PEATLAND PLANTS AS BIOINDICATORS OF AIR CONTAMINATION WITH POLYCYCLIC AROMATIC HYDROCARBONS (PAH)

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Abstract

The concentration of 15 polycyclic aromatic hydrocarbons (PAHs) from US EPA list as well as benzo[e]pyrene and perylene were analysed in four plant species characteristic for raised bogs, i.e. in pine (*Pinus sylvestris*), Dutch Myrthe (*Ledum palustre*), cotton-grass (*Eriophorum vaginatum*) and bog billberry (*Vaccinium uliginosum*). Plant samples were collected from peatlands localised in Masurian District and Bieszczady Mountains. Pine possessing the ability of sorption of organic compounds due to high wax content, is commonly used bioindicator of PAHs contamination level. The aim of this study is to compare the bioindication ability of different peatland plant species. The highest level of the contamination with PAHs was demonstrated in plants originating from peatland Wołosate localised in Bieszczady Mountains. The perylene was absent in the most collected plant samples. The total concentration of PAHs in Dutch Myrthe samples exceeded many times the concentration of PAHs in pine samples collected on the same peatland. In the most of investigated peatlands Dutch Myrthe sorbed more PAHs than surface peat layers, whereas pine and bog billberry showed the similar PAHs level as established in surface peat layers. In cotton-grass samples the PAHs level was about 10 times smaller, comparing to concentration of PAHs in surface layer of peat. The obtained results suggested that Dutch Myrthe is better bioindicator than pine, whereas bioindication ability of bog billberry is comparable to the bioindication feature of pine.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are common pollutants in the environment. They can derive from both natural and athropogenic sources (1,2,3). Perylene present in the environment can derive from people activity, however it is formed mostly from natural processes. Ones emitted, PAHs are distributed atmospherically and deposited on the soil and plants surfaces (4). Vegetation, predominantly pine needles (but also leaves from some other plant species) due to their high wax content and ability of sorption of lipophylic organic compounds has been used by many authors as good indicators of atmospheric contamination and a reservoir for pollutans, especially PAHs (5,6,7). There are several pathways through which organic pollutants eneter vegetation: by partitioning from contaminated soil to the roots and then translocating in the plant by the xylem, by deposition from the atmosphere by gas- and particle phase onto the waxy cuticle of the leaves or by uptake by the stomata and be translocated by the phloem (5). Hydrophobic, persistent organic contaminants reach plant leaves primarily from the atmosphere, with root uptake and translocation being of very limited importance (7). PAHs may exist in the atmosphere in either gas or particulate phase or both, depending on size of PAH molecules (8). The sorption of organic pollutants from the atmosphere by soil is connected with its physical and chemical features, mostly the content of humic substances, which are present in bigger quantity in organic soils (e.g. peat) than in mineral ones.

The aim of this study is to determine the bioindication ability of different plant species overgrowing peatlands and to compare it with the sorption ability of peat from the surface layer of each investigated peatland. The raised bogs plants selected for investigations vary in the content and composition of waxes. The present study is a continuation of our research dealing with the ability of plants to bioindicate the level of some organic pollutants (9).

Methods

Peat and plant samples were collected in five raised bogs localised in the north-east Poland (Masurian District): Jarka (A), Grądy Węgorzewskie (B), Zdory (C), Skieblewo (partly raised bog D1, partly transition bog D2), Żegary (partly raised bog E1, partly E1), and in four raised bogs localised in Bieszczady Mountains in south-east Poland: Wołosate (F), Łokieć (G), Derwich (H), Tarnawa (I). Masurian District is the area situated in the north-east Poland and created by the Baltic glaciation. It is covered by many lakes and forests. Compared to the rest of Poland the Masurian District is characterised by a considerable variety of site conditions and a high degree of naturalness. The Bieszczady Mountains range is a National Park with a very high forest index ot upto 90%. The Wołosate raised bog (F) is an exception due to its localisation on the forestless area. The Jarka raised bog (reserve) and Grądy Węgorzewskie bogs are located in Suwałki Lake District in the landscape terminal moraine of main Baltic glaciation corresponding to the Pomerania moraines. Jarka reserve is covered by raised bog overgrown with peatland forest. Żegary and Bagna Skieblewskie marshes are different in terms of plant communities, as well as the type of peat deposit (lowland and transition bog). Żegary marsh lies among moraine hills built of rock formation. The bog is located on the boundary between the basin of Czarna Hańcza and Biebrza rivers. Torfowisko Zdory is situated in midlle part of Masurian District in the area covered by agricultural fields and meadows. Masurian District is a region with very little anthropogenic pollution. The raised bog Wołosate is the strict reserve localised in River Wołosatka Valley inside the Bieszczady National Park. The other Bieszczady Mountains peatlands are situated in the River San Valley

Subsequent description of peat deposit character and distribution in the peatlands was based on a specialist of peat documentation. A special „Russian sampler" (container length 50 cm) was used to take peat samples from each peat- bog. The peat samples were stored at - 20˚C until analysis. Pine needles (*Pinus sylvestris*) were collected from peatlands: A, B, E2, F, G, I; Dutch Myrthe leaves (*Ledum palustre*) were collected from each peatlands studied except bog B; cotton- grass (*Eriophorum vaginatum*) and bog billberry (*Vaccinium ulignosum*) leaves were collected only in two peatlantd (C and F). Leaves were taken from several plants and wrapped in aluminium foil and were stored at - 20˚C until analysis.The samples were dried at room temperature for 2 days at 50ºC for periods of 2-3 hours. After drying they were sieved through a 2 mm mesh to remove large particles and organic debris (only peat), and stored at 5ºC prior to analysis.

The PAH content analysis in plant and peat material was performed using a gas chromatograph (5890 II) equipped with a mass selective detector (GC/ MSD Hewlett-Packard) and a non- polar capillary column HP- P (length 24 m, diameter 0.2 mm, 0.33 µm diphenyl – 95% dimetylpolysiloxane film). Temperature programming was applied: 70ºC at 10ºC min $^{-1}$ to 200ºC, at 2.5ºC min $^{-1}$ to 300ºC (7 min). The detector temperature was 280ºC.The liquid extraction was performed with the use of dichloromethane in a Soxhlet apparatus in boiling temperature by 4 hrs. Further purification was carried out by column chromatography on Florisil. The quantitative analysis was performed using the external standard method were the certified PM-612 standard (ULTRA Scientific Ltd.) was applied. The following PAHs were determined: acenaphtene (Ace), acenaphtylene (Acf), fluorene (Fl), phenantrene (Fen), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benzo[a,h]anthracene (BaA), chrysene (Ch), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[123-cd]pyrene (IndP), dibenzo[ah]anthracene (DahA), and benzo[ghi]perylene (Bper) – (15 PAHs from US EPA list) – as well as benzo[e]pyrene (Bep) and perylene.

Result and discussion

Table 1 presents the concentration of individual PAHs in investigated plant and peat samples. It was found that, in all peat samples, the concentration of 16 anthropogenic PAHs was between 82 and 277 ng/g whereas perylene was present only in peat from peatlands A, B and D2 (10 – 30 ng/g) as well as in pine needles collected from peatlands Wołosate (60 ng/g) and Łokieć (15 ng/g) The presence of perylene only in two plant samples could be connected with the longer time of exposition of pine needles than the leaves of other plant species and with the highest level of contamination in some part of Bieszczady Mountains than in Masurian District. The concentration of anthropogenic PAHs (except perylene) in investigated plant samples were as follows:

- *Pinus sylvestris* 130 – 227 ng/g (the exception is pine sample from Wołosate (F) 2721 ng/g
- *Ledum palustre* 232 – 1017 ng/g (peatland F 4343 ng/g)
- *Eriophorum vaginatum* 83 ng/g (Masurian peatland C) and 851 (Bieszczady peatland F)
- *Vaccinium uliginosum* 203 ng/g (peatland C) and 2113 ng/g (peatland F)

A noticeably high fluorene concentration in *Ledum palustre* leaves was found at most of sites. Benzo[a]pirene which is the most cancerogenic from all anthropogenic PAHs is present only in plants of peatland Wołosate(F), however it is absent in surface layer of peat from this peatland. In the most of investigated peatlands *Ledum* *palustre* sorbed more PAHs than other plant species and surface peat layers. *Vaccinium uliginosum* and *Pinus sylvestris* showed the similar PAHs levels as established in surface peat layers. The only exception is the peatland Wołosate (F) where the concentration of PAHs is about 100 times lower in peat than in plants. We hypothesised that for such concentration of PAHs in plants from Wołosate are responsible the combustion sources from tourist and sport centres located close to peat land as well as the charcoal production factories. The Wołosate peatland is located in deforestation area and it can also affect for concentration of PAHs (10).

Conclusions

In order to summarise the above results it should be stated that the level of PAHs in plants in the investigated peatlands is generally higher than in peat (especially in Wołosate), suggesting anthropogenic pollution. The obtained results suggested also that Dutch Myrhe is much better bioindindicator than pine, whereas bioindication ability of bog bilberry is comparable to the bioindication feature of pine.

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References

1. S. L. Simonich , R. A. Hites. Organic pollutant accumulation in vegetation. Environmental Science and Technology **29**, 2905-2914 (1995).
2. B. Simoneit. "Biomarker PAHs in the Environment". PAHs and Related Compounds. Chemistry Vol. 3 Springer-Verlag Berlin Heidelberg New York (1998).
3. P. Coleman, R. Lee, R. Alcock , K. Jones. Observations on PAH, PCB, and PCDD/F trends in U.K. urban air, 1991-1995. Environ. Sci. Technol., **31** (7) 2120-2124 (1997).
4. W. Wilcke. SYNOPSIS Polycyclic Aromatic Hydrocarbons (PAHs) in Soil – a Review. J. Plant. Nutr. Soil. Sci., **163** 229 – 248 (2000).
5. I. Holoubek , P. Kořínek , Z. Šeda , E. Schneiderová, I. Holoubková, J. Tříska, P. Cudlín , Čáslavský J. The use of mosses and pine needles to detect persistant organic pollutants at local and regional scales. Environmental Pollution, **109** 283-292 (2000).
6. M. Howsam , K. C. Jones, P. Ineson. Dynamics of PAH deposition, cyclic and storage in a mixed deciduous (*Quercus – Fraxinus*) woodland ecosystem. Environmental Pollution, **113** 163-176 (2001).
7. P. Tremolada, V. Burnett, D. Calamari, K. C. Jones. Spatial distribution of PAHs in U.K. Atmosphere Using Pine Needles. Environ. Sci. Technol., **30** 3570-3577 . (1996).
8. D. Martens, J. Maghun , P. Spitzauer, A. Kettrup. Occurrence and distribution of polycyclic aromatic hydrocarbons (PAHs) in an agricultural ecosystem. Fresenius J. Anal. Chem., **359** 546 – 554 (1997).
9. M. Malawska, I. Bojakowska, B. Wiłkomirski. Polycyclic aromatic hydrocarbons (PAHs) in peat and plants from selected peat-bogs in the north-east Poland. J. Plant Nutr. Soil Sci. **165** 286 - 291 (2002).
10. M. Howsam, P. Ineson, K. C. Jones. PAHs associated with the leaves of three deciduous tree species. I – concentration and profiles. Environmental Pollution **108**, 413-424 (2000).

Tab.1. PAHs concentration [ng/ g] in peat and plant samples from selected Polish peatlands

peat - bog	sample	Ace	Acf	Fl	Fen	Ant	Flu	Pyr	BaA	Ch	BbF	BkF	BeP	BaP	IndP	DahA	Bper	perylene	sum of PAHs
Jarka (Mechacz) A	peat	2	2	2	2	2	2	2	4	4	6	6	6	6	10	10	10	6	82
	P.sylvestris	5	5	6	144	0	20	0	0	1	0	0	0	0	0	0	0	0	181
	L. palustre	7	7	793	94	5	71	38	0	2	0	0	0	0	0	0	0	0	1017
Grądy Węgorzewskie B	peat	4	16	29	104	5	24	12	0	4	0	0	0	0	13	24	30	12	277
	P.sylvestris	0	29	25	120	9	21	0	0	11	0	0	0	0	0	0	0	0	215
Zdory C	peat	7	17	45	142	6	32	15	0	9	0	0	0	0	0	0	0	0	273
	L. palustre	4	19	25	107	0	73	38	9	30	0	0	0	0	0	0	0	0	305
	E. vaginatum	0	9	11	46	0	11	6	0	0	0	0	0	0	0	0	0	0	83
	V. uliginosum	4	15	22	104	5	29	15	0	9	0	0	0	0	0	0	0	0	203
Skieblewo D1	peat	5	9	19	75	4	25	17	5	12	12	0	9	6	0	0	0	0	198
	L. palustre	0	15	20	85	0	62	31	0	19	0	0	0	0	0	0	0	0	232
Skieblewo D2	peat	0	8	19	82	0	39	25	10	25	27	13	14	9	16	0	15	0	302
	L. palustre	10	16	313	82	0	62	32	0	22	0	0	0	0	0	0	0	0	537
Żegary E1	peat	6	14	35	134	6	33	17	0	8	0	0	0	0	0	0	0	0	253
	L. palustre	7	15	692	135	5	38	21	0	9	0	0	0	0	0	0	0	0	922
Żegary E2	peat	4	10	25	92	4	28	16	0	10	9	0	0	0	0	0	0	0	198
	P.sylvestris	0	0	145	4	32	0	0	0	0	0	0	0	0	0	0	0	0	181
	L. palustre	20	50	931	358	14	84	48	0	18	0	0	0	0	0	0	0	0	1523
Wołoste F	peat	5	11	28	89	4	34	20	6	12	14	6	7	0	11	0	0	0	247
	P.sylvestris	15	29	71	205	13	360	306	127	227	228	112	218	227	188	34	241	60	2721
	L. palustre	4	31	786	380	17	599	473	200	357	371	203	259	212	186	0	265	0	4343
	E. vaginatum	0	15	23	156	5	95	75	39	72	89	52	64	68	48	0	50	0	851
	V. uliginosum	8	20	34	255	12	351	293	18	260	277	186	0	56	158	31	154	0	2113
Łokieć G	peat	5	10	30	113	5	40	22	6	1	13	6	8	7	0	0	0	0	266
	P.sylvestris	0	5	7	132	5	34	17	0	12	0	0	0	0	0	0	0	15	227
	L. palustre	0	21	1093	222	4	37	22	0	12	0	0	0	0	0	0	0	0	1411
Derwich H	peat	3	7	20	69	3	25	15	4	17	23	8	12	0	16	0	0	0	222
	L. palustre	0	14	439	179	0	23	16	0	11	0	0	0	0	0	0	0	0	682
Tarnawa (Sychła) I	peat	11	7	18	62	3	19	10	0	5	0	0	0	0	0	0	0	0	135
	P.sylvestris	4	6	4	81	0	21	14	0	0	0	0	0	0	0	0	0	0	130
	L. palustre	0	20	509	172	0	32	18	0	11	0	0	0	0	0	0	0	0	762