



Volatilization and oxidative artifacts of PM bound PAHs collected at low volume sampling (1): Laboratory and field evaluation

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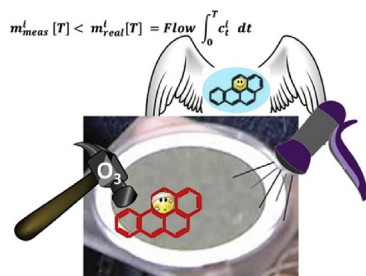
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HIGHLIGHTS

- Sampling artifacts of PM bound PAHs were assessed by laboratory and field tests.
- All PAHs were affected by degradation when exposed to typical sampling ozone doses.
- Further studies are necessary concerning 5-rings PAHs losses at $2.3 \text{ m}^3 \text{ h}^{-1}$ sampling.
- Dedicated field tests evidenced a lack of temporal auto-consistency in PAH sampling.
- 24-h and cumulated 2×12 -h samplings showed comparable losses in hot and cold seasons.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 7 November 2017

Received in revised form

14 February 2018

Accepted 15 February 2018

Available online 17 February 2018

Handling Editor: R Ebinghaus

Keywords:

Atmospheric PM

PAHs

Volatilization

Oxidative degradation

EU sampling reference method

ABSTRACT

Laboratory and field studies were carried out to assess the effects of oxidative degradation and volatilization on PM₁₀ bound polycyclic aromatic hydrocarbons (PAHs), collected at low volume condition according to the EU sampling reference method EN12341:2014 (flow rate $2.3 \text{ m}^3 \text{ h}^{-1}$), on 47 mm quartz filters. For the laboratory experiments, pairs of twin samples were collected in field and, after treatments favoring decomposition or/and volatilization of PAHs on one sample, the PAH amount was compared with that of the corresponding untreated sample. Ozone exposure caused a general PAHs decay with more marked effects on benzo [a]pyrene, perylene and benz [a]anthracene; these compounds showed, similarly to benzo [ghi]perylene, correlations between ozone dose and losses. Treatments with zero air exhibited losses due to volatilization even for 5-ring PAHs up to benzo [a]pyrene, whereas a linear dependence was observed between filter PAH load and losses for benzo [a]anthracene, chrysene and benzo[fluoranthene]. Concentrations on samples collected simultaneously over 48, 24, 12 and 6 h were compared. Results confirmed a lack of temporal auto-consistency in the PAHs sampling methodology here adopted. In particular higher atmospheric PAH concentrations were ascertained on samples constituted by cumulative filters exposed over shorter sampling times. When 24-h and 2×12 -h samples were compared, comparable losses were evaluated in the hot and cold seasons. This finding shows that, although in summer meteorology conditions favor sampling artifacts, the effectiveness of these

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phenomena continue in the winter, probably due to the larger amount of PAH available on the sampling filter (total PAHs ~ 10 vs 0.5 ng m⁻³).

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of organic compounds whose structure is formed by two or more condensed aromatic rings. PAHs are produced by both anthropogenic and biogenic sources through incomplete combustion or pyrolytic processes. PAHs are bioaccumulative and widespread in the environment, thus due to their ascertained carcinogenic, mutagenic and allergenic properties, several of them are known to pose a risk for human health (Ravindra et al., 2006; Keyte et al., 2013; Kim et al., 2013). PAHs are monitored in biota and ambient matrices and the achievement of their accurate determination is of major concern both for scientists and legislation. With regards to atmosphere, in the 1990 Clean Air Act Amendment (CAAA, 1990), US included PAHs in the list of the 187 hazardous air pollutants for which a reduction of sources and of population exposure is mandatory, meanwhile the 1998 Aarhus Protocol on Persistent Organic Pollutants obliges Parties to reduce their emissions (UNECE, 1998). Similarly, European Union regulates the PAH concentrations in the atmosphere and establishes the procedures to be applied to carry out the measures. In particular benzo [*a*]pyrene (BaP) is chosen as marker for the carcinogenic risk associated to PAHs occurring in ambient air and the target value of 1 ng m⁻³ averaged over a calendar year is fixed for its content in the PM₁₀ fraction of suspended particulates. In addition benzo [*a*]anthracene (BaA), benzo [*b*]fluoranthene (BbF), benzo [*j*]fluoranthene (BjF), benzo [*k*]fluoranthene (BkF), indeno [1,2,3-*cd*]pyrene (IPY), and dibenz [*a,h*]anthracene (DBA) must be monitored at a limited number of sites over national territories, in order to assess the respective contributions to the whole ambient air toxicity and, by consequence, the relative importance of BaP (Directive, 2004/107/EC, 2004).

A correct determination of PM bound PAHs is mandatory whenever the PAH associated toxicity and the effectiveness of regulatory/mitigation measures must be assessed, as well as in case source apportionment techniques based on distribution pattern of the congeners are used to determine the emission sources affecting a study area (Tobiszewski and Namieśnik, 2012; Cecinato et al., 2014). PAHs are present at trace levels in the atmosphere and scrupulous attention is paid to the reliability of analytical procedures adopted for their determination (Su and Hung, 2010). On the contrary, less concern is dedicated to the sampling step, which usually consists in collecting airborne particulate onto a filtering membrane; despite this, the accurate measure of PAHs can be compromised already at this stage by volatilization and degradation artifacts (Menichini, 2009; Wang et al., 2015; Melymuk et al., 2016). In fact, during the sampling, particulate PAHs collected on the filter can undergo degradation effects due to reaction with gaseous oxidants present in the air flow crossing the collection membrane (Melymuk et al., 2017). This phenomenon can result in significant losses of the target substances. It is worth to note that some PAHs are particularly prone to oxidation, and that benzo [*a*]pyrene is among them (Goriaux et al., 2006). Among all atmospheric oxidants (OH and NO₃ radicals, nitrogen oxides, NO₂, N₂O₅) ozone is recognized as the most efficient one with regards to PAH degradation due to higher atmospheric concentration and reactivity (Bedjanian et al., 2005, 2010; Bedjanian and Nguyen, 2010; Keyte et al., 2013). Additionally, during the sampling phase PAHs

can be subjected to volatilization (Tsapakis and Stephanou, 2005). PAHs are semi-volatile substances and light congeners can evaporate from the collection substrate due to pressure drop across the filter, and can be stripped by the air flow. A further phenomenon interfering the correct evaluation of the particle bound PAH determination is the adsorptive partitioning of gaseous compounds onto the filter. The artifact effectiveness are influenced by ambient conditions during the sampling and by procedures adopted. Temperature, humidity, atmospheric concentrations of atmospheric oxidants and target compounds, origin and quality of the carrier particles play key roles together with sampling duration, face velocity and typology of the collection filters. The estimation of relative importance of blow off and adsorption during the sampling is very difficult to be achieved, however the process looks influenced by the collection membrane type with the highest efficiency of adsorption associated to quartz (Turpin et al., 2000; Mader and Pankow, 2001; Parshintsev et al., 2011). Different approaches have been applied to understand and quantify the PAHs degradation reactions and the effects of volatilization. Concerning oxidative degradation, most studies were focused on BaP but neglected other PAHs. Two principal experimental approaches were used: in most cases, real or fortified samples were exposed to in-situ generated ozone during field sampling or in laboratory tests (Borström et al., 1983; Van Vaeck and Van Cauwenberghe, 1984; Coutant et al., 1988; Galarneau et al., 2006; Perraudin et al., 2007; Bedjanian and Nguyen, 2010); in a few studies, pairs of samples collected simultaneously through lines with and without ozone denuders were compared (<http://www.sciencedirect.com/science/article/pii/S0045653505009550>; Tsapakis and Stephanou, 2003; Schauer et al., 2003; Liu et al., 2006, 2014; Goriaux et al., 2006; Melymuk et al., 2017). Most of the studies aimed at assessing the impact of volatilization were performed by means of denuders or adsorbing cartridges located along the sampling line, or comparing samples collected according to different sampling programs (Mader and Pankow, 2002; Melymuk et al., 2016). Both oxidative degradation and filter blow off of 3–4 ring PAHs are usually associated with high flow rate and long sampling time. The sampling procedures adopted for the investigation of volatilization and oxidative degradation artifacts were rarely based on low flow rates and 24-h collection periods, which are instead usually adopted in the Air Quality Monitoring Networks to collect PM₁₀. The main goal of this research was to investigate, for the first time, the winter and summer impact of oxidative degradation and volatilization on PAH collection according to the sampling procedure widely adopted in the Air Quality Monitoring Networks of the EU Member States and worldwide. For this reason the investigation has been carried out by using procedures in compliance with the European reference methods for sampling and analysis of PAHs (Commission Directive (EU) 2015/1480 of 28, 2015). Twin sampling lines operated simultaneously at a flow rate of 2.3 m³ h⁻¹ were used in the field experiments. The PAH substances investigated were those known as “carcinogenic” and taken in account by regulation, i.e. BaP, BaA, BbF, BjF, BkF, IPY, and DBA, all belonging to Group 1, 2A and 2B according to IARC classification (IARC, 2017); furthermore chrysene (CHR) and benzo [*ghi*]perylene (BPE) together with benzo [*e*]pyrene (BeP) and perylene (PE), often used to identify the pollution sources and belonging to group 3 of the IARC classification (not classifiable as to

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