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Preservation of coal-waste geochemical markers in vegetation and soil on self-heating coal-waste dumps in Silesia, Poland

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ABSTRACT

Occurrence and distributions of geochemical markers on vegetation and in soils covering two self-heating coal waste dumps were investigated with gas chromatography-mass spectrometry (GC–MS) and compared with those of bitumen expelled on the coal waste dump surface. Presence of biomarkers, alkyl aromatic hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), and such polar compounds as phenols indicate that components of self-heating coal wastes indeed migrate to soils and plants surface and their characteristic fingerprints can be applied in passive monitoring to investigate migration of contaminants from self-heating coal wastes. Moreover, results allow to discriminate between the Upper- and Lower Silesian coal basins, notwithstanding value shifts caused by heating. Mechanisms enabling the migration of geochemical compounds into soils include mixing with weathered coal-waste material, transport in gases emitted due to self-heating and, indirectly, by deposition of biomass containing geochemical substances. Transport in gases involves mostly lighter compounds such as phenols, methylnaphthalenes, methylbiphenyls, etc. Distributions and values of geochemical ratios are related to differences in their boiling temperatures in the case of lighter compounds but preserve geochemical features in the case of heavier compounds such as pentacyclic trierpanes.

1. Introduction

Over the last 25 years, vegetation has been used as a passive sampler of persistent organic pollutants (POPs), among them polycyclic aromatic hydrocarbons (PAHs), volatile organic compounds (VOCs), magnetic particles, and heavy metals emitted to the air by traffic and industry (e.g., Franzarig and van der Eerden, 2000; Piccardo et al., 2005; Alfani et al., 2005; Lehndorff et al., 2006; Lehndorff and Schwark, 2008; De Temmerman et al., 2009; Abril et al., 2014). Plants exposed to dry- and wet pollutants over extended periods of time can act as sinks for inorganic- and organic compounds, accumulating them in their lipid-rich cuticles. It has been estimated that significant amounts of atmospheric PAHs are scavenged by plants acting as natural air scrubbers (Wagrowski and Hites, 1997). Most models of plant POP uptake are based on the assumption that it occurs through the lipophilic cuticle, with root uptake of organic compounds from contaminated soil considered sufficiently low to be ignored (Edwards, 1986; Cousins and Mackay, 2001). However, such factors as physical properties and partitioning of POPs between vapour phase and particulate matter, climate (temperature, wind speed), dry- versus wet deposition, POP degradation and removal from plant tissues may influence results (Barber et al., 2004; Boll et al., 2008).

Significant factors bearing on the scavenging efficiency of POPs are physiological features of leaves such as morphology and cuticle chemistry, number and distribution of stomata, and the presence or absence of hairs (Howsam et al., 2000; Barber et al., 2004). Thus the ability to scavenge and retain POPs varies for different species. Plants and their parts used in biomonitoring include mosses (Ötvös et al., 2004), lichens (Augusto et al., 2010, 2013), evergreen leaves such as *Quercus ilex* (Alfani et al., 2005), deciduous trees (Howsam et al., 2000), grasses (Meharg et al., 1998), and most commonly, due to their efficiency in pollutant entrapment and common occurrence, conifer needles (Lehndorff and Schwark, 2004; Piccardo et al., 2005; Wang et al., 2005; Lehndorff and Schwark, 2009; Augusto et al., 2010; Ratola et al., 2011). As plant morphology affects biomonitoring, results of PAHs recovery from different plant species and families have been compared to select

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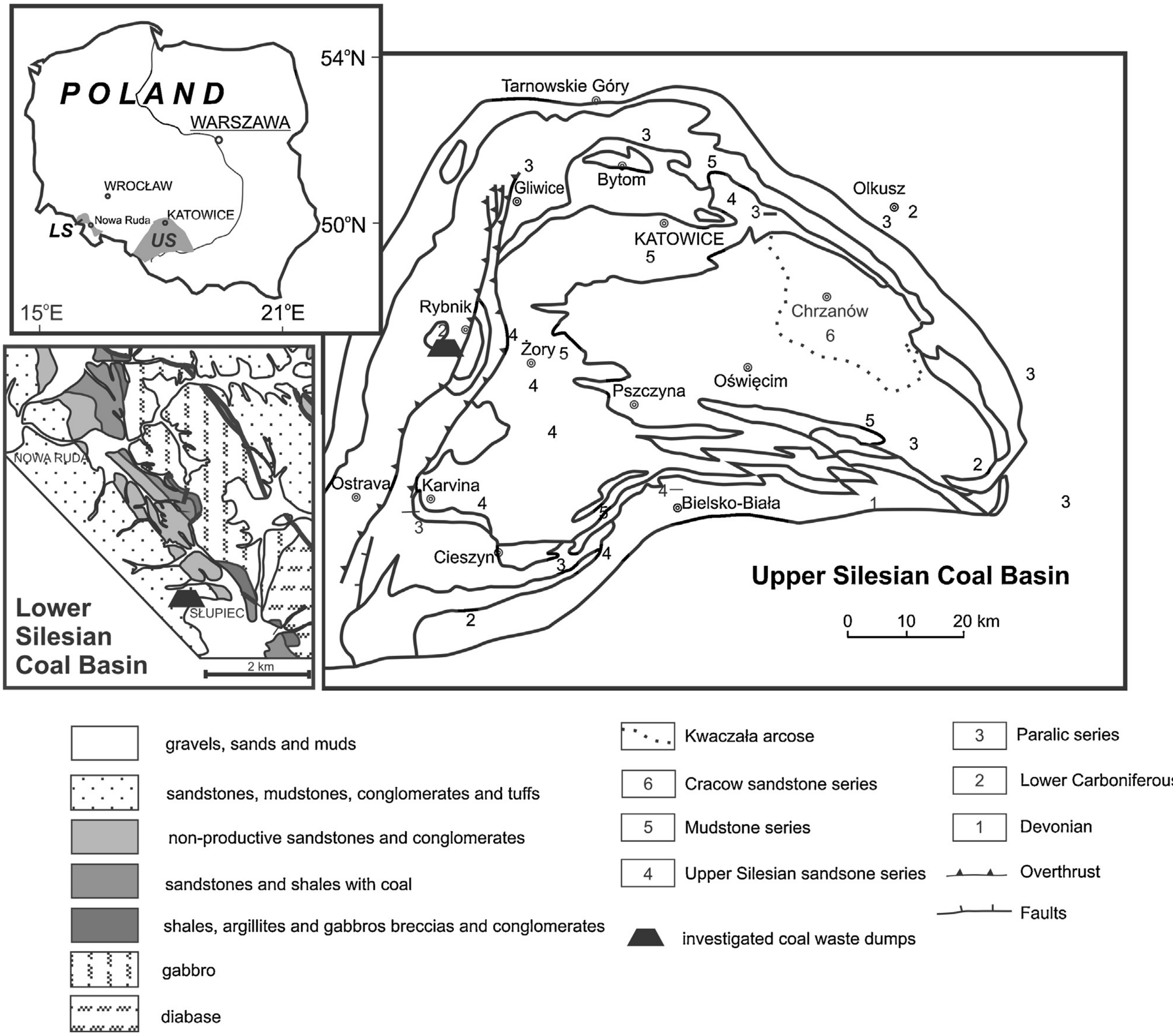

Fig. 1. The sketch of the geological formation of the Lower Silesian Coal Basin (LS) and Upper Silesian Coal Basin US (modified, after Gabzdyl 1994) with investigated dumps locations.

the best species for biomonitoring (e.g., Migaszewski et al., 2002; Augusto et al., 2010). Others have compared extraction methodologies (Tomaniová et al., 1998), and assessed PAHs destruction due to photolysis (Wang et al., 2005).

Despite the diagnostic potential of the method, biomonitoring with plants growing in urban- and industrial settings has concentrated mostly on unsubstituted PAHs to define their profiles in plants, spatial distribution, fate in the environment and rate of transfer to soils (Howsam et al., 2000; Lehndorff and Schwark, 2004; Piccardo et al., 2005; Augusto et al., 2010). Lehndorff and Schwark (2009) proposed the use of akyl PAHs monitoring to improve source identification. Significantly fewer studies have concerned chlorinated compounds such as dioxins and polychlorinated biphenyls (Ockenden et al., 1998; Welsch-Pausch and McLachlan, 1998; Kylin and Sjödin, 2003; Augusto et al., 2007).

In this research, the focus is on coal waste dumps located in two industrial- and highly urbanized regions in Poland, namely, Upper Silesia and Lower Silesia where intensive coal mining began over 150 years ago (Fig. 1; Ciesielczuk, 2015). In most of the dumps, self-heating processes are on-going (Fig. 2; Misz-Kennan, 2010; Misz-Kennan et al., 2013). As a consequence, a variety of gaseous-, liquid- and solid contaminants are produced (Finkelman, 2004; Kuenzer et al., 2007; Ribeiro et al., 2012). One of the products formed in oxygen-depleted conditions is bitumen with chemical features similar to those of coal tars – pyrolysates (Misz-Kennan and Fabiańska, 2010, 2011; Rein, 2011). Commonly, it permeates dump surfaces above self- heating zones forming 'hot spots' with elevated surface temperatures that are characterized by high moisture levels, strong bitumen odour, crusts of mineral blooms around vents, and an absence of vegetation (Fig. 2a,b,e and f; Fabiańska et al., 2013a; Ciesielczuk et al., 2014). The range of organic pollutants emitted from these coal wastes is little known. Neither is it known how far they migrate nor the extent to which they may affect the environment and health.

In this research, the biomonitoring method is used to establish:

(a) Whether it can be successfully applied to monitor the surroundings of coal-waste dumps and self-heating products.
(b) What chemical compounds (if any) migrate from self-heating coal waste to plants and soils and if their profiles are indicative of contamination originating from coal waste.
(c) What changes occur in the distributions of geochemical markers during their transport and catchment in soil and in plant cuticular wax.