species to Cd and Zn accumulation was also noted by other authors (Berg and Steinnes 1997; Halleraker et al. 1998) but this is not a rule (Reimann et al. 2001).

An interesting part of biomonitoring studies conducted in the HCM has been connected with the determination of REE. This group includes lanthanides (La to Lu), and according to IUPAC (International Union of Pure and Applied Chemistry) also Y and Sc. These elements are mainly of geogenic origin and can be used as environmental tracers (Agnan et al. 2014). Some of them (La, Yb) were determined in plant samples collected during 1994–1996, but no significant relationships were found. For the first time, the REEs were determined in mosses collected in the vicinity of Kielce in 2008 and subsequently in 2011 (Dołęgowska and Migaszewski 2013; Dołęgowska et al. 2013). As expected, the highest concentrations were obtained for La and Ce, which have the highest natural concentrations among the REE (La 0.490, 0.789 mg kg^{-1}; Ce 0.930, 1.54 mg kg^{-1} in 2008 and 2011, respectively). The NASC-normalized REE concentration patterns displayed a positive Eu anomaly (Eu/Eu_{NASC} 1.2), which suggested the dominance of Eu^{3+} over Eu^{2+} (Dołęgowska and Migaszewski 2013; Ding et al., 2006). The comparison of shale-normalized patterns of mosses and soil subhorizons Ofh or mixed humic-eluvial horizon (AE) showed an interesting relationship. The deeper soil horizon AE had a negative Eu anomaly (0.8) that disappeared in the overlying subhorizon Ofh, and then turned into a positive anomaly in mosses (1.2) (Dołęgowska and Migaszewski 2013). A similar relationship was also observed by Krzciuk and Gałuszka (2019) who determined REE in shoots and roots of *Juncus effusus* L. collected from natural habitats of the HCM. These authors found a slightly negative Eu anomaly in some roots (0.8–1.1) and a strong positive Eu anomaly in all shoots (1.4–20.6). The presence of positive Eu anomaly in vegetation is known from other sites, but the explanation of its origin is not so obvious. Several hypotheses were proposed, including substitution of Ca by Eu due to the similar ionic radii (Brioschi et al. 2013), precipitation of Eu in the presence of phosphates in plant organs (Ding et al. 2006), or reduction of trivalent to divalent ions (Censi et al. 2014). The study of Krzciuk and Gałuszka (2020) from the HCM gave another explanation on the origin of Eu anomaly connecting it with the light-dependent fluctuations of the redox potential in the rhizosphere of *J. effusus*. This may indicate why the Eu anomaly is not so common in plants even in the presence of Eu^{3+} ion reduction. In non-vascular plants, which have no roots and take up elements mainly from the atmosphere, the observed fractionation of Eu is probably linked to changes in redox conditions of topsoil containing REE-bearing particulates derived from dry deposition.

Scientific projects carried out in the years 1994–2008 were related mainly to air quality biomonitoring, but chemical analysis of different plants collected during subsequent sampling campaigns (Table 1) covered also other environmental aspects, including the (i) negative effects of road de-icers on roadside vegetation (Gałuszka et al. 2011), (ii) influence of acid mine drainage (AMD) on plant chemistry (Gałuszka et al. 2020), and (iii) as it was mentioned above, accumulation and translocation of REEs in *J. effusus* (Krzciuk and Gałuszka 2019, 2020). The chemical analysis of bark and leaves of four roadside trees: ash (*Fraxinus excelsior* L.), linden (*Tilia cordata* Mill. and *Tilia platyphyllos* Scop.), Scots pine (*P. sylvestris*), and maple (*Acer pseudoplatanus* L.), collected in Kielce in June 2009, showed that changes in soil salinity connected with employing chloride de-icers, such as NaCl, $MgCl_2$, and $CaCl_2$, may disturb a plant growth and development. The use of chloride de-icers increased soil alkalinity and reduced bioavailability of Zn, P, Mn, Cu, and Fe. In addition, these chlorides increased bioavailability of B, which resulted in higher concentrations of this element in leaves. The computed K/Na and Ca/Na ratios were the lowest at these sites where trees showed the most negative symptoms. They varied from 2 to 5 and from 10 to 50, whereas for control site trees were in the range of 5–50 and 75–450, respectively. Interestingly, the bark of roadside trees, similar to that of forest trees, was enriched in Ca and Fe, whereas leaves, like young needles, were abundant in K, Mg, P, and S (Gałuszka et al. 2011).

Biogeochemical studies of several aboveground plant samples collected within an AMD area in 2016 and 2017 aimed at the evaluation of the local spatial variability in trace element contents and stable sulfur isotope ratios, and to select the most suitable species for revegetation of degraded areas (Gałuszka et al. 2020). The study confirmed an impact of AMD waters on plants as evidenced by higher concentrations of As (data for mosses: AMD area 12.4 mg kg^{-1} vs. HCM < 1 mg kg^{-1}), Co (1.45 mg kg^{-1} vs. 0.16 mg kg^{-1}), Cr (67.5 mg kg^{-1} vs. 0.9 mg kg^{-1}), and Ni (31.1 mg kg^{-1} vs. 0.8 mg kg^{-1}) and characteristic patterns of REEs (Gałuszka et al. 2020; Migaszewski et al. 2009). The vascular plants showed a positive Eu anomaly, which in case of mosses was distorted by an influence of AMD waters. The concentrations of other elements, including REEs, were from 8 to 26 times higher in mosses than in other plants (Gałuszka et al. 2020). However, this issue needs more detailed investigation. The major shortcoming of the study was the lack of microscopic investigation.

Identification of solid particles deposited on the moss surface that may not have been removed during washing may explain such high concentrations of REE in these samples.

Nowadays, the main source of most trace elements in the HCM region is the combustion of fossil fuels (bituminous coal) and road traffic. This pattern has changed since the 1990s when emissions from steelworks made up a significant contribution to the pollution budget. Restructuring of Poland's heavy industry that has begun since 1989 was mirrored in changes of concentration profiles of selected trace elements, especially during 1994–1998 (Fig. 7). It should be stressed that there is no characteristic trend of changes, which could

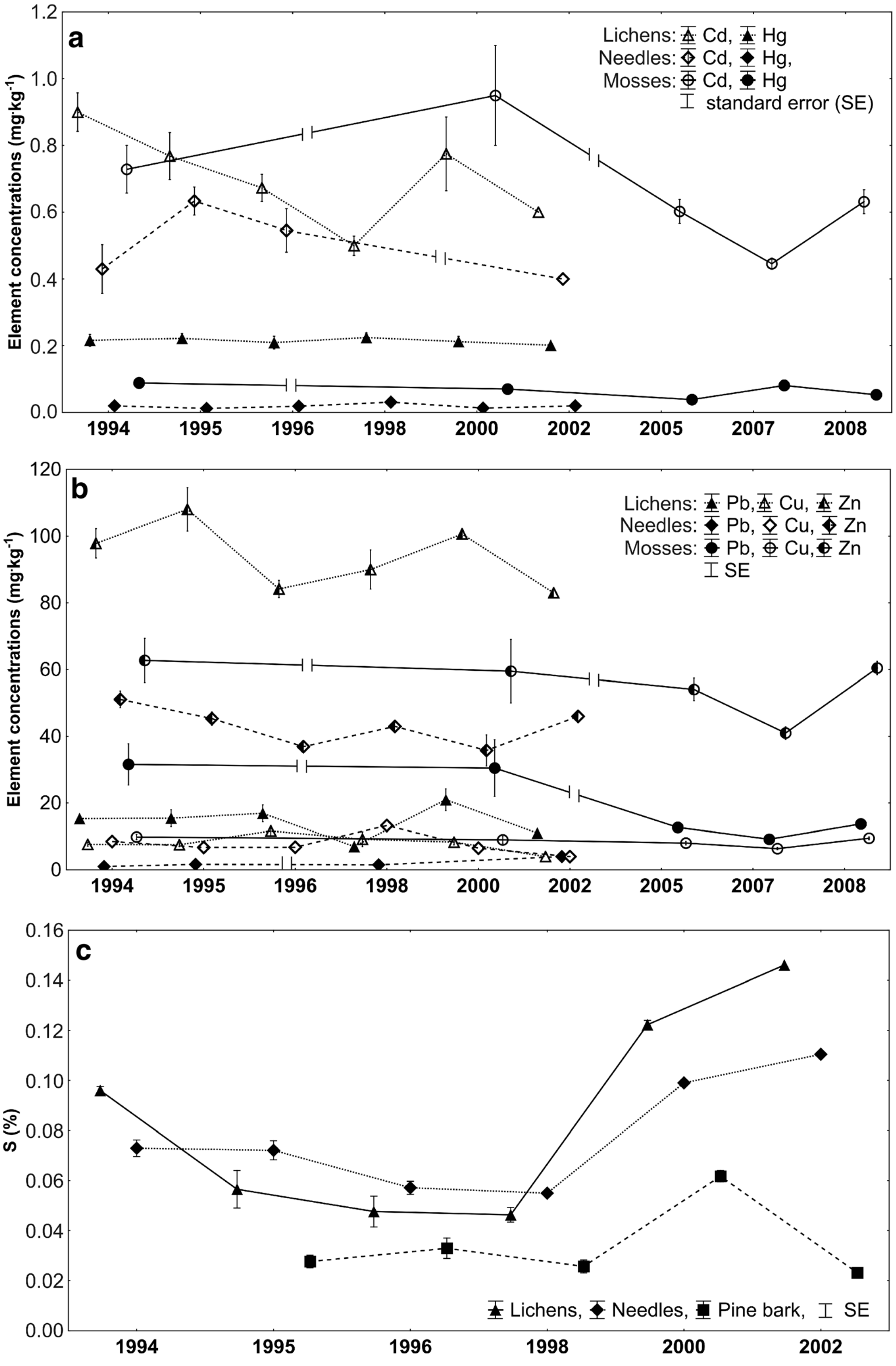

Fig. 7 Temporal variability in concentrations of selected elements (**a** – Cd, Hg; **b** – Pb, Cu, Zn; **c** – S) in: lichens growing on pine trees, 1-year Scots pine needles, Scots pine bark, and *P. schreberi* moss species (data from Dołęgowska et al. 2013; Gałuszka 2005, 2007; Migaszewski 1998; Migaszewski and Pasławski 1996; Migaszewski et al. 2001, 2004, 2009)

be explained by different sampling locations and different bioindicators used. A decrease in Cd contents between 1994 and 1998 was observed in lichens collected from Scots pine trees, and also in 1995–1998 pine needles. However, in the case of other elements (Hg, Zn) this relationship is not so clear (Fig. 7a, b). For example, Zn contents in both lichens and needles decreased during 1994–1996 and then increased again in 1998. It is noteworthy that a somewhat decrease in Hg, Pb, Zn, and Cu contents can be observed in *P. schreberi* moss samples collected during 1994–2007, but the lack of data for the years 1995–1998 makes it difficult to interpret changes over time. Re-increase in the concentrations of Cd, Pb, and Zn in 2008 in comparison to 2007 may be explained by the fact that in 2008 samples were collected mostly within the administrative boundaries of Kielce, while in 2007 sampling sites were located in a relatively pristine forests. Higher concentrations of Cd and Hg in 2000 lichens in comparison to the previous years (Fig. 7a) may be caused by a small number of samples taken in 2000, or by increased combustion of coal resulting from the cold 1999/2000 winter. The same relationship is observed for sulfur. A gradual decrease in its content in the years 1994–1998 in lichens and pine needles was caused by lower coal combustion and reduction of SO_2 emissions, but a significant growth recorded in 2000 and 2002 could be linked to the cold winters, and an increased use of coal by heating plants and detached houses (Fig. 7c). A relatively high concentration of Pb (~ 10 to 20 mg kg^{-1}), higher than in Europe (3.7 mg kg^{-1}) (Harmens et al. 2015), and in the other parts of Poland (6.5–8.2 mg kg^{-1}) (Kłos et al. 2018), resulted from a geochemical anomaly of this element and its presence in Upper Paleozoic and Lower Triassic rocks in the form of galena (PbS).

Stable sulfur isotopes in plant bioindicators of the Holy Cross Mountains

The use of stable sulfur isotopes in bioindication studies dates back to the 1970s when pioneering works of Krouse (1977) and Winner et al. (1978) confirmed an impact of air pollution on the δ^{34}S values in plants. The first complex studies on stable sulfur isotopes in different plant bioindicators (*H. physodes* thalli, terrestrial moss species, tree bark, pine needles) in the HCM were conducted in the 1990s (Migaszewski 1998; Migaszewski and Pasławski 1996). Since that time, stable sulfur isotopes have been determined in this area in plant bioindicator samples collected from the forest ecosystems (Gałuszka 2001, 2005; Migaszewski et al. 2010a). The study conducted by Gałuszka et al. (2020) in an AMD-impacted area unexpectedly showed the low δ^{34}S values in plant samples. The δ^{34}S ranges of plant bioindicators studied in the HCM versus the δ^{34}S values in terrestrial plants (Finlay and Kendall 2007) and local precipitation (Michalik and Migaszewski 2012) are summarized in Fig. 8.

Forest tree bark, Scot pine needles, moss gametophytes, and lichen *H. physodes* thalli were used as bioindicators in the forest ecosystems of the HCM (Gałuszka 2001, 2005; Migaszewski 1998; Migaszewski and Pasławski 1996; Migaszewski et al. 2004, 2010a). The δ^{34}S values varied from 1.1 to 10.5‰ and did not show any significant relationship with sulfur content in the samples examined. Stable isotope sulfur ratios in plant organs may change in a wide range of δ^{34}S values. As shown by Gałuszka (2001), various samples collected from a single Scots pine tree in Wymysłów (central HCM) differed in their δ^{34}S values by 6.3‰ (Fig. 9). Tree bark and *H. physodes* exhibited similar S isotope ratios in the HCM regardless of the tree species, usually in the range of 2.0 to 4.0‰ (Gałuszka 2001, 2005; Migaszewski 1998). Compared to lichens and pine bark, pine needles were enriched in ^{34}S. Moreover, the young Scots pine needles were typically enriched in ^{34}S isotope, regardless of the type of habitat; for example, the 1996-age class needles displayed the δ^{34}S values in the range of 2.5 to 7.2‰, with a mean of 4.4‰ ($n = 21$), whereas the 1995- and 1994-age class needles showed the similar δ^{34}S values: from 1.3 to 6.2‰ (mean of 3.3‰) and from 1.1 to 5.9‰ (mean of 3.2‰), respectively. This diversity may be induced by removal of an excessive amount of sulfur through stomata in the form of isotopically lighter H_2S (Migaszewski 1998), thus confirming upshots obtained by Case and Krouse (1980). Another option, namely, remobilization of sulfur from older pine needles and twigs combined with isotope fractionation, is difficult to prove.

In contrast to forest trees and lichens, terrestrial moss samples showed a broader range of δ^{34}S values (2.7 to 10.5‰) (Gałuszka 2005; Migaszewski 1998; Migaszewski et al. 2010). It is interesting to compare the results of stable sulfur isotope measurements in the moss species *H. splendens* and *P. schreberi* performed in different years. Results obtained in the late 1990s showed the lower δ^{34}S values (2.7 to 4.2‰) than in the 2000s (4.4 to 6.9‰ (Gałuszka 2005); 3.7 to 10.5‰ (Migaszewski et al. 2010)). This trend may be explained by decreased emissions of isotopically lighter sulfur from industrial sources to the atmosphere. The lack of such trend in forest trees is caused by a delay in response of vascular plants to reduced atmospheric emissions. Mosses take up sulfur from precipitation, whereas vascular plants mostly from soils. Thus, a reaction of moss to lower S emissions is expected to be faster than that of vascular plants.

All plant bioindicators collected in forests of the HCM in the years 1998–2010 had positive δ^{34}S values. In contrast, the most recent study conducted in a mining area impacted by acid mine drainage (Gałuszka et al. 2020) showed that all plant samples had negative δ^{34}S values (Fig. 8). In this study, seventeen samples of plants (vascular plants, fern, and moss species) were collected from an area near the tailings pile

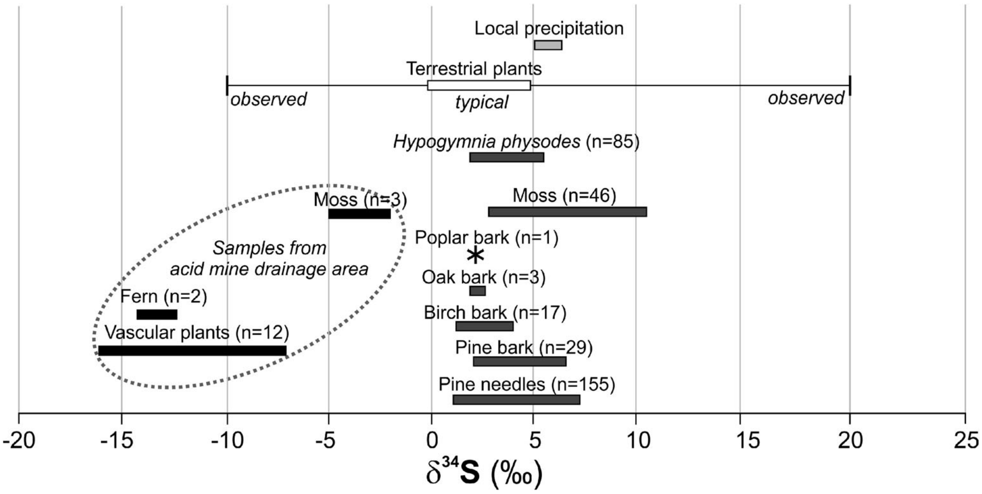

Fig. 8 The δ^{34}S ranges in plant bioindicators from the Holy Cross Mountains versus the δ^{34}S values in terrestrial plants (Finlay and Kendall, 2007) and local precipitation (Michalik and Migaszewski, 2012)

seeps. Weathering of pyrite (FeS_2), which is an abundant mineral in the study area, causes acidification and pollution of mining water with SO_4^{2-}. Because local pyrite is strongly enriched in ^{32}S (δ^{34}S from − 41.4 to − 23.6‰), these negative δ^{34}S values are also recorded in AMD waters (Migaszewski and Gałuszka 2019; Migaszewski et al. 2018) and plants

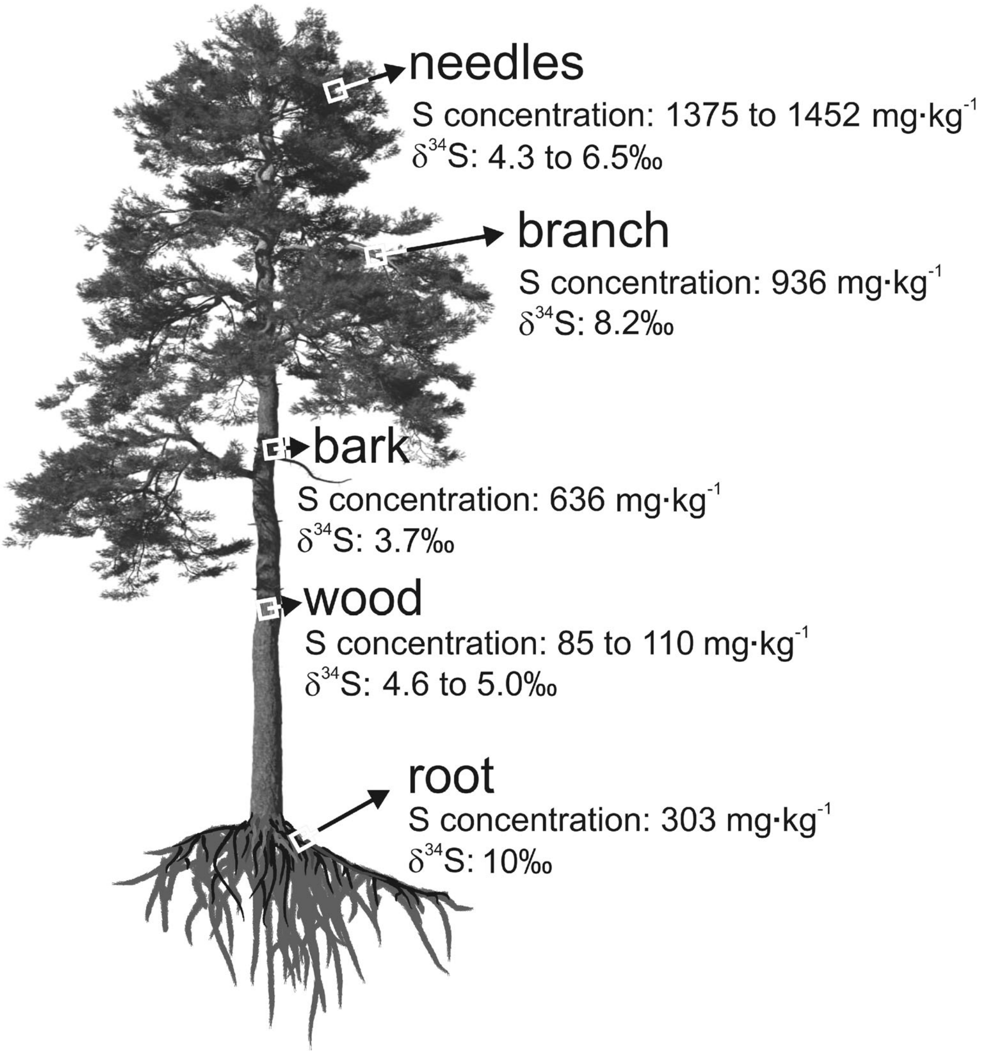

Fig. 9 Concentrations of sulfur and δ^{34}S values in different samples from a single Scots pine (*P. sylvestris*) tree (data from Gałuszka, 2001)

(Gałuszka et al. 2020). The examined plant samples encompassed *P. sylvestris* needles. They contained 1370 mg/kg sulfur, which is a typical concentration in pine needles of the HCM, but its δ^{34}S value was − 7.1‰. Such low δ^{34}S value has not been recorded in pine needles in the HCM. Similarly, three moss species growing near the tailings pile seep (*P. schreberi*, *H. splendens*, and *Drepanocladus aduncus* (Hedw.) Warnst.) showed S concentrations in the range of 1100–1400 mg/kg, which are also typical for moss bioindicators in the HCM, but their isotopic composition showed a substantial enrichment in the light sulfur isotope (δ^{34}S from − 7.7 to − 2.0‰) compared to the moss species collected within forest areas of the HCM (δ^{34}S from + 2.7 to + 10.5‰) (Gałuszka 2005; Migaszewski 1998; Migaszewski et al. 2010). Unlike plant bioindicators from the HCM forest ecosystems, a statistically significant positive correlation ($R^2 = 0.87$) between the reciprocal S concentrations and the δ^{34}S values was observed in plants from the AMD area. For the first time, the negative δ^{34}S values were noted in plants from south-central Poland. These values diverge significantly from those of typical terrestrial plants which vary from 0 to + 5‰ (Fig. 8; Finlay and Kendall 2007).

The study of plant bioindicators in the HCM showed that stable sulfur isotopes are useful for tracing sources of sulfur taken up by plants. Two distinct sets of δ^{34}S values were recorded in plant bioindicators growing in the forest ecosystems (+ 1.1 to + 10.5‰) and in acid mine drainage area (− 16.1 to − 2.0‰). This knowledge is important for better understanding the spatial extent of acid mine drainage pollution.

Methodological issues

Among several methodological aspects that have been taken under consideration, the most important are related to the estimation of uncertainty arising from different steps of biomonitoring studies, like sampling, sample storage, and sample physical preparation (Table 2). The study was conducted in three forest areas (Fig. 3) during 2014–2017. For this purpose, combined and duplicate samples of *P. schreberi* moss species were collected from 27 sampling sites, and after storage in well-defined conditions and preparation, they were analyzed for selected trace elements (Cd, Co, Cu, Fe, Pb, Mn, Ni, Zn) and REEs. The results obtained were used to calculate the level of uncertainty from the time of sampling (Dołęgowska and Migaszewski 2020), sampling strategy (Dołęgowska 2016, 2017), and sample storage and preparation (Dołęgowska and Migaszewski 2019; Dołęgowska et al. 2017). The study showed that, even in the case of samples collected from the same sampling sites, located in natural forest habitats, using the same sampling protocol, the level of uncertainty from different stages of biomonitoring studies can be relatively high. The biggest contribution to the budget of uncertainty is usually linked to the sampling uncertainty which depends on the type of element, its natural concentrations, and diversity in the environment. As regards sample preservation and preparation uncertainties, the most important is the role of element and its affinity to the binding sites. Both these factors affect element accumulation in different fractions and its translocation (Vázquez et al. 2015).

Overall conclusions

Chemical analyses of abiotic media do not provide information on the bioavailability and a detrimental impact of pollutants on biota. Of different bioindicators, vascular and non-vascular plants and lichens enable a better understanding and assessment of the air and/or soil quality. In Europe, the most common moss species employed as bioindicators include *H. splendens*, *P. schreberi*, and *H. cupressiforme*, whereas lichen species include mostly *H. physodes*.

The compilation of results derived from 25-year studies in the HCM area with vascular and non-vascular plants showed the potential of biomonitoring in solving different environmental and methodological issues. It should be stressed that most studies performed in this region can be recognized as a pioneering work. These results from applications of (i) a wide spectrum of determined elements and organics, (ii) complementary analytical methods (geochemical, isotopic, mineralogical), and (iii) a variety of the examined media (plants, soils, rocks, waters). A broad scope of studies, and a variety of plants used, has been unprecedented for such a relatively small area. This research included classical biomonitoring of air quality and solving different issues like a response of plant bioindicators to variable pollution levels and an influence of environmental factors on plant chemistry. The use of plant bioindicators and soils, representing biotic and abiotic systems, provided a more holistic assessment of the quality of the environment.

Comparison of results derived from long-term biomonitoring has revealed how useful this method is in identifying pollution sources as well as in tracking variations of spatial and temporal distribution of elements and organics and stable sulfur isotope ratios over time. However, due to the presence of inter- and intra-species differences, a selection of a specific plant bioindicator was one of the most important issues, especially when it comes to interregional comparisons. A scope of studies also encompassed methodological aspects regarding the quality control assurance of individual biomonitoring steps. It was shown how crucial the precise definition and standardization of sampling, handling, and storage procedures are. However, even being consistent at each stage of environmental studies, it is impossible to eliminate uncertainties arising from environmental variables and individual features of plant species.

Another issue that requires a more detailed investigation, constituting a research perspective, is a study of plants growing under physiological stress conditions (e.g., from AMD areas). The study conducted by Gałuszka et al. (2020) displayed how unusual adaptations and defense mechanisms had been developed by plants living in heavily pollution-impacted areas, e.g., inhibition of toxic element uptake and detoxification of metal(loid)s in the aboveground parts of plant (Küpper and Andersen 2016). Chemical analysis of such plants provided data not only on the quality of the environment but also on the possibility to find naturally growing organisms (plant (hyper)accumulators) that could be used for revegetation of AMD or other post-mining areas.

Most of the studies in the HCM provided a regional framework and an interpretative scientific database for environmental agencies, mining companies, and land management agencies involved in evaluating anthropogenic vs. geogenic pollution sources, and geochemical landscape patterns and processes. An understanding of bedrock and soil origin, mineralogy, and geochemistry is critical to the assessment and interpretation of results derived from biogeochemical study. This holistic approach to the environment needs, in turn, employing a broad variety of instrumental methods. Only by combining all these components, we will be able to better evaluate the quality of the environment and its impact on biota and humans.

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Authors' contributions S.D. made substantial contributions to the conception and design of the manuscript. A. G and Z.M.M. were involved in drafting the manuscript and revising it critically for important intellectual content. All authors reviewed the final version of the manuscript.

Data availability Not applicable.

Compliance with ethical standards

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