

# The Use of Wetlands for the Monitoring of Non-Point Source Air Pollution

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## Abstract

The distribution of polycyclic aromatic hydrocarbons (PAHs) in plant and organic soil from 14 peatland sites in NE Poland and 7 peatland sites in SE Poland have been investigated. The total PAH concentration in the leaves of *Ledum palustre* collected from peatlands in NE Poland ranged from 232 ng/g to 1523 ng/g and was higher than the total PAH concentration in pine needles (*Pinus sylvestris*) taken from those same peatlands (the values ranged from 181 to 307 ng/g). A similar trend was observed in the case of plants from the peatlands in SE Poland, except that the overall PAH concentration in the majority of the plant samples was found to be higher than those found in NE Poland.

Phenanthrene and fluoranthene had the biggest share in the overall PAH concentration in all the peat and plant samples. The lack of 5- and 6-ringed PAHs in the plant and soil material indicates the lack of any direct emission sources of these compounds in regions adjacent to those examined in the study. Total sum of PAH pollution levels in peats and plants as well as vertical distribution of the concentrations in the soil profile of particular study sites integrates long-range pollution sources. To compare natural and anthropogenic PAH input in the peatlands, we have used parent PAH ratios: ANT/(ANT&PHE); FLT/(FLT&PYR). Our data suggest that PAHs with four and more rings do not allow a simple segregation into combustion or petroleum sources.

**Keywords:** PAHs, biological monitoring, air pollution, wetlands.

## Introduction

Over the last few years a series of studies has been conducted aimed at deepening and broadening our knowledge concerning the behavior of a group of compounds – commonly called persistent organic pollutants (POPs) – in the environment. Of the numerous compounds belonging to this group, polycyclic aromatic hydrocarbons (PAHs) have been included on the EU List of Priority Pollutants due to their negative (mutagenic, carcinogenic, and teratogenic) effect upon living organisms. The PAHs and some selected heavy metals belong to substances under-

going the regulations in a future, derived directive of the Council Directive 96/62/EC on Ambient Air Quality Assessment and Management. According to EU directives, the concentrations of PAHs in the air should be constantly monitored.

Polycyclic aromatic hydrocarbons (PAHs) are introduced into the terrestrial environment by both natural processes (e.g. forest fires, volcanoes) and anthropogenic sources (mainly through incomplete combustion of organic materials, such as coal, wood, oil or fossil fuels). In view of the overall contamination, the amount of PAHs in the environment originating from natural sources is minimal in comparison to the amount resulting from human activity. PAHs are byproducts created as part of various chemical processes. In essence, every process involving the extreme

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heating or incomplete combustion of organic compounds can lead to the emission of PAHs. The main sources of PAH emission involve the incomplete combustion of fossil fuels (coal and crude oil) and wood, as well as the burning and recycling of waste, activities which create dust and ash that become airborne. PAHs also originate in heavy industry – e.g. at coke processing plants, ironworks, and oil refineries – where coal and crude oil are processed. Vehicle fuel exhaust also plays a large role. PAH concentration in the air is dependent upon the distance from the source of emission, the current meteorological conditions and the time of year.

PAHs are highly volatile compounds. Adsorbed on dust particles created due to industrial production processes, they can travel significant distances. It is mainly the 2- and 3-ringed PAHs that travel as gasses during the gas phase, while those that have five or more rings travel as adsorbed non-volatile PAH compounds. The current phase of a given PAH is determined by its vapor pressure and the ambient temperature [1]. In order to determine regional and global pollution trends, vegetation samples are used to identify the sources of POPs. This is because it is relatively easy to obtain plant material, as opposed to using dosimeters for measuring contamination in the air. Conti and Cechetti maintain that “*bioaccumulators must have the same contaminant concentration level correlation as the surrounding environment at every site studied and under any condition. This must be true for all organisms examined*”. [2]

Material from various plant species such as lichens [3-7], mosses [8-13], tree leaves [14-16] and pine needles [17-25] have been used in biomonitoring studies concerned with measuring air pollution.

Of all the various types of vegetation, pine trees are probably one of the most often studied plants [26]. The pine (*Pinus sp.*) is the plant most often used in the biomonitoring of organic pollutants, due to:

1. Its common occurrence in various geographic zones;
2. The year-round availability of its needles;
3. The ease of determining the age of the needles and the resulting possibility of tracking the seasonal changes of the PAH concentrations in the air.

In temperate climates, evergreen plant species are chosen because they do not lose their leaves in the winter, which enables researchers to track changes in PAH emissions over time. This is the reason why conifers – (*Pinus sp.*, *Picea sp.*) – are the species most often chosen for study.

The mechanism by which the plants take up PAHs from the air, so that the compounds accumulate in their tissues, is dependent on several abiotic and biotic factors, including: vapor-particulate partitioning (which takes place in the atmosphere), ambient temperature, the octanol-air partitioning coefficients, leaf surface area and lipid concentration in plant tissues [27-29]. It is therefore reasonable to expect that plants present in the same area are going to accumulate various quantities of contaminant substances.

The results presented here follow from the study of PAH concentrations in pine needles and in the leaves of Dutch Myrthe (*Ledum palustre*) encountered in various peatland

ecosystems. The peatlands chosen for the study were located at a significant distance from direct sources of PAH emissions, so it would be possible to measure the impact of long-term atmospheric transport on pollution. We used comparative analysis of the PAH concentrations in two plant species and in the topsoil to determine which of the plant species studied is the better bioaccumulator and can be used to measure the PAH concentrations present in the air.

## Experimental Procedures

The plant and soil samples were collected from 14 peatland sites in NE Poland and 7 peatland sites in SE Poland in the period from June to August 2000. The investigated peatlands are predominantly covered by forests and meadows.

The NE region of Poland, described as the country’s “green lungs,” is in large part composed of areas unaltered by human activity (forests, peatlands and lakes). Industry has not been developed there and the population density is relatively low. A relatively insignificant portion of the region is covered by grassland and agricultural fields, cultivated predominantly by extensive farming methods. The majority of the peatlands studied is located within the buffer zones that surround the system of protected national forests (or “landscape parks,” as they can also be called), and some of the peatlands are protected nature reserves in themselves.

The peatlands studied in the SE of Poland are located within the Bieszczady National Park, at the foot of the Bieszczady Mountains, in the valley of the San River and its tributary, the Wołosatka. This region is very sparsely populated, with no large cities in the vicinity. One of the activities that the local population subsists on is the production of wood charcoal. The charcoal is burned at locations at the edge of the forest, outside the area of the National Park.

The localization of investigated peatlands is illustrated on the map in Fig. 1.

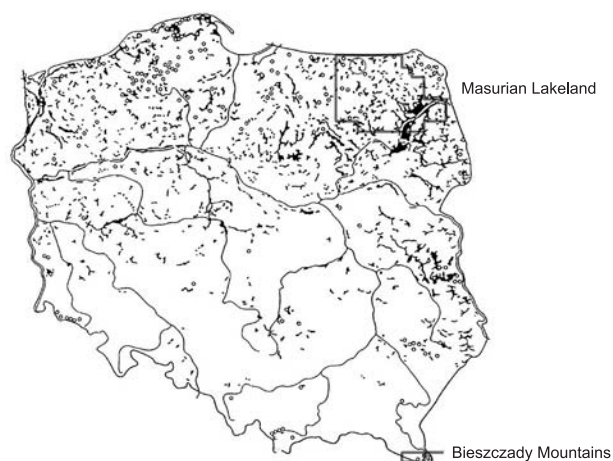


Fig. 1. The main peatlands in Poland and localization of sampling areas.

The species collected were *Pinus sylvestris* (13 needle samples) and *Ledum palustre* (19 leaf samples), in addition to 21 peat samples. *Ledum palustre* was not present at 3 of the sites studied, and *Pinus sylvestris* was not found at 6.

Peat samples were collected with the Instorf sampler (container length 50 cm) from different depths in the stratigraphic profile of each peat deposit. Peat cores were sectioned into the peat samples according to genus of peat.

The plant and soil samples were wrapped in aluminum foil and transported to the laboratory at ca. 4°C. They were stored at -20°C prior to being analyzed. The peat samples were dried at 5°C, sieved through 2 mm mesh in order to remove large particles and undecomposed plant debris, and stored at 5°C prior to analysis. The extraction procedure was carried out on defrosted plants.

Extraction was performed in a Soxtec apparatus, by the use of dichloromethane. Further purification was carried out using solid-phase extraction by glass column chromatography packed with Florisil® as a silica-based stationary phase. Quantitative analysis was performed using the external standard method, in which the certified standard (Ultra Scientific Ltd.) was applied.

The analysis of the PAH concentrations in peat and plant material was performed using a gas chromatograph (5890 II) equipped with a mass selective detector (GC/MSD Hewlett – Packard) and a non-polar capillary HP-5 column (length 24 m, diameter 0.2 mm, film thickness 0.33 µm diphenyl – 95% dimethylpolysiloxane). The following temperature programming was applied: 70°C at 10°C/min to 200°C, at 2.5°C/min to 300°C (7 min). The detector temperature was 280°C. The detection limit was ca. 0.1 ng/g dry weight, assuming 10 g of sample used.

The following PAHs were determined to be present: acenaphthene (Ace), acenaphthylene (Aceph), fluorene (Fl), phenanthrene (Phe), anthracene (An), fluoranthene (Flu), pyrene (Pyr), benzo[a]anthracene (BaAnt), chrysene (Chry), benzo[b]fluoranthene (BbFlu), benzo[k]fluoranthene (BkFlu), benzo[a]pyrene (BaP), benzo[e]pyrene (BeP), indeno[123-cd]pyrene (IndPyr), dibenzo[ah]anthracene (DbahAnt), benzo[ghi]perylene (BghiPer) and perylene (Peryl).

#### Quality Assurance and Quality Control (QA/QC)

The procedures described above were checked for recoveries and reproducibility according to the standards of PAH determination. PAHs were quantified using external standard solution. For all the compounds, recovery results were in the range of 79 to 94%. The reproducibility of individual PAHs was calculated by replicate analysis, giving an error between 3.1 and 8.4%. Ten percent of the samples were extracted and analyzed in duplicate. Following the analysis of every 10 samples, a standard samples with known PAH concentrations were analyzed. A solvent blank was analyzed after every 20 samples, to verify the response of the gas chromatograph.

## Results and Discussion

Table 1 presents total PAH concentrations in the peat and plant samples taken from the studied locations.

The total PAH concentration in the leaves of *Ledum palustre* collected from peatlands in NE Poland ranged from 232 ng/g to 1523 ng/g and was higher than the total PAH concentration in pine needles taken from those same peatlands. A similar trend was noted in the case of plants from the peatlands in SE Poland, except that the overall PAH concentration in the majority of the plant samples there was found to be higher than in NE Poland. The PAH concentrations were much lower in the soil than in leaves at all the peatlands studied, with the exception of peatlands E2 and J, where the PAH concentrations were found to be slightly higher in the soil than in pine needles. The low PAH concentrations in the surface layer of the peat deposits relative to the PAH concentrations in plants suggests that these compounds migrate from the soil surface by evaporating. Aamot et. al. compared the PAH concentrations in peat core samples from two ombrogenous peatlands in Norway to PAH concentrations in forest soils and concluded that the compounds accumulate in much greater amounts within the surface layers of peat [30]. They allege that many of these compounds do not decompose in organic soils. Further, they suggest that the peat soils that form at peat bogs (in an anaerobic environment, where the activity of microorganisms is low) provide an excellent medium for the study of changes in PAH concentration. Our study, conducted at the three chosen peatlands in different parts of Poland, has shown that the average PAH concentration in peat soils was significantly higher than the PAH concentration in mineral (forest) soils collected from the immediate vicinity of the peatlands [31].

Numerous authors have stated that PAHs accumulate much more readily in soils that are rich in humic compounds [30, 32-34]. The duration of these compounds' presence in the soil depends in large part on how fast they evaporate from the soil surface, undergo irreversible sorption by organic compounds, get washed out, accumulated by plants, or undergo biodegradation [35-38]. The PAHs' low solubility in water and their strong sorption on organic (humic) compounds limits their evaporation and spread into the deeper layers of the soil. The breakdown of PAHs in mineral soils takes place mainly through the agency of soil bacteria, while peat, due to its low pH, is characterized by little microbial activity [39,40]. According to the reports of Giraud et al., however, it does appear that some mushroom species may play a role in the process of biodegradation in peat [39].

Fig. 2 presents the min./max. extent and average PAH concentration for the studied plant and soil material from the peatlands in the northeast and southeast of Poland.

It was shown that the average PAH concentration (excluding that of perylene) in the top level of the soil at the peatlands studied (excluding Wolosate peat bog) was 172 ng/g; with a min. value of 31 (at peatland F1) and a max.







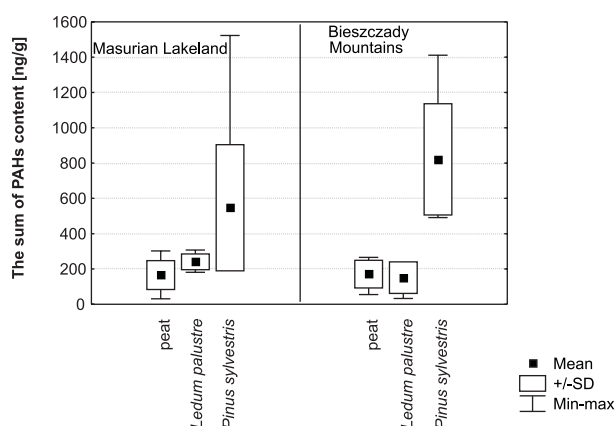


Fig. 2. Concentrations of total PAHs (mean  $\pm$  SD, min-max) in peat and plant samples at different sampling regions.

of 302 ng/g (at peatland D2). In NE Poland, the values of PAH concentrations in pine needles taken from the peatlands ranged from 181 to 307 ng/g, with an average of 248 ng/g. In comparison, pine needles collected at peatlands in SE Poland had PAH concentrations which ranged from 33 to 2721 ng/g, with an average of 149 ng/g. Relative but similar proportions were found in the case of *Ledum palustre*. Here the PAH concentrations in leaves found in NE Poland ranged from 232 to 1523 ng/g, while in leaves from SE Poland the PAH concentrations were from 491 to 1411 ng/g. Only at the Wolosate peat bog were PAH concentrations within plant and soil samples very high.

What is notable are the large differences between the PAH concentrations in different plant species occurring within the same peatland area. No significant difference was detected between the average PAH concentration values in peat samples taken from peatlands in NE and SE Poland. The majority of peatlands studied were ombrogenous, with a thick bryophytic cover over the top layer of soil, created by way of peat formation. Most of the studied peat bogs are hummock-and-hollow plant communities, composed in large part of *Sphagnum* mosses and various heath types. This vegetation constitutes an excellent insulating (sorption) layer, capable of preventing PAHs from penetrating deeper into the peat deposits throughout most of the year. At times when the water level is low, the peatlands become dry and PAHs collected on the mosses may evaporate. The results obtained by the authors following the study of the PAH concentrations in peat core samples seem to support this thesis [41]. The PAH concentration decreases with the depth of the peat deposits and vice versa. This negative correlation is a testament to the low degree of PAH migration into the deeper peat deposit layers.

The high PAH concentrations in the vegetation are an indication that these compounds constantly travel into the area by air. Organic compounds (including PAHs) may be taken up by plants from the soil, but various studies point out that the effects of this process are insignificant in com-

parison to the effects of the plants' accumulation of these compounds taken in through the leaves, directly from the atmosphere [35, 42]. Simonich and Hites state that the accumulation of PAHs in various sections of a plant (mainly the root system and the leaves) depends on the specific octanol:water ratio of the particular PAH [43]. Those PAHs which have a log Kow > 6 most often are absorbed from the air by the leaves of the plant, while those which have a log Kow < 2.5 may be taken up from the soil by the plant through its root system and then transported via the xylem. That the PAH concentration may vary among leaves collected from the same area has been very well documented [15, 16, 29]. The authors have concluded that the mechanism by which plants take in organic contaminants depends on the given compound's physicochemical properties (molecular weight, solubility in water, volatility), environmental conditions (including temperature and distance from the source of emission) as well as the species of plant and structure of the plant's organs.

In studying how PAHs that are present in the air accumulate in plants, Howsam et al. take into account various leaf characteristics such as leaf size, thickness, morphology, the concentration and chemical composition of epicuticular wax, and the presence of epicuticular hairs [15]. It is a well-known fact that the POP concentrations found in different plant species originating from the same area may vary significantly. The kinetics of the uptake of organic compounds have been described using a one-compartment model for the entire leaf, with no distinction being made between the outer (cuticular) and the inner leaf compartments [1]. It is also possible that volatile, low-molecular-weight PAHs found inside the leaves reach the inner compartment by gaseous diffusion through the open stomata. Many studies have shown that wax occurring in plants is an active sorbent of PAHs. The chemical composition of plant wax depends not only on the type of plant, but also varies with the plant's location. The epicuticular waxes of higher plants consist of complex mixtures of long chain aliphatic and cyclic components, including hydrocarbons, primary and secondary alcohols, aldehydes, ketones, esters, fatty acids and triterpenoids [44-47]. Chain length distributions of wax components change with variation in environmental conditions such as temperature, light intensity and air pollution [48-50, 44]. The epicuticular waxes of plants growing at polluted sites are the first foliar components to be attacked by both gaseous and particulate pollution. The formation of epicuticular waxes can be restrained and their composition and distribution changed.

In studying the changes in PAH concentrations over time in various tree species, Howsam et al. asserts that how many PAHs a given plant species accumulates depends on the surface area of its leaves, as well as on the lipid concentration in the leaves [29]. In any case, pine seems to be a particularly good bioindicator for measuring organic contamination coming in from the air, not only because it can be used for monitoring the atmospheric PAH concentration year-round, but also due to the rela-

tively thick epicuticular wax layer of its needles, which is a good absorber of organic pollutants.

Table 2 presents the total PAH concentrations in the plant samples taken from the (sub)urban areas and from places of different human (industrial/rural) activities.

Total PAHs concentrations in plant samples from the investigated peatlands are similar to those in plants from other urban/rural and industrial areas. The urban plant concentrations are similar to the concentrations in the plant samples from peatlands. However, the differences in PAH-concentrations in plants from the selected peatlands are caused by differences in plant characteristics of two investigated species but not by PAH sources. In this study, the higher PAH concentrations determined for *Ledum palustre* in comparison to pine serve as evidence that the compounds collect more readily in the former species of plant. *Ledum palustre* is a heath commonly found at peat bogs. It is a perennial evergreen plant, but

since it is also most often covered by snow in the winter, it does not collect organic compounds from the air during that time. Compared to pine needles, its leaves are somewhat shorter and more flat. Additionally, the leaf wax layer is much thicker in *Ledum palustre*, making it much more difficult for organic contamination to be washed away by precipitation. These features of the *Ledum palustre* leaf most likely promote the accumulation of PAHs in the plant.

Fig. 3 presents data on the 16 PAH compounds in addition to perylene, found in the peat and in the leaves of the studied plants.

It was determined that in all the samples studied, 3- and 4-ringed compounds were the most numerous. Five-ringed compounds were slightly less common, while 6-ringed compounds were found in only a couple of the samples. The Wolosate peatland was the exception. There, 6-ringed compounds were present in all the plant samples

Table 2. Total concentrations of PAHs (ng/g) in different plant species from locations of human (industry/rural) activities.

Plant species	Number of PAHs	Total range [ng/g]	Site	References
<i>P.sylvestris</i>	17 *	31 – 563	urban/industrial and rural	H.-M. Hwang et al. (2003)
<i>P.sylvestris</i>	16	0.3 – 19251	industry	Holoubek et al. (2000)
<i>P.sylvestris</i>	14	270	rural	Migaszewski (2002)
<i>P.sylvestris</i>	5	86 – 492	urban/industrial and rural	Weissflog and Wenzel (1997)
<i>P.sylvestris</i>	25	410 – 6100	urban/industrial and rural	Kylin (1996)
<i>P.sylvestris</i>	10	64 – 141	forest	Lang et al.(2000)
<i>P.sylvestris</i>	10	600 – 1600	urban	Simonich and Hites (1994)
<i>P.sylvestris</i>	17	1126	urban/industrial	Hwang et al. (2003)
<i>P.sylvestris</i>	16	19 – 3091	rural	Tremolada et al. (1996)
<i>P.sylvestris</i>	16	0.3 – 18590	background	Holoubek et al. (2000)
<i>P.sylvestris</i>	14	19 – 3091	urban/industrial	Tremolada et al. (1996)
<i>P.strobus</i>	10	137 -859	urban	Lang et al. (2000)
<i>P.strobus</i>	10	64 – 141	mountain	Lang et al. (2000)
<i>P.sylvestris</i>	16	0.3 – 18590	rural	Holoubek et al. (2000)
<i>P.sylvestris</i>	16	85 – 19251	industrial	Holoubek et al. (2000)
<i>Quercus ilex</i>	18	106 – 4607	urban/industrial and natural	Alfani et al. (2001)
grass (mixed species)	7	2000	industrial	Bakker et al. (2000)
<i>Plantago major</i>	7	8000	industrial	Bakker et al. (2000)
<i>Pine</i>	17	31 – 563	rural/urban/industrial	Hwang et al. (2003)
<i>Pine</i>	18	51 – 410	urban	Lehndorf and Schwark (2004)
<i>Quercus robur; Q.petrea</i>	23	43-267	rural	Howsam et al. (2000)
<i>Fraxinus excelsior</i>	23	39-146	rural	Howsam et al. (2000)
<i>Corylus avellana</i>	23	35-239	rural	Howsam et al. (2000)

\* – 16 PAHs with methylphenanthrene

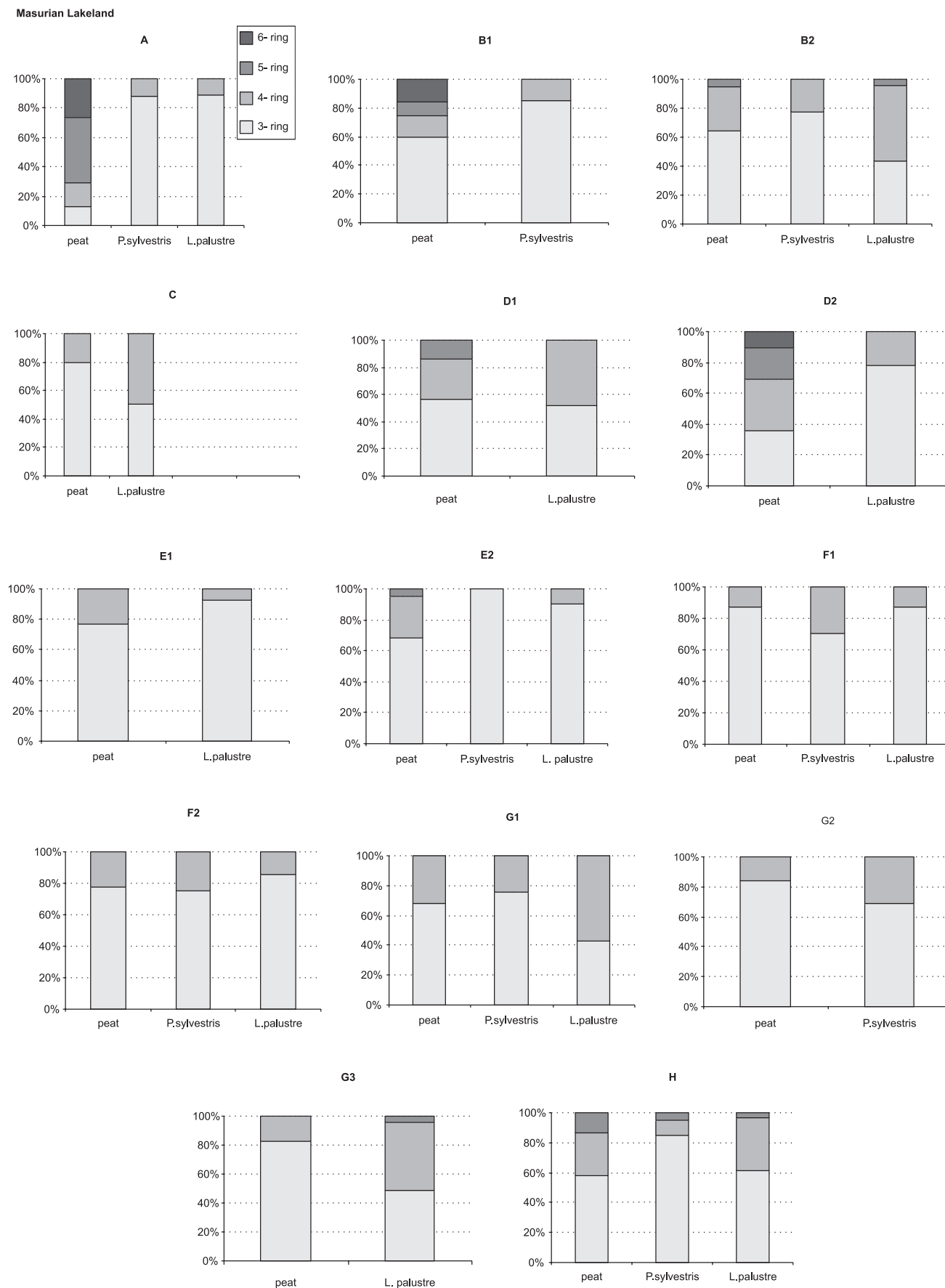


Fig. 3. The percentage content of 2, 3, 4, 5, and 6-ring PAHs in peat and plant samples in different study regions.



## Bieszczady Mountains

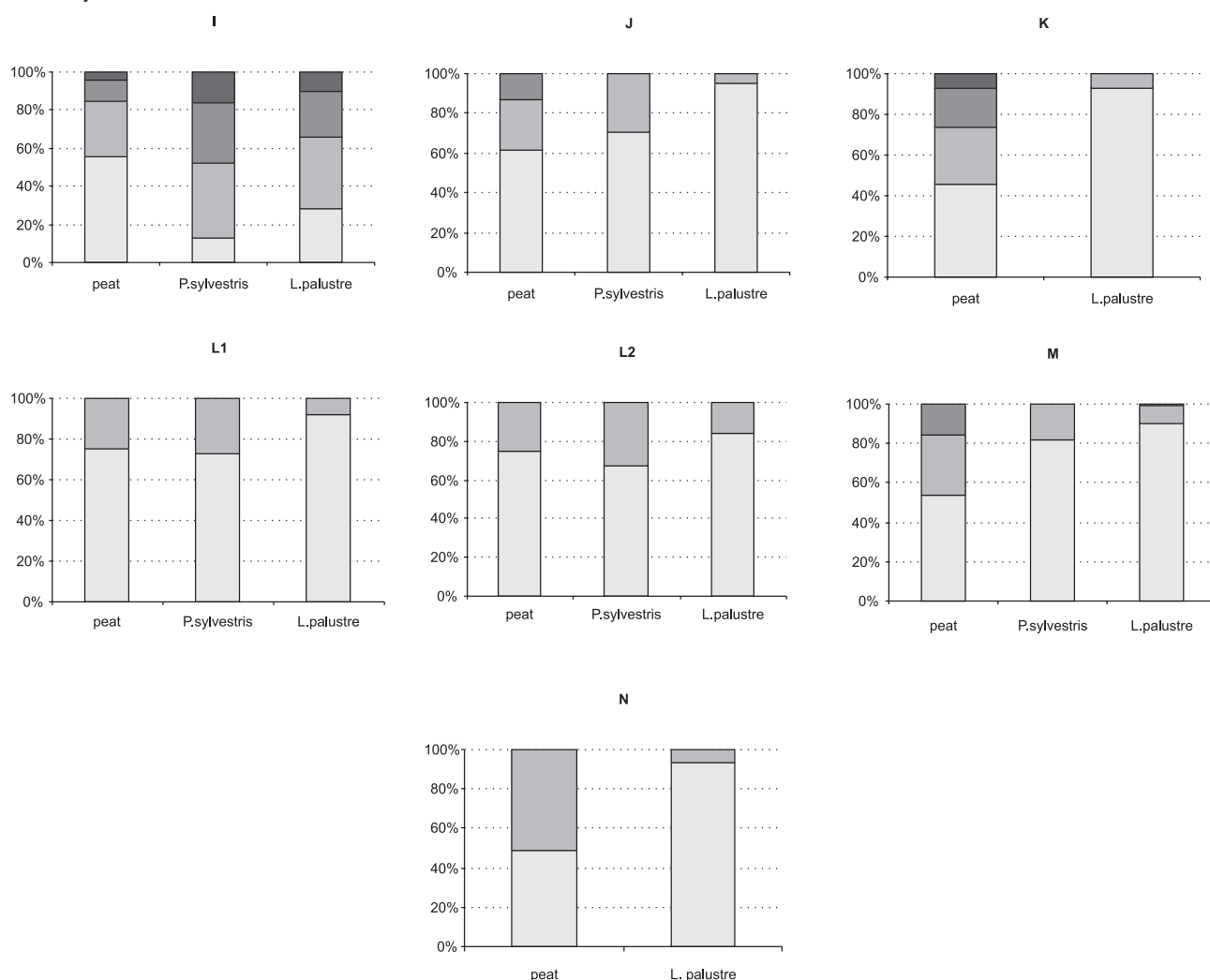


Fig. 3. continued

and in the peat sample. It was determined that in the peat samples, 3-ringed PAHs were present in concentrations from 10 to 217 ng/g, while 4-ringed PAHs in concentrations from 4 to 99 ng/g. Slightly higher concentrations of these compounds were found in the vegetation samples. For *Ledum palustre*, 3-ringed PAHs had concentrations of 109 to 1373 ng/g, while 4-ringed PAHs had concentrations of 50 to 1629 ng/g. In pine needles, the concentrations of 3- and 4-ringed PAHs were slightly lower than in *Ledum palustre* leaves: 27 to 333 ng/g, and 21 to 1020 ng/g, respectively. Phenanthrene and fluoranthene had the biggest share in overall PAH concentration in all the peat and plant samples. In *Ledum palustre*, the fluoranthene concentration was many times the amount it was in any other plant species in the case of all the study areas. This may be tied to the specific characteristics of this plant species.

Research done by Howsam et al. showed that 3- and 4-ringed PAHs constituted over 60% of the total PAHs in all the plant species he studied [15]. He determined that the samples he studied most often contained the greatest amounts of phenanthrene, as well as other 4-ringed PAHs

(fluoranthene and pyrene). Other authors confirm that high levels of phenanthrene and anthracene are characteristic of leaf samples [51, 52]. Fluoranthene has been reported to be the dominant compound in PAH concentrations present in plants of the temperate zone [53]. Holoubek et al. determined a high concentration of fluoranthene in the needles of the Norway spruce (*Picea abies*) [11].

In the analysis of the PAH concentrations within the plant and soil samples from peatlands in both NE as well as SE Poland, what is notable are the low concentrations of 5- and 6-ringed PAHs. The Wołosate peatland, where their concentrations were very high, is the exception. This peatland, which is also a nature reserve, is located near a road known for increased automobile traffic during certain periods. The presence of the 6-ringed benzo[ghi]perylene in samples from the environment is considered to be a particular marker of contamination from fuel exhaust [20, 54, 55]. Similarly to benzo[ghi]perylene, benzo[a]pyrene was also present in the vegetation taken from the peatland at Wołosate, but not in the peat sample collected there from the topmost layer of peat. At all the remaining peatlands

Table 3. PAH ratios in peat and plant samples from different study sites.

Region	Study site	Sample	Ant/(Ant&Phe)	Flu/(Flu&Pyr)	BaAnt/ (BaAnt&Chry)	Indpyr/ (Indpyr&BgHiPer)
Masurien	A	peat	0.5	0.5	0.5	0.5
		<i>P.sylvestris</i>	0	1	0	0
		<i>L. palustre</i>	0.05	0.95	0	0
	B 1	peat	0.05	0.7	0	0.3
		<i>P.sylvestris</i>	0.07	1	0	0
	B 2	peat	0.04	0.6	0	0
		<i>P.sylvestris</i>	0	0.7	0	0
		<i>L. palustre</i>	0	0.3	0	0
	C	peat	0.04	0.8	0	0
		<i>L. palustre</i>	0	0.4	0.2	0
	D 1	peat	0.05	0.5	0.3	0
		<i>L. palustre</i>	0	0.4	0	0
	D 2	peat	0	0.4	0.3	0.5
		<i>L. palustre</i>	0	0.9	0	0
	E 1	peat	0.04	0.7	0	0
		<i>L. palustre</i>	0.04	1	0	0
	E 2	peat	0.04	0.6	0	0
		<i>P.sylvestris</i>	0.03	0	0	0
		<i>L. palustre</i>	0.04	1	0	0
	F 1	peat	0	1	0	0
		<i>P.sylvestris</i>	0	0.6	0	0
		<i>L. palustre</i>	0	0.9	0	0
	F 2	peat	0.12	0.7	0	0
		<i>P.sylvestris</i>	0	0.6	0	0
		<i>L. palustre</i>	0.04	0.9	0	0
	G 1	peat	0.07	0.6	0	0
		<i>P.sylvestris</i>	0.05	0.7	0	0
		<i>L. palustre</i>	0	0.3	0	0
	G 2	peat	0	1	0	0
		<i>P.sylvestris</i>	0.05	0.6	0	0
	G 3	peat	0.19	0.8	0	0
		<i>L. palustre</i>	0	0.4	0	0
	H	peat	0	0.7	0	0
		<i>P.sylvestris</i>	0.04	1	0	0
		<i>L. palustre</i>	0	0.8	0	0
	Bieszczady Mountains	I	peat	0.04	0.6	0.3
<i>P.sylvestris</i>			0.06	0.2	0.4	0.4
<i>L. palustre</i>			0.04	0.6	0.4	0.4

Bieszczady Mountains	J	peat	0.04	0.6	0.9	0
		<i>P.sylvestris</i>	0.04	0.3	0	0
		<i>L. palustre</i>	0.02	1	0	0
	K	peat	0.04	0.6	0.2	1
		<i>L. palustre</i>	0	1	0	0
	L 1	peat	0.05	0.6	0	0
		<i>P.sylvestris</i>	0	0.2	0	0
		<i>L. palustre</i>	0	1	0	0
	L 2	peat	0.04	0.6	0	0
		<i>P.sylvestris</i>	0	0	0	0
		<i>L. palustre</i>	0.02	0.7	0	0
	M	peat	0	0.6	0	0
		<i>P.sylvestris</i>	0.2	1	0	0
		<i>L. palustre</i>	0	1	0	0
N	peat	0	0.5	0	0	
	<i>L. palustre</i>	0	1	0	0	

in this study, this compound occurs only in the topmost layer of peat, if at all.

According to many authors, which PAHs are present in the examined vegetation and soil material and in what concentrations depends on the type of pollution source and the distance to it [56-58]. In the study by Milukaite, it was determined that the concentration of benzo[a]pyrene was 24.3 ng/g, 200 m from the street, while at a distance of 10 m and less, it was 103 and 280 ng/g [59]. The most comprehensive analysis of the effects of distance on PAH accumulation in vegetation was published by Meharg et al. [60]. In it, the highest PAH concentration was observed at a sampling point located ca. 3.2 km from the source. Points beyond 3.2 km and up to 4.5 km away were still characterized by elevated PAH concentrations that declined only slightly, relative to the increasing distance. The authors suggested that PAH concentrations should be considered within the framework of atmospheric conditions and the sampling distance of plant specimens.

The investigated PAH ratios (Ant/(Ant&Phe); Flu/(Flu&PYR); BaAnt/(BaAnt&Chry) and IndPyr/(IndPyr&BghiPer) are presented in Table 2.

PAHs with molecular masses of 178 (anthracene) and 202 (fluoranthene) are commonly used to make the distinction between combustion and petroleum sources. The Ant/(Ant&Phe) ratio <0.1 usually is taken as an indicator of petroleum while a ratio >0.1 indicates the dominance of combustion. But for a mass of 202, Flu/(Flu&Pyr) ratio of 0.5 is usually defined as the petroleum/combustion transition point, [61-63]. In comparing the obtained PAH ratios for the peat samples, it was determined that only in the case of two peatlands in NE Poland did the values of Ant/(Ant&Phe) surpass 0.1. This is while, with the exception

of peatland D2, the values of the Flu/(Flu&Pyr) ratio were greater than 0.5. These data conform to the ideas of Yunker et al., who suggest that PAHs present in peat soil come from combustion processes [63]. This is not confirmed, however, by results pertaining to PAH concentrations in the plants present at those locations. The absence of anthracene made it impossible to compute the Ant/(Ant&Phe), while the Flu/(Flu&Pyr) ratio pointed to a different source of contamination. For most of the remaining peatlands, the Fl 202 indicator is different for the plants as well as the soil from the same areas. Only at 6 out of the 21 peatlands studied were the values of the Flu/(Flu&Pyr) ratio greater than 0.5 in all three cases (peat, *Ledum palustre* and *Pinus sylvestris*), which would point to the same source of PAH contamination. Our data suggest that PAHs with four and more rings do not allow simple segregation into combustion or petroleum sources.

Bucheli et al. have suggested that, in the environment, anthracene degrades faster than phenanthrene, which would lead to reduced marker numbers [64]. For this reason, the usefulness of anthracene as an emission marker has been doubted by Hwang et al. [22]. Additionally, it seems that the processes – by which PAHs (brought in by air from distant emission sources) accumulate in plants, as well as are sorbed by humic substances present in the soil – are mainly connected to the distribution of PAHs in the environment. Simonit and Hites estimate that about 40% of PAHs are transported through the air over long distances [1]. Considering that most of these compounds are 3- and 4-ringed PAHs, it can be expected that in areas where there are no immediate emission sources, they will be the dominant pollutants in both the soil and vegetation.

## Conclusions

In order to summarize the above results, it should be stated that the level of PAHs in plants at the examined peatlands is generally higher than in the peat (especially at Wołosate), which implies that there is an anthropogenic source of pollution. Total sum of PAH pollution levels in peats and plants as well as concentration profiles of particular study sites integrates long-range pollution sources. The lack of 5- and 6-ringed PAHs in the plant and soil material indicates the lack of any direct emission sources of these compounds in regions adjacent to those examined in the study. The results obtained show that *Ledum palustre* is a much better bioindicator than pine in the wetland ecosystems (especially for treeless ombrotrophic bogs), and may be used as a biomonitoring tool for comparing the concentrations and the spatial distribution of airborne pollutants such as PAHs.

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