Seasonal variation of PAHs concentration and source attribution through diagnostic ratios analysis

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Abstract

An extensive monitoring campaign was conducted between November 2011 and July 2012 at schools, homes, offices and Regional air quality network stations in Rome, within the LIFE+ EXPAH Project. This study allowed to improve the knowledge of actual concentrations and percent composition of Polycyclic Aromatic Hydrocarbons (PAHs) over the city area. High concentrations of all PAH congeners were observed during winter colder periods, e.g. benzo[a]pyrene weekly average concentration reached 3.0 ng/m³, while much lower values were recorded in summer (<0.1 ng/m³), with seasonal variability (winter-to-summer ratios R) exceeding 10. This latter value was larger than that recorded for other pollutants including PM2.5 (R ~ 2.5). Also the percent composition of PAHs in particulates and the rates of diagnostic concentration ratios between selected congeners changed along the year, allowing to draw insights about the predominant sources and their respective importance. In particular, biomass burning for heating purposes was identified as the prevailing PAH source during winter and vehicle traffic in summer. Discrepancies between PAH profiles estimated from the emission inventory and observations were detected, with possible implication for modelling of PAH congeners.

1. Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) are carcinogenic and mutagenic pollutants formed during the incomplete combustion and pyrolysis of organic substances (Kameda et al., 2005; Manahan, 1994). Heavy PAH congeners are air contaminants bond to fine particulate matter for their prevailing mass fraction. Benzo[a]pyrene (BaP) has been recently classified as carcinogen for humans (group 1) by IARC (IARC, 2012). Some other PAHs have been identified in 2010 as probable (dibenz[a,h]anthracene and Dibenz[a,i]pyrene) or possible (benz[a]antracene, benzo[b,ij]fluoranthenes, benzo[c]phenanthrene and indeno[1,2,3-cd]pyrene) carcinogens for humans. Further possible health effects include intrauterine growth restriction, bronchitis, asthma and asthma-like symptoms, fatal ischemic diseases, neurodevelopmental problems (Bostrom et al., 2002; WHO, 2010).

Abbreviations: PAH, polycyclic aromatic hydrocarbon; DR, diagnostic concentration ratio; MW, molecular weight; BaA, benz[a]anthracene; BbF, benzo[b]fluoranthene; BjF, benzo[j]fluoranthene; BkF, benzo[k]fluoranthene; BghiF, benzo[ghi]perylene; BPE, benzo[ghi]perylene; BaP, benzo[a]pyrene; CH, chrysene; DBA, dibenz[a,h]anthracene; IP, indeno[1,2,3-cd]pyrene; PE, perylene.

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PAHs can be released in the atmosphere by either natural (e.g., volcanic activity and forest fires) or anthropogenic sources (industrial processes, traffic and residential heating, spill of petroleum products). (Baek et al., 1991; Zhang and Tao, 2009; Tsapakis and Stephanou, 2005; Mantis et al., 2005; Albiet et al., 2007). In highly urbanised areas, mobile sources and domestic heating are usually regarded as the largest contributors of PAHs, with diesel fuelled vehicles emitting more than gasoline fuelled cars (Ravindra et al., 2008; Zhang and Tao, 2009). The recent literature about airborne PAHs and their health effects highlights the importance of biomass combustion for heating and cooking (Fuller et al., 2014; Shen et al., 2013; Piazzalunga et al., 2013; Gianelle et al., 2013). PAH concentrations in urban areas are important due to the relevant population exposure potentially affecting densely inhabited areas (Gariazzo et al., 2015). Their fine characterisation has acquired great relevance to identify the principal sources of air quality and health impact, in the light of supporting planning of mitigation measures.

The European policies concerning PAHs are regulated by the Directive 2008/50/EC of the European Council and Parliament on Ambient Air Quality and Cleaner Air for Europe (EU, 2008), which includes the previous 4th European Daughter Directive on Air Quality (EU, 2004). Benzo[a]pyrene (BaP) is used to index the total load of PAHs in the air. The Directive establishes that the mean annual concentration of BaP cannot exceed 1 ng/m³ and reports that the long-term objective of 0.1 ng/m³ must be achieved by January 1, 2020. PAHs have been included in the United Nations Economic Commission for Europe (UNECE) Protocol on Persistent Organic Pollutants (http://www.unece.org/env/lrtap/pops_h1.html), which suggests to consider the following four indicator compounds into emission inventories: benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, and indeno[1,2,3-cd]pyrene.

Exposure to PAHs is of growing concern due to their ascertained presence even in remote regions, to the awareness of health risk associated with their exposure, and to their growing concentration trend detected in different areas of the world. The European Environmental Agency, in its 2014 report on the air quality (EEA, 2014), identified BaP as the only monitored pollutant showing increasing concentration in large parts of Europe. At this regard, the emissions of BaP have been calculated to raise by 21% in the EU-28 countries between 2003 and 2012. The positive emission trend is mainly attributed to solid fuels (e.g., wood) for domestic heating that has been favoured, during the latest years, by both incentives promoting the use of renewable energy and increasing costs of other energy sources. In this perspective, the use of source apportionment techniques appears crucial to identify the principal contributions to PAH release in the atmosphere of cities.

The PAH measurements performed in urban environment for regulatory purposes provide rather discontinuous data, which cannot support a thorough evaluation of urban population exposure. To fill this knowledge gap, the LIFE+ EXPAH project (Population EXposure to PAHs, 2010–2014; http://www.ispesl.it/expah/) has been finalised to assess the environmental and health effects induced by the emission, dispersion and transformation of PAHs in the urban environment of Rome and to evaluate the effectiveness of possible mitigation strategies. The EXPAH project experimental activities provided extensive PAHs monitoring in many locations within the urban area. The availability of a large number of heavy PAH measurements supported the use of specific PAH congeners concentration ratios, also called diagnostic ratios (DR), to support source identification and assessment.

Molecular signatures are used since long time for source attribution (see e.g. Sawicki, 1962; Ravindra et al., 2008; Tobiszewski and Namieśnik, 2012; Bhupander et al., 2012; Guillon et al., 2013). This analysis method has been criticised (Zhang et al., 2005), but it can be considered reliable provided that reactivity, gas-to-particle partition, particle size distribution, meteorology, and water solubility are taken in account (see the comprehensive discussion provided by Cecinato et al., 2014, and references therein).

The present paper analyses the seasonal variability of PAH concentrations in the urban area of Rome and examines PAH DRs to draw information about the pollution sources.

### 2. Materials and methods

#### 2.1. PAH monitoring in airborne particulates

The routinely available PAHs measurements performed to fulfil the European Union (EU) Air Quality Directives requirements are limited to BaP and do not provide a clear insight into space and time variability of concentrations over large conurbations. To complement the information supplied by the regional air quality monitoring network (http://www.arpalazio.gov.it/) for the city of Rome, the EXPAH project carried out extensive experimental field campaigns that allowed to assess the PAH exposure and its seasonal variability, to investigate the possible source contribution and verify the representativeness of emission profiles included in the emission inventories.

EXPAH field campaigns have been carried out from November 2011 to July 2012 in both indoor and outdoor environments. PAH concentrations were determined from airborne particulates (PM_{2.5}) with collection and PAHs analysis techniques described in details by Romagnoli et al. (2014) and Cecinato et al. (2012). Briefly, daily particulates were pooled into weekly samples, solvent extracted in ultra-sonic bath, fractioned through alumina column chromatography and chemically characterised through gas chromatography coupled with mass spectrometric detection operated in electron impact, selected-ion-monitoring. The use of internal standards (perdeuterated homologues of target compounds) allowed to account for recovery and detector efficiency. No blank interferences were found for any of target PAHs. The following PAHs were determined: benz[a]anthracene (BaA), benzo[b]fluoranthene (BbF), benzo[j]fluoranthene (BfJ), benzo[k]fluoranthene...
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