THE PEAT CORES AS AN ARCHIVE OF PAHS SOURCES IN THE QUATERNARY SEDIMENTS.

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) are important and dangerous pollutants that have been identified in diverse environmental matrices world- wide. 15 US EPA PAHs are major products of incomplete combustion of fossil fuels and organic matter, but the perylene is formed from non- specific precursor materials by biotic or abiotic transformation processes.

Peat samples were collected in three peat-bog complex: Gązwa, Sychła and Bruch. The highest level of 15 US EPA PAHs (2586 ng/g) were determinated in peat from Bruch bog (antropogenic pollution). The peat sample from upper level of stratygrphic profile was most polluted. In deeper levels contamination was lower, but there was more perylene. In Gązwa and Sychła bogs the 15 US EPA PAHs concentration in upper level were more then ten times less. In all investigated stratigraphic profiles of peatlands the 15 US EPA PAHs content ranges between 67- 149 ng/g. There is no detected perylene in upper levels of Sychła and Gązwa bogs. The highest content of perylene was determinated in bottom level of Sychła bog (1141 ng/g); in Gązwa bottom level of bog, concentration of perylene were between 121- 631 ng/g. The peat cores could be taken as the archives of information about the PAHs sources in sediments.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are commonly occuring, as well as more and more intensively studied organic compounds, which constitute a significant pollutant in natural environments. In various concentrations, they have been detected not only in polluted industrial and urbanized environments, but also in soil, water sediments and derivative rocks in areas of different antrophogenic pressure (*Coleman* et. al., 1997; *Ollivon* et. al., 1995; *Bradley* et. al., 1994; *Bojakowska* and *Sokołowska*, 1998). A vast majority of polycyclic aromatic hydrocarbons is introduced into the environment from anthropogenic sources (*Harvey*, 1998; *Howsam* and *Jones*, 1998; *Lichtfouse* et. al., 1997), whereas relatively small proportions of PAHs derive from natural sources (*Simoneit*, 1998; *Wilcke*, 2000; *Capacioni* et. al., 1995). The hydrocarbon that is the most frequently created as a result of natural biogeochemical processes in sediments is perylene (*Silliman* et. al., 1998; *Thiele* and *Brümmer*, 2002; *Wilcke* et. al., 1999).

The literature contains very few papers concerning the presence of PAHs in peat (*Sanders* et. al., 1995; *Bojakowska* et. al., 2000). In Poland there are about 51 thousand peatlands covering the total surface area of slightly more than 13,000 km^2. The aim of this paper is to present information concerning the 15 US EPA PAHs and perylene contents in peat samples according to stratigraphic profile of different ombrotrophic bogs.

Methods

Study sites

The peat samples were collected from peatlands: Gązwa bog (north- eastern part of Poland, in the area relatively free of contamination, since no heavy industry is concentrated there, and forests and lakes cover a high percentage of land), Sychła bog (south- eastern Poland, Bieszczady Mountains, charcoal distillating manufactures are concentrated there), Bruch bog (Silesian, very polluted area with coal and metal mining industry).

Peat sampling

Peat samples were collected in June and September 2000 (Gązwa, Sychła) and June 2002 (Bruch). Subsequent description of peat deposit character and distribution in peatlands was based on specialist peat documentation. Points for the collection of biogenic sediment cores (with the Russian sampler, container length 50 cm) were selected on the basis of geological documentation. Peat samples were collected from a different depth of the stratigraphic profile of peat deposit.

In the three selected sites 14 peat samples were collected. The botanical classification of peat genus revealed that the samples represented different genetic types of various botanical origin and decomposition rates, namely:

- 2 samples of Sedge-Moss (*Carici Bryaleti*), belonging to ***Hypnum*** **Moss Peat (*Bryalo-Parvocaricioni*)**,
- 2 samples of Sedge Peat *(Cariceti*) belonging to **Sedgeous Peat (*Magnocaricioni*)**,
- 9 samples of high-moor peat belonging to poorly decomposed *Cuspidato-Sphagneti* (2 sample), *Eriophoro-Sphagneti* (6 samples), and *Pino- Sphagneti* (1 sample). The all peat were classified by *Sphagnum* Moss Peat (*Ombro-Sphagnioni*),
- 1 sample of totally decomposed Gyttja typical of raised bogs

Identification of polycyclic aromatic hydrocarbons (PAHs) in peat.

The samples were dried at room temperature for 2 days then at 50˚C for 2-3 hours, sieved through a 2-mm mesh to remove large particles and organic debris, and stored at 5˚C until preparation for analysis was undertaken.

The PAH content in 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- 5 (length 24 m, diameter 0.2 mm, o.33 μm diphenyl- 95% dimethylpolysiloxane film). Temperature programming was applied: 70˚C at 10˚C min^{-1} to 200˚C, at 2˚C min^{-1} to 300˚C (7 min). The detector temperature was 280˚C. The detection limit was ca. 0.1 ng g^{-1} dry weight, assuming 10 g of sample. The liquid extraction was performed with the use of dichloromethane in a Soxtec apparatus in boiling temperature by 4 hrs. Further purification was carried out by column chromatography on Florisil. The quatitative analysis was performed using the external standard method where the certified PM-612 standard (ULTRA Scientific Ltd.) was applied.

The following PAHs were determined: Acenaphthene (ACE), Acenaphtylene (ACY), Fluorene (FLU),Fluoranthene (FLA), Phenanthrene (PHE), Anthracene (ANT), Pyrene (PYR), Benzo[a]anthracene (BAA), Chrysene (CHRY), Benzo[b]fluoranthene (BBFLA), Benzo[k]fluoranthene (BKFLA), Benzo[a]pyrene (BAP), Indeno[1,2,3-cd]pyrene (IND) Dibenzo[ah]anthracene (DBAH), Benzo[ghi]perylene (BGHI) and perylene (PER)- (15 PAHs from US EPA list)- as well as Benzo[e]pyrene (BeP) and Perylene.

Quality assurance and quality control

The procedures described above were checked for recoveries and reproducibility. Prior to extraction, the extraction was investigated by spiking peat samples with four increasing amounts of standards. For all the compounds analyzed, recovery, recovery results were in the 81 and 96% range. Reproducibility was calculated on replicate analyses, giving an error between 3.1 and 8.4%. ten percent of samples were extracted and analyzed in duplicate. After an analysis of each 10 samples, standard samples with a known PAHs content were analyzed. Solvent blank was analyzed after every 20 samples as a check on the response of the gas chromatography.

Results

The peat cores collected from various depth of stratigraphic profiles of three raised bogs were investigated. In Gązwa bog the sum of antropogenic PAHs was between 63 – 168 ng/g (table I). The highest concentration was found in surface level of the peat deposit. The concentration of perylene in peat of this bog varied from 121 and 631 ng/g. However in three upper levels (from 5 to 200 cm) the perylene was absent. The highest concentration of perylene was found in moss peat (*Bryaleti)*.

In Sychła bog the total concentration of anthropogenic PAHs was similar in all peat samples through the stratigraphic profile, varied in the narrow range (135-166 ng/g). The concentration of perylene was none in surface level, small (65 ng/g) in medium level and very high 1141 ng/g in the bottom level of deposit.

A noticeably high concentration of anthropogenic PAHs (2768 ng/g) was found in the surface layer of peat collected from Bruch bog. The other layers of peat were characterised by much smaller concentration (92-160 ng/g) of anthropogenic PAHs. The content of perylene was very low in all investigated samples collected from this bog.

The concentrations of Pahs with different numbers of ring are presented in Figure 1.
In all peat samples from Gązwa and Sychła raised bogs were dominated 3-ring and 4-ring PAHs. Five-ring and 6-ring PAHs only occur in top layers of peat bog Bruch and this is connected with very high air pollution in this Region of Poland.

Conclusions

1.The very high content of anthropogenic Pahs was found in the surface level of peat deposit in raised-bog Bruch, what suggest the great anthropogenic pollution of this area.

2. The content of perylene was higher in bottom layers of peat deposits than in surface ones.

3. The highest content of perylene was found in wooden peat (*Pineti)*. This probably due to intensive biotransformation of perylene precursors.

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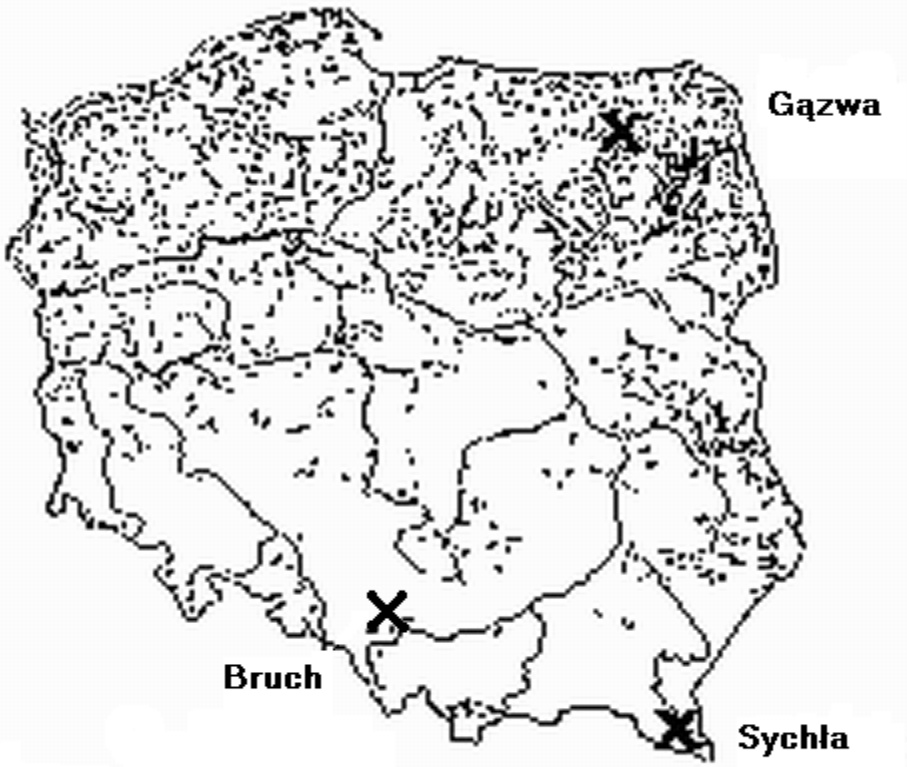

Figure 1: Main peat bogs in Poland and localization of the study areas

SITE	Genus of peat	Depth of peat [cm]	Acenaphtylene	Acenaphthene	Fluorene	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Benzo[a]anthracene	Chrysene	Benzo[b]fluoranthene	Benzo[k]fluoranthene	Benzo[e]pyrene	Benzo[a]pyrene	Indeno[1,2,3-cd]pyrene	Dibenzo[ah]anthracene	Benzo[ghi]perylene	The sum of PAHs	Perylene
GĄZWA	ers	005-050	0	10	20	68	0	18	10	0	19	23	0	0	0	0	0	0	168	0
	car	050-090	0	0	7	14	54	0	13	7	0	0	0	0	0	0	0	0	95	0
	eus	150-200	0	8	16	49	0	11	6	0	0	0	0	0	0	0	0	0	90	0
	ers	300-360	0	10	12	35	0	9	6	0	0	0	0	0	0	0	0	0	72	351
	bry	500-540	0	14	14	37	0	7	0	0	0	0	0	0	0	0	0	0	72	631
	cab	550-600	0	7	10	34	0	8	4	0	0	0	0	0	0	0	0	0	63	272
	car	605-650	0	6	11	36	0	10	4	0	0	0	0	0	0	0	0	0	67	121
SYCHLA	ers	020-060	11	7	18	62	3	19	10	0	5	0	0	0	0	0	0	0	135	0
	ers	110-150	5	13	27	82	4	19	10	0	6	0	0	0	0	0	0	0	166	65
	pis	160-200	3	11	20	73	4	18	10	0	5	0	0	0	0	0	0	0	144	1141
BRUCH	eus	005-025	5	9	23	349	20	453	264	97	325	287	171	182	113	253	390	178	2768	17
	ers	070-120	0	2	7	48	2	11	5	0	3	0	0	14	0	0	0	0	92	0
	ers	160-185	0	1	4	33	1	7	3	0	0	0	0	0	0	0	0	18	67	7
	gyttja	185-205	0	3	14	98	4	20	8	0	2	0	0	0	0	0	0	11	160	15

Table 1: Concentrations of 17 PAHs in the peat samples (ng g^{-1})

The percentage content of 3-ring, 4-ring, 5-ring, 6-ring in peat samples