Technical note

Stability of polycyclic aromatic compounds in polyurethane foam-type passive air samplers upon O₃ exposure Narumol Jariyasopit^a, Yongchun Liu^b, John Liggio^a, Tom Harner^{a,*}^a Air Quality Processes Research Section, Environment Canada, Toronto, Ontario, M3H 5T4 Canada^b 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 O₃.
- Some degradation of PAHs occurred under low relative humidity (RH).
- The majority of the PACs were stable upon O₃ 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 O₃ exposure was studied in a flow tube. A wide range of PACs was evaluated by spiking PUF disks with PACs and exposing to O₃ at concentrations that were equivalent to two months exposure, a typical deployment period for these passive air samplers. Ambient concentrations of O₃ (~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 O₃ 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

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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, NO₃ radicals, N₂O₅, nitrogen oxides, and O₃ 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 O₃ 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 O₃ 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 O₃ exposure. The studied PACs included a number of alkylated PACs whose reactivities toward O₃ have been rarely reported. A flow tube reactor was used to simulate the air sampling conditions in which PUF disks were exposed to O₃ at concentrations and durations that were approximately equivalent to exposing PUFs at ambient O₃ 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 ¹³C-phenanthrene were purchased from Cambridge Isotope Labs (Andover, MA). The isotopically labeled recovery PAH surrogates included d₁₂-2,6-dimethylnaphthalene, d₁₀-acenaphthene, ¹³C-phenanthrene, d₁₀-anthracene, d₁₀-benzo(b)naphtho(2,1-d)-thiophene, d₁₂-chrysene, d₁₂-benzo(b)fluoranthene, d₁₂-benzo(e)pyrene, d₁₄-dibenz(a,h)anthracene, d₁₂-indeno(123-cd)pyrene. The labeled PAH internal standards included d₁₀-fluorene and d₁₂-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. O₃ 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) O₃ 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. O₃ 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 O₃ 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 O₃ concentrations were approximately equivalent to exposing the PUFs to an ambient O₃ concentration of ~50 ppb for two months. A clean blank filter was also placed in the flow tube and exposed to O₃ 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 O₃ 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 O₃, 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 N₂ 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%)

Table 1

List of target analytes and their abbreviations.

PACs		
Naphthalene (NAP)	Acenaphthylene (ACY)	Acenaphthene (ACE)
Fluorene (FLU)	Phenanthrene (PHE)	Anthracene (ANT)
Dibenzothiophene (DBT)	Retene (RET)	Fluoranthene (FLA)
Pyrene (PYR)	Benz(a)anthracene (BaA)	Chrysene (CHR)
Benzo(b)fluoranthene (BbF)	Benzo(k)fluoranthene (BkF)	Benzo(a)pyrene (BaP)
Perylene (PER)	Indeno(1,2,3-c,d)pyrene (IcdP)	Dibenzo(a,h)anthracene (DahA)
Benzo(ghi)perylene (BgHiP)		
Alk-PACs		
C1 FLU - Fluorene 9-methyl (9MFLU), Fluorene 2-methyl (2MFLU)		
C2 FLU - Fluorene 9-ethyl (9EFLU), Fluorene 1,7-dimethyl (1,7DMFLU)		
C3 FLU - Fluorene 9-n-propyl (9PFLU)		
C4 FLU - Fluorene 9-n-butyl (9BFLU)		
C1 PHE - Phenanthrene 1-methyl (1MPHE), Phenanthrene 9-methyl (9MPHE)		
C2 PHE - Phenanthrene 1,3-dimethyl (1,3DMPHE), Phenanthrene 3,6-dimethyl (3,6DMPHE)		
C3 PHE - Phenanthrene 9-n-propyl (9PPHE), Phenanthrene 1,2,6-trimethyl (1,2,6TMPHE)		
C4 PHE - Phenanthrene 1,9-dimethyl-7-/1,9-dimethyl-5-ethyl (1,9DM7EPHE/1,9DM5EPHE), Phenanthrene 1,2,6,9-tetramethyl (1,2,6,9TMPHE)		
C1 ANT - Anthracene 1-methyl (1MANT), Anthracene 9-methyl (9MANT)		
C2 ANT - Anthracene 2,3-dimethyl (2,3DMANT), Anthracene 9,10-dimethyl (9,10DMANT)		
C1 DBT - Dibenzothiophene 2-methyl (2MDBT)		
C2 DBT - Dibenzothiophene 2,8-dimethyl (2,8DMDBT), Dibenzothiophene 2,3-dimethyl (2,3DMDBT)		
C3 DBT - Dibenzothiophene 2,4,7-trimethyl (2,4,7TMDBT), Dibenzothiophene (1:1) 2,3,7-/2,3,8-trimethyl (2,3,7TMDBT/2,3,8TMDBT)		
C4 DBT - Dibenzothiophene 4,6-diethyl (4,6DEDBT), Dibenzothiophene 2-butyl (2BDBT)		
C1 FLA - Fluoranthene 2-methyl (2MFLA)		
C2 FLA - Fluoranthene 3-ethyl (3EFLA)		
C1 PYR - Pyrene 1-methyl (1MPYR)		
C2 PYR - Pyrene 4,5-dimethyl (4,5DMPYR), Pyrene 2,7-dimethyl (2,7DMPYR)		
C2 BaA - Benz(a)anthracene 3,9-dimethyl (3,9DMBaA), Benz(a)anthracene 7,12-dimethyl (7,12DMBaA)		
C1 CHR - Chrysene 6-methyl (6MCHR), Chrysene 4-methyl (4MCHR)		
C2 CHR - Chrysene 6-ethyl (6ECHR)		
C3 CHR - Chrysene 6-n-propyl (6PCHR), Chrysene 1,3,6-trimethyl (1,3,6TMCHR)		
C4 CHR - Chrysene 6-n-butyl (6BCHR)		

for the 0% RH and 50% RH experiments, respectively (Figure SI.1, Tables SI.1 and SI.2, Supporting Information). In both cases, the lowest recoveries were attributed to naphthalene (NAP) which exists primarily in the gas phase. Higher percent recoveries of other volatile and semi-volatile PACs containing 3–4 rings (mean of 105% and 111% at 0% RH and 50% RH, respectively) indicated that the PUF disks have a high sorptive capacity and are able to retain the majority of the compounds that have significant fractions in the gas phase. Excluding NAP, average percent recoveries were 101% and 105% at 0% RH and 50% RH, respectively, suggesting that volatilization of these compounds from PUFs was minimal during the course of the experiment.

To correct for the evaporation losses for compounds with higher volatilization, the amount of individual PAC degraded after exposure to O₃ was calculated by dividing the average masses in the exposed samples by those in the control samples. Fig. 2A and B shows the PAC_{exposed}/PAC_{unexposed} ratios for the exposures at 0% RH and 50% RH, respectively. The means and standard deviations of PAC masses are given in Tables SI.1 and SI.2, Supporting Information. An asterisk indicates a statistically significant difference in mass after exposure to O₃, as compared to the control (p -value < 0.05, student's t -test). A filled dot denotes a statistically significant difference between the exposed masses at 0% RH and 50% RH (p -value < 0.05, student's t -test). At 0% RH, the mean

Fig. 1. Experimental setup for the flow tube chamber.

Fig. 2. Ratios of A. alk-PAC_{exposed}/alk-PAC_{unexposed} and B. parent PAC_{exposed}/parent PAC_{unexposed} for the O₃ exposures at RH 0% and RH 50%. A red asterisk denotes a statistically significant difference between the unexposed and exposed masses. A solid blue circle denotes a statistically significant difference between the exposed masses at 0% RH and 50% RH. See Table 1 for chemical names. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

PAC_{exposed}/PAC_{unexposed} ratios were 0.66 and 0.70 for the parent PAHs and alk-PACs, respectively (Fig. 2A and Table S1.1, Supporting Information). The most reactive parent PAHs and alk-PACs were (see Table 1 for compound names) PER and 9,10DMANT, respectively. Fifteen alk-PACs (C2-FLU, C1-ANT, C2-ANT, alk-DBTs, and C2-BaA) and eight parent PAHs (including ACY, FLU, ANT, DBT, BaA, BaP, PER, DahA) exhibited significant losses (>50%) after the O₃ exposure at 0% RH.

At 50% RH, the mean PAC_{exposed}/PAC_{unexposed} ratios were 0.81 and 0.85 for the parent PAHs and alk-PACs, respectively (Fig. 2B and Table S1.1, Supporting Information). The most reactive parent PAHs and alk-PACs were ACY and 9,10DMANT, respectively. Significant losses (>50%) were found for ACY, 9MANT, 2,3DMAN, 9,10DMANT, DBT, 2MDBT, and 7,12DMBaA. The reactivity of higher ring PAHs (BaA, BaP, PER, DahA) that resulted in significant losses at 0% RH decreased at 50% RH. Despite the decrease in reactivity at 50% RH, 48% of BaP mass reacted after the exposure. Except for PHE and IcdP, for the case where PAC masses were statistically different (p -value < 0.05) between the 0% RH and 50% RH, the ratios of PAC_{exposed}/PAC_{unexposed} at 50% RH were higher than those at 0% RH. This implies that water vapor played a significant role in stabilizing the PACs in PUFs. The observed humidity dependence is consistent with previous studies which attributed the decreases in PAC reactivity to the competitive adsorption of water vapor and O₃ on surfaces which could interfere with the heterogeneous reactions of PACs with O₃. (Pitts et al., 1986; Pöschl et al., 2001) It is also possible that water condensed in the pores of the PUF could have slowed down the diffusion of O₃. However, the O₃ degradation of the reactive PACs, including ACY and DBT, 2,3DMAN, 9,10DMANT,

2MDBT, was less dependent on RH. We note that in a few instances PAC_{exp}/PAC_{unexp} values exceeded 1.0 (Fig. 2) which could be attributed to experimental and analytical variability as shown in Figure S1.1.

Overall, this study demonstrates that the majority of PACs (77% of the studied PACs), under the simulated conditions, were stable (PAC_{exposed}/PAC_{unexposed} > 0.7) upon O₃ exposure at 50% RH. However, significant chemical losses of some volatile PACs were observed at 50% RH. The degree of degradation by O₃ in PUFs varies depending on the molecular structure and humidity. There was no distinguishable relationship between reactivity and degree of alkylation. For the reactive PACs, the results could lead to an underestimation of air concentrations which may have important implications for compounds that are used in air quality guidelines, such as BaP. As such, the underestimation of PAC concentrations in air can also be expected from active air sampling where O₃ and gas-phase compounds are drawn through PUF plugs, when a denuder is not installed, allowing PAC transformation.

It is important to note that the observed degradation in this study represents the upper limit or worst case scenario as PUFs were openly exposed to oxidants and chemicals that were applied onto the PUF disks were not bound to particles. In the real environment, PACs with more than 4 rings, including reactive BaP, PER, and DahA, are mainly associated with particulate matter (Su et al., 2006; Yamasaki et al., 1982) and hence suffer from O₃ degradation to a lesser extent as they are partially shielded from gaseous oxidants by black carbon, organic matter, and the accumulation of atmospheric reaction products on the surface. (Jariyasopit et al., 2014; Lammel et al., 2009; Zhou et al., 2012) Furthermore, it is

also likely that in ambient air, the fraction of the reactive PACs on freshly emitted particles that are available for chemical reactions would have already partially reacted in the atmosphere prior to collection. (Jariyasopit et al., 2014) These particle-bound PACs will become less available for further degradation as particles are photochemically aged. Additionally, as shown in previous studies (Pitts et al., 1986; Pöschl et al., 2001) and this study, humidity can potentially promote the stability of the PACs by suppressing O_3 reactions. For instance, under the conditions in the Athabasca oil sands region where the relative humidity annual mean was 67%, (Jung et al., 2011) it is expected that most of the PACs accumulated on PUF disks will be stable toward O_3 degradation during the two-month sampling collection period.

4. Conclusions

In summary, the results show that the passive PUF disk samplers are capable of accurately reflecting PAC concentrations in air; however, the reactive PAC (acenaphthylene, 2,3-dimethylanthracene, 9,10-dimethylanthracene, dibenzothiophene, and 2-methyldibenzothiophene) concentrations should be interpreted with caution. Although it has been shown that O_3 was an effective oxidant for heterogeneous reactions of particle-bound PACs (Jariyasopit et al., 2014), it should also be noted that in a real world environment the coexistence of O_3 and other atmospheric oxidants (e.g. OH radicals, NO_3 radicals, NO_2 , N_2O_5) could complicate the degradation reactions of the PACs associated with PUF disks. Moreover, the experiments are based on the assumption that the kinetics of heterogeneous reactions are linear with O_3 concentration. Deviation from linearity may be possible under ambient conditions. In the future, it would be useful to conduct similar studies to assess the stability of other priority chemicals frequently collected using PUF disk samplers and to consider different oxidant types under varying concentrations and exposure times.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.atmosenv.2015.08.088>.

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