

PAHs and nitrated PAHs in air of five European countries determined using SPMDs as passive samplers

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Received 5 August 2004; received in revised form 20 October 2004; accepted 10 November 2004

Abstract

The gas phase polycyclic aromatic hydrocarbons (PAHs) and nitro-PAHs in the atmosphere of five European countries (Austria, the Czech Republic, Poland, Slovakia and Sweden) were measured simultaneously during two 21-day passive sampling campaigns using semipermeable membrane devices (SPMDs). SPMD samplers, consisting of a pair of SPMDs covered by a metal umbrella, were deployed at 40 locations ranging from remote and rural to urban and industrial, at a similar time during each of the two sampling campaigns (autumn 1999, except in Poland, winter 1999, and summer 2000). The total amounts of PAHs and nitro-PAHs found in the SPMDs ranged between $5.0\text{--}1.2 \times 10^3$ and $1.1 \times 10^{-3}\text{--}4.0 \text{ ng SPMD}^{-1} \text{ day}^{-1}$, respectively. The measured environmental sampling conditions were similar between sites and, thus, the variations in the SPMD data reflected the spatial differences in gas phase concentrations of nitro-PAHs and PAHs within and between countries. The gas phase concentrations of nitro-PAHs and PAHs found in East Europe (Slovakia, the Czech Republic and Poland 1999) were 10 times higher than those measured in Sweden, Austria and Poland in 2000. In each country, the levels of PAHs and nitro-PAHs differed by one–three orders of magnitudes amongst sampling sites. The highest within-country spatial differences were found in Poland where levels of PAHs and nitro-PAHs were about one and two orders of magnitudes, respectively, higher in winter 1999 than in summer 2000, probably due to increasing emissions of coal combustion for residential heating. Differences in PAH-patterns between sites were visualized by the multivariate projection method, principal component analysis (PCA). However, no specific source patterns were found, probably since imissions rather than emissions were measured, so the PAHs detected at many sites originated from multiple sources.

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Keywords: Air monitoring; Diffusive sampling; PCA; Spatial variation; Analysis

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic, moderately to highly lipophilic pollutants that are widely distributed in the environment. They are present in the atmosphere due to emissions from gasoline- and diesel-powered vehicles, municipal and commercial incinerators, residential heating systems that combust fuels such as coal, wood, gas and oil, various industrial processes and volatilization from polluted grounds. The main concern of PAHs is that some PAHs are reported to have carcinogenic properties that are associated with increasing size of the molecule (species with compounds of four or more benzene rings being especially carcinogenic) and their metabolic transformation to reactive dihydrodiol epoxides. Nitrated PAHs (nitro-PAHs) were first detected in atmospheric particulate matter in the 1970s (Pitts et al., 1978). The main concerns regarding these compounds are that many of them are reported to have direct mutagenic activity and carcinogenicity (Durant et al., 1996; Tokiwa et al., 1994). Nitro-PAHs are present in the atmosphere, originating from both primary sources, such as emissions in diesel vehicle exhaust (Bamford et al., 2003; Nielsen, 1984), and reactions of the parent PAHs in the atmosphere. Gas phase reactions of the parent PAHs are initiated by hydroxyl (OH) radicals during the day and by nitrate (NO₃) radicals (in the presence of NO_x) during the night (Arey et al., 1986; Atkinson et al., 1987; Atkinson and Arey, 1994; Nielsen, 1984). Parent PAHs associated with aerosols react with N₂O₅ or HNO₃ to produce nitro-PAHs (Kamens et al., 1990; Nielsen, 1983). Different nitro-PAH isomers are formed in the gas phase reactions (radical-initiated reactions) than those formed via particle phase reactions or emitted from primary sources (electrophilic nitration) (Atkinson et al., 1987; Atkinson and Arey, 1994; Feilberg et al., 1999, 2001; Gupta et al., 1996; Nielsen, 1983, 1984). Feilberg et al. (1999) analyzed diesel exhaust for the two nitronaphthalenes 1-nitronaphthalene (1-NN) and 2-nitronaphthalene (2-NN) and found only 1-NN in it, whereas Atkinson et al. (1987) found that gas phase reactions between naphthalene initiated by OH radicals produced 1-NN and 2-NN in nearly equal abundance. Concentration ratios can therefore be used to assess whether direct emissions or gas phase reactions have produced atmospheric nitro-PAHs (Bamford and Baker, 2003; Feilberg et al., 2001). In the atmosphere, both PAHs and nitro-PAHs display a wide range of gas–particle partitioning characteristics. PAHs with two or three rings, which have relatively low log *K*_{OA} values, are mainly associated with the vapor phase, 4-ring PAHs occur in both the gas and particle phases, whereas PAHs with five rings or more, which have high log *K*_{OA} values, are mostly bound to particles. Dimashki et al. (2000) measured nitro-PAHs in the atmosphere of

two cities and detected 2-ring nitronaphthalenes only in the vapor phase, the 3-ring nitro-PAH 9-nitroanthracene (9-NA) in both the gas and particle phases, whereas nitro-PAHs with four benzene rings or more (1-nitropyrene (1-NP), 2-nitrofluoranthene (2-NF) and 7-nitrobenz[*a*]anthracene (7-NBa)) were mainly bound to particles. Further, Feilberg et al. (1999) studied the gas–particle partitioning of 2-ring nitro-PAHs in a chamber and found that these compounds partition mainly to the gas phase. Nitro-PAHs appear to have lower vapor pressure than PAHs with corresponding numbers of benzene rings in their molecular structure since the 2-ring nitro-PAHs 1-NN and 2-NN elute between the 3-ring PAHs fluorene and phenanthrene from a DB-5 gas chromatographic column (J&W).

When measuring the atmospheric distribution of organic pollutants such as PAHs and nitro-PAHs at multiple sites on a global scale, passive air samplers are preferred to conventional active air samplers since they do not require electricity or maintenance and are less expensive. Passive air samplers can also be exposed for a long period of time and time-weighted average (TWA) concentrations can be determined. Many studies have used plant samples, e.g. bark (Simonich and Hites, 1995), lichen or pine needles (Kylin and Sjödin, 2003; Hellström et al., 2004; Ockenden et al., 1998b; Tremolada et al., 1996), to monitor ambient air concentrations of organic pollutants on a large scale, assuming that their spatial pollution distribution in the plants and the atmosphere will be closely related. However, the concentration capacity and sampling rate of plant tissues vary with the plant species and age, location and season. Therefore, these kinds of plant data are subject to several uncertainties, which complicate their interpretation and limit the potential of plants as monitoring tools. For this reason, man-made passive air samplers are preferred, despite their additional costs and that they have to be deployed, since the variability of samplers at different locations is low, and the sampling period can be controlled. In 2004, for instance, Jaward et al. (2004a, b) used man-made passive samplers to simultaneously monitor the atmospheric distribution of PAHs, polychlorinated naphthalenes (PCNs), polychlorinated biphenyls (PCBs), polybrominated diphenylethers (PBDEs), and organochlorine pesticides across Europe in a defined time period.

Semipermeable membrane devices (SPMDs) are passive samplers that have been used in spatial surveys of the atmospheric gas phase concentrations of organic pollutants by, for instance, Lohmann et al. (2001) and Meijer et al. (2003). The SPMD sampling rate (*R*_S) is affected by the physicochemical properties of the compound sampled. Furthermore, Söderström and Bergqvist (2004) found that high wind speeds/turbulences affect the amounts sequestered by the SPMDs. Chemicals bound to particles or aerosols can be trapped

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