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Characterization and classification of complex PAH samples using GC–qMS and GC–TOFMS

Magnus Bergknut *, Kristina Frech, Patrik L. Andersson, Peter Haglund, Mats Tysklind

Environmental Chemistry, Department of Chemistry, Umeå University, SE-90187 Umeå, Sweden

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Abstract

The aim of this study was to compare the polycyclic aromatic hydrocarbon (PAH) contents in a number of complex samples, including soil samples from industrial sites, anti-skid sand, urban dust and ash samples from municipal solid waste incinerators. The samples were characterized by routine analysis of PAHs (gas chromatography–quadrupole mass spectrometry) and gas chromatography–time of flight mass spectrometry (GC–TOFMS). Classification of the samples by principal component analysis (PCA) according to their composition of PAHs revealed that samples associated with traffic and the municipal incinerator formed homogeneous clusters, while the PAH-contaminated soils clustered in separate groups. Using spectral data to resolve co-eluting chromatographic peaks, 962 peaks could be identified in the GC–TOFMS analysis of a pooled sample and 123–527 peaks in the individual samples. Many of the studied extracts included a unique set of chemicals, indicating that they had a much more diverse contamination profile than their PAH contents suggested. Compared to routine analysis, GC–TOFMS provided more detailed information about each sample and in this study a large number of alkylated PAHs were found to be associated with the corresponding unsubstituted PAHs. The possibility to filter peaks according to different criteria (e.g. to include only peaks that were detected in the analysis of another sample) was explored and used to identify unique as well as common compounds within samples. This procedure could prove to be valuable for obtaining relevant chemical data for use in conjunction with results from various biological test systems.

Keywords: Soil; Anti-skid sand; Urban dust; Traffic; Creosote; Peak deconvolution; PCA

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) comprise a large group of organic contaminants that are formed and emitted as a result of incomplete combustion of organic material. PAHs are composed of two or more fused benzene rings and contain only carbon and hydrogen atoms. However, alkyl-substituted PAHs, heterocyclic PAHs containing nitrogen, sulfur and oxygen, and oxidation products of PAHs (oxy-PAHs) including PAH ketones, PAH quinones, and hydroxylated PAHs are often grouped together with the unsubstituted PAHs and are then referred to as polycyclic aromatic compounds (PACs). Routine analysis is often limited to the 16 PAHs regarded as priority pollutants by the US EPA. However, over a hundred PACs have been identified in various matrixes, including contaminated soil (Mueller et al., 1989; Meyer et al., 1999; Lundstedt et al., 2003), sediments (Fernandez et al., 1992), diesel exhaust (Choudhury, 1982), airborne particulates (Casellas et al., 1995; Allen et al., 1996, 1997), emissions from wood combustion (Hedberg et al., 2002), and ash from municipal waste incinerators (Akimoto et al., 1997a,b). From a risk assessment perspective, it is important to consider all of the compounds and the biological effects of a complex mixture found in environmental matrixes, such as soils contaminated with PACs. It is however difficult to identify and quantify all of the PACs in such complex mixtures and most methods for analyzing

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* Corresponding author. Tel.: +46 90 786 93 39; fax: +46 90 12 81 33.
E-mail address: magnus.bergknut@chem.umu.se (M. Bergknut).

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complex PAC samples are based on fractionation of the samples using liquid chromatography or similar strategies. Analysis is often performed using high performance liquid chromatography (HPLC) coupled with fluorescence or UV detectors, or using gas chromatography (GC) coupled to mass, C-, S- or N- selective detectors (Hale and Aneiro, 1997). By using a chromatographic technique it may however become difficult to maintain adequate peak separation as the number of compounds increase. One solution to this is to use peak deconvolution, i.e. use spectral data to resolve co-eluting chromatographic peaks.

The aim of the study presented here was to compare a number of complex PAH-containing samples, including samples from current and former industrial sites, anti-skid sand, urban dust and ash samples from municipal solid waste incinerators. The samples were characterized by routine analysis of PAHs using gas chromatography–quadrupole mass spectrometry (GC–qMS) in the selected ion monitoring (SIM) mode and by comprehensive analysis using gas chromatography–time of flight mass spectrometry (GC–TOFMS). GC–TOFMS was used for the extensive characterization since it can provide a full mass spectrum for each chromatographic point (thus eliminating spectral skewing) and high sampling rates (up to 500 spectra/second), making TOFMS data very suitable for peak deconvolution. Data from all of the samples were evaluated by principal component analysis (PCA; Wold et al., 1984, 1987). PCA visualizes dominant patterns and trends in datasets and has previously been used for classifying, assessing sources, and evaluating the composition of diverse PAH-containing samples (Yunker et al., 1996; Naes and Oug, 1997; Yunker et al., 1999; Arzayus et al., 2001; Carlon et al., 2001; Wingfors et al., 2001). The data was evaluated focusing on (i) similarities and differences in the samples chemical composition, (ii) the relationships between the samples contamination profiles and source(s) of contamination, and (iii) similarities and differences between the data obtained by the routine and comprehensive analyses.

2. Materials and methods

2.1. Chemicals

Silica gel 60 (0.063-0.200 mm) was purchased from Merck (Darmstadt, Germany), rinsed with methanol and dichloromethane, activated for 48 h at 130 °C and deactivated with 10% water prior to use. Sodium sulphate, also from Merck, was activated for 48 h at 550 °C. Celite 545 was obtained from VWR Prolabo (Umeå, Sweden) and cleaned by Soxhlet extraction using toluene prior to use. All solvents used were of HPLC grade from Merck or J.T. Baker (Deventer, Holland). A [$^2H_{10}$]fluoranthene (30 µg/g in toulene) syringe standard was prepared using a solution supplied by Cambridge Isotope Laboratories (Andover, MA, USA). A NIST (Gaithersburg, MD, USA) SRM 2260 certified reference standard (7–10 µg/g in toluene) was used for quantification, containing: naphthalene, 1-methylnaphthalene, biphenyl, 2,6-dimethylnaphthalene, acenaphthylene, acenaphthene, 2,3,5-trimethylnaphthalene, fluorene, phenanthrene, anthracene, 1-methylphenanthrene, fluoranthene, pyrene, benz[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*e*]pyrene, benzo[*a*]pyrene, perylene, indeno[1,2,3-*cd*]-pyrene, dibenz- [*a,h*]anthracene, and benzo[*ghi*]perylene.

2.2. Samples and sample extraction

PAH-contaminated soil was collected from former gasworks and wood preservation sites. A soil sample from a current coke production facility was also collected. Each sample was passed through a 2 mm sieve and the <2 mm fraction was collected and used in the analysis. The water content (overnight incubation at 105 °C) and organic matter content (6 h at 550 °C) ranged between 0.5–12.9% and 0.9–14.7% respectively. A reference material, CRM 103-100, Lot RQ 103 of PAH-contaminated soil (Resource Technology Corp., RTC, Laramie, WY, USA), was also included and run in triplicate. Ash, fly ash and soot from municipal solid waste incinerators (Umeå and Sundsvall, Sweden) were kindly donated by Lisa Lundin and Stellan Marklund, of the Environmental Chemistry section, Umeå University. Anti-skid sand was collected in the springtime with the assistance of the Swedish Road Administration (SRA) and included samples from roads, trenches running alongside the roads and storm drains collecting run-off from the roads. Samples of two reference sands, collected from remote areas (Röbäck, Hössjö, Sweden), were also included in the study. Dust from urban areas with high volumes of traffic was collected from horizontal surfaces, including window-ledges, walls, and low roofs in the vicinity. Both the urban dust and the anti-skid sand samples were collected in, or close to, the city of Umeå, Sweden, which has a population of about 110 000 people. Wet samples were air-dried for 24 h prior to extraction.

All samples were extracted by pressurized liquid extraction (PLE) using a Dionex ASE 200 accelerated solvent extractor (Dionex, Sunnyvale, CA, USA) equipped with 11 ml stainless steel extraction cells. The extraction procedure included in-cell clean-up, as described by Ong et al. (2003), using 4 g of silica gel 60 on a cellulose filter placed at the bottom of each cell. For most extractions 1 g of sample was then added, and the remaining part of the cell was filled with sodium sulphate. However, for extractions of samples from the municipal incinerators, 0.5 g of each sample mixed with 0.5 g Celite 545, was used instead, and a thin layer of Celite 545 was placed between the sample and the silica gel. A thin layer of Celite 545 was also used for the dust samples. Extraction was performed using a 1:1 (v:v) mixture of *n*-pentane and dichloromethane, and the following PLE program: 7 min thermal equilibration, during which the cells were heated to 150 °C and pressurized to 4 MPa, followed by 7 min static extraction, a 100% flush with fresh solvent (10 ml), and finally a 60 s purge with gaseous nitrogen. Laboratory blanks ($n = 3$) were prepared by