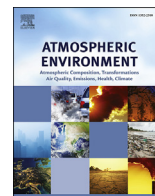




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## Technical note

# Stability of polycyclic aromatic compounds in polyurethane foam-type passive air samplers upon O<sub>3</sub> exposure

Narumol Jariyasopit <sup>a</sup>, Yongchun Liu <sup>b</sup>, John Liggio <sup>a</sup>, Tom Harner <sup>a,\*</sup><sup>a</sup> Air Quality Processes Research Section, Environment Canada, Toronto, Ontario, M3H 5T4 Canada<sup>b</sup> State Key Joint Laboratory of Environment Simulation and Pollution Control, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 100085, China

## HIGHLIGHTS

- Stability of polycyclic aromatic compounds (PACs) on PUF disks is evaluated.
- Flow tube chamber was used to simulate 2 months exposure to O<sub>3</sub>.
- Some degradation of PAHs occurred under low relative humidity (RH).
- The majority of the PACs were stable upon O<sub>3</sub> exposure at 50% RH.
- PUF disk sampler is validated for measuring PACs in air under typical conditions.

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## ABSTRACT

Stability of polycyclic aromatic compounds (PACs) in polyurethane foam (PUF) disks upon O<sub>3</sub> exposure was studied in a flow tube. A wide range of PACs was evaluated by spiking PUF disks with PACs and exposing to O<sub>3</sub> at concentrations that were equivalent to two months exposure, a typical deployment period for these passive air samplers. Ambient concentrations of O<sub>3</sub> (~50 ppb) at 0% and 50% relative humidity (RH) were applied. At 0% RH, 23 of 68 PACs yielded more than 50% loss after exposure. The mean percent loss was 30% with perylene and 9,10-dimethylanthracene the most reactive polycyclic aromatic hydrocarbons (PAHs) and alkylated PAHs, respectively. At 50% RH, 77% of the studied PACs was stable upon O<sub>3</sub> exposure ( $PAC_{\text{exposed}}/PAC_{\text{unexposed}} > 0.7$ ). The mean percent loss was 17% and only 7 of 68 PACs yielded greater than 50% loss. In general, the reactivity of most of the PACs decreased at higher RH, except for the reactive PAHs (acenaphthylene, 2,3-dimethylanthracene, 9,10-dimethylanthracene, dibenzothiophene, and 2-methyldibenzothiophene) which demonstrated lower RH dependence. The experimental conditions in this study represent a worst case scenario for the stability of PACs sorbed to PUF. In reality, the sampling of PACs in ambient air represents an 'aged' component of PACs where the most reactive species have already partially been removed. Also, PACs in ambient air will be associated with the particle phase to varying extents that will help to enhance their stability. Therefore, under regular operating conditions, over a 2-month exposure, we expect a minimal error in the measurement of total concentration of PACs in air using the PUF disk passive sampler.

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## 1. Introduction

Passive air sampling has been widely used in air monitoring for persistent organic pollutants (POPs) (Bartkow et al., 2004; Harner et al., 2006; Jaward et al., 2004; Schuster et al., 2015) as it is convenient, inexpensive, and does not require electricity to operate.

Chemicals, both gas-phase and particulate-phase, are passively accumulated in sampling media being deployed for months at a time. The sampling media include semipermeable membrane devices (SPMDs), polyurethane foam (PUF) disks, and XAD resin. Given that they are easy to handle, polyurethane foam (PUFs) disks are commonly used in a number of air monitoring programs, (Jaward et al., 2004; Klánová et al., 2006; Motelay-Massei et al., 2005; Pozo et al., 2004; Schuster et al., 2015) including the Joint Canada/Alberta Implementation Plan on oil sands Monitoring

\* Corresponding author.

E-mail address: [tom.harner@ec.gc.ca](mailto:tom.harner@ec.gc.ca) (T. Harner).

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Under JOSM, the passive sampling monitoring network was initiated to measure polycyclic aromatic compounds (PACs) across the oil sands region. The PACs being monitored include parent polycyclic aromatic hydrocarbons (PAHs), alkylated PAHs (alk-PAHs), dibenzothiophene (DBT) and alkylated DBTs. (Schuster et al., 2015) Released from pyrogenic (e.g. combustion processes) and petrogenic (e.g. bitumen and upgrading activities) sources, these compounds are ubiquitous and potentially carcinogenic and mutagenic. (Baird et al., 2005) Compared to pyrogenic sources, chemical composition of bitumen is relatively enriched with alk-PACs, DBT, and alk-DBTs, (Hawthorne et al., 2006; Yang et al., 2011) therefore, they are used as an indicator of petrogenic sources.

A concern regarding the passive sampling method is the potential reactions of PACs with atmospheric oxidants such as OH radicals, NO<sub>3</sub> radicals, N<sub>2</sub>O<sub>5</sub>, nitrogen oxides, and O<sub>3</sub> during field deployment. This raises a question of whether or not they are capable of accurately reflecting contaminant concentrations in air. Long deployment periods may allow chemicals trapped in the sampling media to undergo transformation reactions with oxidants, which can alter the relative abundances of PACs in air. For example, field observations have found that particulate-bound PAH concentrations measured using conventional high volume active air samplers could be underestimated by up to 100% or more, compared to the concentrations measured by denuders. (Goriaux et al., 2006; Schauer et al., 2003) However, limited data exist for the stability of PACs associated with passive sampling substrates. Bartkow et al. reported the photodegradation of PAHs in SPMDs that were not protected from sunlight. (Bartkow et al., 2006) There are several studies investigating heterogeneous reactions of surface-bound PAHs with gaseous oxidants using various substrates including silica, graphite, soot particles, particulate matter, and glass fiber filters. (Bedjanian and Nguyen, 2010; Esteve et al., 2004; Jariyasopit et al., 2014; Nguyen et al., 2009; Perraudin et al., 2007; Pöschl et al., 2001; Ringuet et al., 2012) The results from previous studies suggest that O<sub>3</sub> was an effective oxidant for degrading surface-bound PAHs (Jariyasopit et al., 2014; Pitts et al., 1986). As a result, for passive sampling methods where PUFs are protected from direct sunlight, wet precipitation, and strong wind inside sampler housings, it is likely that heterogeneous reactions with O<sub>3</sub> will play an important role in degrading PACs associated with PUFs.

The objective of this study was to evaluate the stability of PACs associated with PUF disks upon O<sub>3</sub> exposure. The studied PACs included a number of alkylated PACs whose reactivities toward O<sub>3</sub> have been rarely reported. A flow tube reactor was used to simulate the air sampling conditions in which PUF disks were exposed to O<sub>3</sub> at concentrations and durations that were approximately equivalent to exposing PUFs at ambient O<sub>3</sub> concentrations (~50 ppb) for two months, the typical deployment period for these passive samplers. To our knowledge, this is the first laboratory study to evaluate stability of PACs in PUF-type passive air samplers. The outcomes of this study will be relevant not only for passive air sampling using PUF and other substrates but also for active air sampling studies in which PUFs, used for collecting gas phase compounds, are exposed to oxidants.

## 2. Materials and methods

### 2.1. Chemicals and materials

The monitored PAH, alkylated PAHs, and dibenzothiophene and its alkylated homologs are listed in Table 1. Standards for the parent PAHs were purchased from Cambridge Isotope Labs (Andover, MA)

and Chiron (Trondheim, Norway). Deuterium-labeled PAHs and <sup>13</sup>C-phenanthrene were purchased from Cambridge Isotope Labs (Andover, MA). The isotopically labeled recovery PAH surrogates included d<sub>12</sub>-2,6-dimethylnaphthalene, d<sub>10</sub>-acenaphthene, <sup>13</sup>C-phenanthrene, d<sub>10</sub>-anthracene, d<sub>10</sub>-benzo(b)naphtho(2,1-d)-thiophene, d<sub>12</sub>-chrysene, d<sub>12</sub>-benzo(b)fluoranthene, d<sub>12</sub>-benzo(e)pyrene, d<sub>14</sub>-dibenz(a,h)anthracene, d<sub>12</sub>-indeno(123-cd)pyrene. The labeled PAH internal standards included d<sub>10</sub>-fluorene and d<sub>12</sub>-benz(a)anthracene. PUF disks (TE-1014, 14 cm diameter × 1.35 cm thick) were purchased from Tisch Environmental (Village of Cleves, OH).

### 2.2. O<sub>3</sub> exposures

PUFs were pre-cleaned before use using a previously published protocol. (Schuster et al., 2015) A pipet was used to distribute 320 ng of the individual PACs in 0.5 ml of isooctane evenly onto a cleaned PUF disk. The spiked PUFs were air-dried in a fume hood for 5 min to allow solvent to evaporate before being placed in the flow tube chamber. An illustration of the experimental setup for the flow tube chamber is shown in Fig. 1. The flow tube was of electro-polished stainless steel with an inner diameter of 19.8 cm and length of 255 cm. The setup consisted of three air streams delivered into the flow tube: (1) O<sub>3</sub> generated by a TG-10 Ozone Generator (Ozone Solutions, IA), (2) zero air for dilution generated by a zero air source (AADCO Model 737), and (3) humid air generated by passing zero air through a gas-washing bottle filled with deionized water. O<sub>3</sub> concentrations were monitored by an Ozone analyzer (Model 205, 2B Technologies, CO). A probe was used to measure relative humidity (RH) of the mixture in the flow tube chamber. The PUFs were exposed for ~4.5 h with the average O<sub>3</sub> concentrations at ~40 ppm (total flow of 11 LPM) and ~14 ppm (total flow of 4 LPM) at 0% RH and 50% RH respectively. The experiments at 0% RH and 50% RH were conducted in triplicate. In both cases, total O<sub>3</sub> concentrations were approximately equivalent to exposing the PUFs to an ambient O<sub>3</sub> concentration of ~50 ppb for two months. A clean blank filter was also placed in the flow tube and exposed to O<sub>3</sub> for ~4.5 h to test for background contamination. The result showed that there was no significant PAC contamination in the flow tube system or the laboratory.

Losses of PACs from PUF disks in the flow tube system could be caused by reaction with O<sub>3</sub> and evaporation. Control experiments at 0% RH and 50% RH were carried out in triplicate by passing a stream of zero air across PUFs spiked with the PACs in the chamber to determine losses from evaporation, in the absence of O<sub>3</sub>, occurring inside the flow tube chamber over the course of exposure.

### 2.3. Sample preparation and analysis

Samples were prepared and analyzed using methods described previously. (Schuster et al., 2015) Briefly, PUFs were spiked with the labeled recovery PAH surrogates and extracted with pressurized liquid extraction using petroleum ether and acetone (75:25, v:v; 2 cycles). The extracts were evaporated under a purified N<sub>2</sub> stream with a Turbovap II (Biotage, NC). Sample extracts were spiked with the labeled PAH internal standards and were analyzed using gas chromatography mass spectrometry (Agilent 6890 coupled with an Agilent 5975 MSD), in electron impact in selected ion monitoring mode, on a DB-XLB column (30 m × 0.25 mm I.D., 0.25 μm film thickness, Agilent Technologies).

## 3. Results and discussion

Percent recoveries of the PACs from the control experiments averaged 100% (ranging from 54% to 144%) and 104% (59%–153%)

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