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Fossil fuel compounds from fly dust in recent organic matter of southern Poland peats

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ABSTRACT

Several samples of peat from 6 bogs located in southern Poland were investigated for occurrence and distribution types of biomarkers present in their extractable organic matter fraction. It was found that there are inputs from two different sources of organic compounds differing in their characteristics and origin: (1) recent immature peat organic matter deposited *in situ* which is the source of all polar functionalized compounds, most of *n*-alkanes, and acyclic isoprenoids, and (2) mature fossil fuels, most probably bituminous coals from the Upper Silesia Coal Basin of vitrinite reflectance equivalent values of 0.9–1.1%. The latter compounds were most probably transported with fly ash to bogs from nearby settlements utilizing such fuel in domestic ovens. This group includes pentacyclic triterpenoids (hopanes and moretanes), minor amounts of *n*-alkanes, and numerous alkyl naphthalenes and alkyl phenanthrenes. All these compounds show distributions and values of geochemical ratios characteristic for mature organic matter confirming there *ex situ* origin.

1. Introduction

Peat is defined as immature terrestrial sedimentary organic matter, mostly of the Holocene age (Keddy, 2010). It is ranked as a fuel of the lowest coalification stage being at the beginning of diagenesis. Total peat resources of the world are roughly estimated at over 1000 billion tons (dry weight), covering some 275 ← 10^6 ha (2.7% of the land surface of the earth). The richest deposits occur in the Northern Hemisphere, in the temperate boreal climate, but they also can be found in the other climatic zones, from arctic to tropical (Twardowska et al., 1999; Lappalainen, 1996). In Poland the peatland total area is estimated to be about 1.3×10^6 ha, with peat resources have been estimated as 18×10^9 m^3. These deposits are located in three provinces of Poland: the southern Baltic seashore province of high-moor peatlands; northern Poland and Polish–northern German provinces of low-moor and high-moor peatlands (Ilnicki, 2002). The database developed by the Institute of Land Reclamation and Grassland Farming in Falenty, Poland, currently comprises 50.807 peat bogs, predominantly (82.5%) of the low-moor type.

1.1. Peatlands as natural archives

Peatlands belong to ecosystems most sensitive to environmental changes. Their sediments have registered and stored the history of changes which occurred during their several thousands of years of functioning as a kind of natural archives. This comes from the way of its formation by accumulation of primary organic material with only limited decomposition. Peat ordered stratigraphy allows to investigate the ways of peat accumulation, biological sources of organic material, sedimentary conditions and its subsequent changes in biogeochemical reactions.

Since the end of 19th century they have became an object of scientific research in the regard of changes in shifts in plant communities, or changes in climatic and hydrological conditions. This is documented by works concerning moors in Germany (Weber, 1899) or Scandinavia (Sernander, 1892). Investigations of well preserved animal and plant macro- and microfossils such as pollen grains, plant macro remains, frustules of diatom and Testacea or remains of insects and crustaceans are commonly applied to reconstruct changes occurring in the environment, both natural and caused by human activity (Bindler, 2006). Moreover, peatlands, having the wide geographical distribution, with most of them located in lands of the northern hemisphere, where most of heavy industry is also located, can be applied as spatial and temporal records of the industrial pollution (e.g. Jones and Hao, 1993; Brännvall et al., 1997; Weiss et al., 1997; West et al., 1997; Twardowska et al., 1999). Atmospheric contaminants have been deposited there in wet or dry deposition since the Industrial Revolution (ca 1985) (Renberg et al., 2001). For more than 30 years also geochemistry has been included into the range of research methods to document changes in atmospheric pollution (Scheffler, 2004; Bindler, 2006). Up to now the most of investigations concentrated mainly on occurrence of various metals, their distribution and

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concentrations in peats related to natural processes and human-induced changes in such metal cycling as mercury, lead, strontium, zircon, titanium, or zinc (e.g. Brännvall et al., 1997; Shotyk et al., 1997; Weiss et al., 1997; West et al., 1997; Twardowska et al., 1999; Renberg et al., 2001; Syrovetnik et al., 2004; Ettler et al., 2008). Also changes in sulphur concentration has been applied to reconstruct its historical changes in emission to the atmosphere (Coulson et al., 2005).

However, in many of these studies the assumption is made that elements, once absorbed in peat organic matter, are immobile, being strongly bound to the organic macromolecule. Based on this, it was concluded that changes in the element's accumulation or sometimes concentrations are caused by changes in atmospheric pollution input (Biester et al., 2012).

Ombotrophic bogs built of different *Sphagnum* species, are considered the best for investigation of contaminants from atmospheric deposition (Clymo et al., 1990; Jones and Hao, 1993; Berset et al., 2001). This is due to such their features as the absence of input contaminants from local groundwater and surface waters, high hydrophobic sorption capability, weakly acidic interstitial waters and low oxygen level leading to low bacterial decay of anthropogenic organic contaminants (Berset et al., 2001).

It is only recently that also organic compounds transported *ex situ* to the peat have been investigated. They include a wide variety of compounds, both emitted in fossil fuel and biofuel combustion or other industrial processes (Bojakowska et al., 2000; Berset et al., 2001). However, comparing to numerous references concerning metal distributions in peat, research of organic pollutants in peat organic matter is rather limited.

Polycyclic aromatic hydrocarbons are the commonest compounds investigated in such research due to their well known high carcinogenic activity (White et al., 1998; Pufulete et al., 2004). These ubiquitous persistent organic contaminants are formed in industrial processes, incomplete combustion of various fuels, natural fires, oxygenation of natural products present in plants such as resins or in thermal evolution of organic matter in sediments (Simoneit, 1998; WHO, 1998). Mechanisms of their formation, occurrence and profiles are commonly studied in atmospheric particulate matter (e.g. Rehwagen et al., 2005; Wu et al., 2006; Tham et al., 2008; Kim et al., 2012), soils (e.g. Aamot et al., 1996; Trapido, 1999; Ping et al., 2007), aquatic sediments (e.g. Pereira et al., 1999; Chen et al., 2007; Das et al., 2008; Wang et al., 2011), and peats (e.g. Bojakowska et al., 2000; Berset et al., 2001; Tam et al., 2001; Malawska et al., 2006; Zaccone et al., 2009; Pontevedra-Pombal et al., 2012) all over the world. The PAHs profiles related to their source were also investigated to determine characteristic features of their distributions caused by material combusted (e.g. Zou et al., 2003; Kozielska and Konieczyński, 2007).

Bojakowska et al. (2000) applied distributions of polycyclic aromatic hydrocarbons (PAHs) in peat form several bogs trying to differentiate anthropogenic and natural distributions of these compounds, depend on bog distance from the nearest settlements (i.e. pollution sources). According to Berset et al. (2001) the highest PAHs concentrations are found at depth 20–25 cm, with concentrations decreasing with depth. Several authors reported changes in historical trends of organic contaminants in peat. Pontevedra-Pombal et al. (2012) investigated PAHs profiles in pre-industrial bogs of the Iberian Penninsula. They indicated that anthropogenic PAHs emitted in biomass burning related to the Medieval expansion of the agricultural frontier show a predominance of low molecular weight PAHs (<252 g/mol) in distribution whereas high molecular weight PAHs (>252 g/mol) predominated in peats deposited

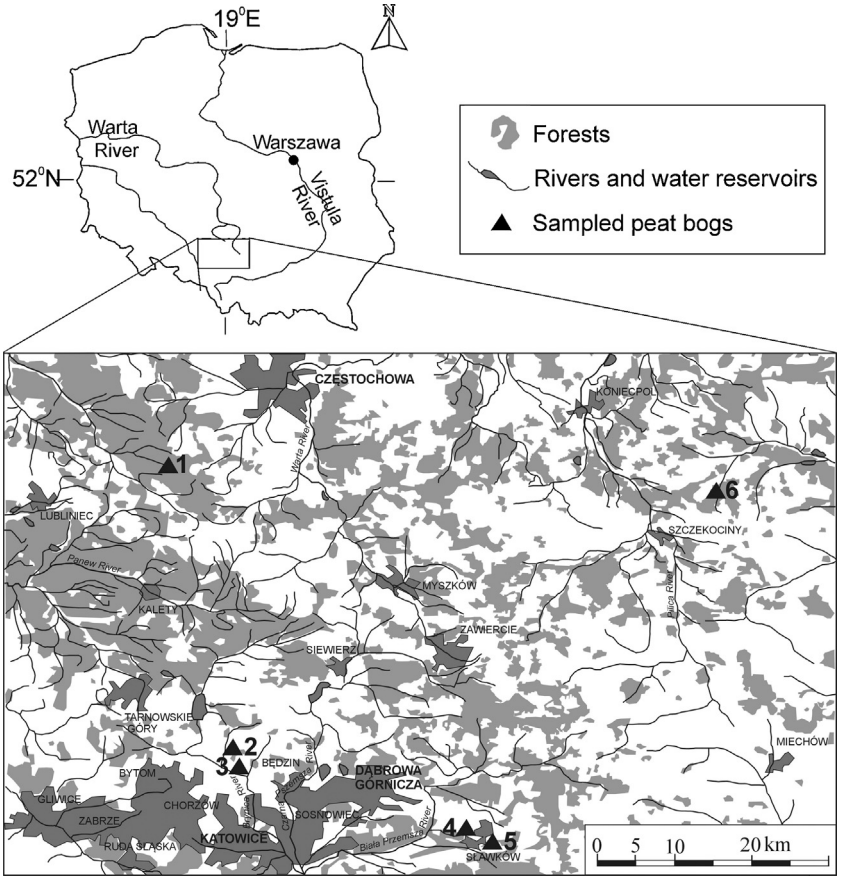

Fig. 1. Locations of sampled peat bogs. (1) Olszyna, (2) Rogoźnik, (3) Wojkowice, (4) Sławków 1, (5) Sławków 2, (6) Mękarzów.