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Particulate-bound polycyclic aromatic hydrocarbon sources and determinants in residential homes[☆]

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ABSTRACT

Human exposure to polycyclic aromatic hydrocarbons (PAHs) in indoor environments can be particularly relevant because people spend most of their time inside buildings, especially in homes. This study aimed to investigate the most important particle-bound PAH sources and exposure determinants in $PM_{2.5}$ samples collected in 19 homes located in northern Italy. Complementary information about ion content in PM_{10} was also collected in 12 of these homes. Three methods were used for the identification of PAH sources and determinants: diagnostic ratios with principal component and hierarchical cluster analyses (PCA and HCA), chemical mass balance (CMB) and linear mixed models (LMMs). This combined and tiered approach allowed the infiltration of outdoor PAHs into indoor environments to be identified as the most important source in winter, with a relevant role played by biomass burning and traffic exhausts to be identified as a general source of PAHs in both seasons. Tobacco smoke exhibited an important impact on PAH levels in smokers' homes, whereas in the whole sample, cooking food and natural gas sources played a minor or negligible role. Nitrate, sulfate and ammonium were the main inorganic constituents of indoor PM_{10} owing to the secondary formation of ammonium sulfates and nitrates.

1. Introduction

The effects of particulate matter (PM) on human health are well known. Because people spend 80–90% of their time in confined environments (Schweizer et al., 2007), indoor residences greatly contribute to total daily exposure, and indoor PM exposure is a relevant health concern. Thus, indoor PM contamination is a matter of public health concern with well-established impacts (WHO, 2014), and the high toxicity of indoor PM has been investigated (Oeder et al., 2012). Different sources may contribute to the increase in PM concentrations indoors, including infiltration from outdoors, cooking, tobacco smoke, human activities, wood burning, and indoor photochemistry (Urso et al., 2015). Furthermore, some adverse health effects arising from indoor exposure can be strictly correlated to the chemical composition of PM, which contains classes of hazardous compounds—such as polycyclic aromatic hydrocarbons (PAHs)—generated by the incomplete combustion or pyrolysis of organic substances.

PAHs are semivolatile compounds originating from natural sources (volcanism and wildfires) and anthropogenic combustion of wood, waste and fossil fuels, some of which have been recognized as human carcinogens (IARC, 2010; Kim et al., 2013) and priority indoor air pollutants (WHO, 1998, 2010). When present in the atmosphere, PAHs with low molecular weights tend to occur in the gas phase, and those with high molecular weights occur as particulates. Gas-phase PAHs are less carcinogenic, and their equivalent toxicity, calculated with respect to benzo(a)pyrene (BaP), is practically negligible with respect to that of particle-bound PAH (Gregoris et al., 2014). Thus, the quantification of particle-phase PAHs is a key aspect in the assessment of health risks for humans exposed to air pollution.

As a general rule, the identification of pollutant sources is crucial for risk management purposes and for developing effective policies and risk mitigation plans for the protection of public health. Among

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sources, the infiltration and penetration of PAHs of outdoor origin into indoor environments should be first considered. Outdoor air, influenced by emissions from vehicular traffic (Dunbar et al., 2001; Perrone et al., 2014; Slezakova et al., 2010), domestic heating (Marchand et al., 2004), oil refining, waste incineration (Harrison et al., 1996), industrial activities, asphalt production, agricultural burning of biomass, wood burning and combustion of heavy oils (Masiol et al., 2012), can also be an important source of PAHs in indoor environments. Among the typical indoor sources, second-hand tobacco smoke is one of the most relevant contributors to the increase of PAH concentrations indoors (Castro et al., 2011; Fromme et al., 2004), along with residential heating systems, particularly wood burning stoves and fireplaces (Gustafson et al., 2008; Ozgen et al., 2014; Piazzalunga et al., 2013a), some cooking procedures (Zhu and Wang, 2003), burning of natural gas (Mitra and Ray, 1995), and the use of candles (Derudi et al., 2012, 2014), incenses and insect repellents (Ohura et al., 2005). Other factors associated with increased indoor PAH levels are the floor level, owing to a vertical gradient of outdoor PAH concentrations (Jung et al., 2011), and the age of the house (Li et al., 2005; Ohura et al., 2005).

PAH source apportionment studies are quite common in outdoor environments but scarce on samples collected indoors. However, it is very important to focus on indoor air contaminants to better represent the real exposure of human populations because people spend most of their time in indoor work or life environments. In particular, residential homes are the most relevant environments in terms of time spent, especially for vulnerable populations such as infants, children and the elderly.

Recently, very high PAH exposure levels were reported in China (Duan et al., 2014), more than two orders of magnitude higher than the current levels in indoor environments of the EU and U.S. In Italy, homes were the microenvironments that most widely contribute to PAH exposure in Rome (>58% of daily time), followed by schools for children (Gariazzo et al., 2015), with indoor concentrations sometimes exceeding the EU limit for BaP in ambient air (Romagnoli et al., 2014).

Not only is BaP classified as carcinogenic to humans (group 1) by the International Agency for Research on Cancer, but also several other PAHs are classified as probably and possibly carcinogenic to humans, groups 2A and 2B, respectively (IARC, 2010). However, BaP has been widely used as a marker for the carcinogenic risk of PAH in ambient air and as the reference indicator for cancer risk estimates even for PAH mixtures, combining epidemiological risk assessments with data on exposure restricted only to BaP and a derivation of toxic equivalent factors (TEF) using bioassays or animal experiments (Bostrom et al., 2002). Estimations using accepted unit risk factors for chemical carcinogens showed that PAH can give an important contribution to the excess mortality and reduced life expectancy attributable to the exposure to urban air pollution (Harrison et al., 2004).

The present work is aimed to investigate sources of particulate-bound PAHs in residential homes and other possible factors associated with increased PAH levels indoors, to collect useful information for effective risk mitigation to protect public health.

2. Materials and methods

2.1. PM sampling

Twenty-four-hour $PM_{2.5}$ and PM_{10} samples were collected in the living rooms of homes located in the Province of Lodi (Northern Italy) by means of GK2.05 and GK2.69 samplers (BGI Inc., Waltham, MA, USA) during both summer 2007 and winter 2007–2008. Filters were kept at 20 °C for 48–96 h according to international standards and then weighed and stored at 3 °C before analysis. Thus, a limitation of this study could be the partial loss of some PAHs due to volatilization and/or oxidation processes that may have occurred during the conditioning of filters at 20 °C for gravimetric determination and subsequent storage at 3 °C. Detailed instrumental information is reported in Cattaneo et al., 2011. In this study, a subset of 29 homes was investigated, and the corresponding winter and summer samples were analyzed.

$PM_{2.5}$ samples were used for the analysis of PAHs, whereas PM_{10} samples were used for the quantification of the main ion content. In Supplementary Table S1, the identification code (ICH) for the 29 selected homes is reported together with the sample identification code (ICS). The information on ion content was available only for 12 of the 19 homes selected for PAH analyses.

Characteristics of the buildings, including location (e.g., proximity to roads, with corresponding traffic volumes, and industries) and heating/conditioning systems were recorded by means of a standardized checklist (Roulet et al., 2006). Furthermore, a time–activity diary was used for recording quantitative data about activities that could influence indoor PM levels (occupant number, HVAC operation time, number of cigarettes smoked, time spent cooking, cleaning activities, open windows, fireplace lit, etc.). More detailed information on the specific data collection using checklists and time–activity diaries is available in Urso et al., 2015.

2.2. Analytical techniques

Fifteen PAHs considered as “priority” for the U.S. EPA were selected for study: naphthalene (Nap), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benzo(a)anthracene (BaA), chrysene (Chr), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), BaP, dibenzo(a,h)anthracene (DahA), benzo(g,h,i)perylene (BghiP) and indeno(1,2,3,cd)perylene (IcdP) and were quantified in both winter and summer by HPLC–FLD according to ISO 16362:2005 (ISO, 2005).

An ultrasonic bath extraction for 15 min was performed using 10 mL of dichloromethane (×3 times), and a solution of 6-methylchrysene and 1-methylanthracene was added as an internal standard. The samples were then filtered using PTFE filters (0.45 μm porosity) and concentrated to known volumes under N_2 flow. Before the step of evaporation, 50 μL of dimethyl sulfoxide (DMSO) was added to retain in solution the lighter hydrocarbons (DMSO has a higher boiling temperature). The evaporation was then completed inside amber vials where CH_3CN was added up to a volume of 100 μL.

The analyses were carried out using a column Vydac 201 TP 52 (Alltech, USA; 25 cm × 4.6 mm internal diameter). The eluent was a mixture CH_3CN/water, using a gradient elution program (0–3 min = 50:50 CH_3CN–H_2O; 3–10 min = linear gradient up to CH_3CN only; 10–18 min = CH_3CN only; 18–20 min = linear gradient up to 50:50 CH_3CN–H_2O), with a total constant flowrate of 1.5 mL min^{-1}, and the sample injection volume was 20 μL. Three replicates were carried out for each standard during calibration to evaluate the precision of the method, which was determined to be less than 5%. The limit of detection (LOD) for each PAH has been calculated from the calibration curves and reported in Supplementary Table S2.

For the ion analysis, an extraction was performed introducing the filter in a test tube to which 3 mL of H_2O and 30 μL of methanol were added; the test tube was then placed in an ultrasonic bath for 1 h. Subsequently, the sample was centrifuged for 5 min, and the solution was filtered (PTFE, 0.45 μm porosity) and analyzed by ion chromatography (IC) through a conductivity detector.

Measurements of cationic (Na^+, K^+, Ca^{2+}, Mg^{2+} and $NH4^+$) and anionic (NO_3^-, SO_4^{2-}, Cl^-) species were carried out by using an