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Gas/particle partitioning of *n*-alkanes, PAHs and oxygenated PAHs in urban Denver

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HIGHLIGHTS

- Gas-phase semi-volatile organic compounds were collected with low breakthrough.
- Gas/particle partitioning of selected species were measured and predicted.
- Theoretically-based partitioning coefficients were compared to measured ones.

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ABSTRACT

In this study, a medium volume sampler equipped with quartz fiber filters (QFFs) and a polyurethane foam (PUF)/XAD-4/PUF sandwich (PXP) was used to collect semi-volatile organic compounds (SVOCs) in both gaseous and particle ($PM_{2.5}$) phases. A backup QFF (bQFF) was used to evaluate possible sampling artifact of particulate organics due to vapor-phase adsorption. A series of *n*-alkanes (molecular weight: 170–562) and PAHs (128–300), and two oxy-PAHs (acenaphthenone, 168; fluorenone, 180) were measured. Breakthrough experiments demonstrated that the PXP could collect all gas-phase target compounds with high efficiency, even the low molecular weight (MW) species (e.g., naphthalene). Comparing species concentrations across different sampling matrices encountered at the Denver, Colorado field site, the light *n*-alkanes (MW < 282) and PAHs (MW < 192) were mostly distributed into the gas phase; while those heavy *n*-alkanes (MW > 324) and PAHs (MW > 202) were primarily in the particle phase (Average temperature, 12.5 ± 10.1 °C). Log values of measured gas/particle (*G*/*P*) partitioning coefficients ($K^{m}_{p,OM}$) of selected SVOCs (docosane, tricosane, fluoranthene, pyrene, acenaphthenone and fluorenone) were linearly regressed to those of theoretically-based partitioning coefficients ($K^{t}_{p,OM}$) for comparison. Prior to $K^{m}_{p,OM}$ calculation, the gas- and particle-phase concentrations of SVOCs were corrected following two different approaches based on bQFF measurements. The first approach assumed that the bQFF associated SVOCs were from the adsorption of gaseous SVOCs (positive artifact); the second approach assumed equal contributions from positive and negative (organics evaporated from top QFF and adsorbed by bQFF) artifacts. Under both corrections, significant correlations ($p < 0.05$) were observed between log $K^{m}_{p,OM}$ and log $K^{t}_{p,OM}$ for the six selected SVOCs, suggesting that the predicted *G*/*P* partitioning can reasonably capture the measured *G*/*P* partitioning behavior. The large deviations (1-2 orders of magnitudes) between $K^{m}_{p,OM}$ and $K^{t}_{p,OM}$ for acenaphthenone and fluorenone might be caused by the assumption of ideality (activity coefficient = 1) and the over prediction of vapor pressures (for $K^{t}_{p,OM}$ calculation). Negative correlations were observed between regression residuals of log $K^{m}_{p,OM}$ vs. log $K^{t}_{p,OM}$ and relative humidity, which might be attributed to the use of a constant activity coefficient and the possibility of phase separation.

1. Introduction

Gas/particle (*G*/*P*) partitioning is a key process affecting the environmental fate and transport of semi-volatile organic compounds (SVOCs), as well as human and ecosystem exposure to harmful SVOCs (Liang et al., 1997). According to *G*/*P* partitioning

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theory (Pankow, 1994a,b), the underlying partitioning mechanisms include particle surface adsorption and particulate organic matter (OM) absorption. The absorptive partitioning into the particulate OM phase has been demonstrated as the dominant mechanism for ambient SVOCs (Liang et al., 1997; Mader and Pankow, 2002) and applied in chemical transport models. The absorptive G/P partitioning coefficient ($K_{p,OM}$, $m^3\ \mu g^{-1}$) of each SVOC can either be measured directly ($K^m_{p,OM}$, Eq. (1)) or calculated from theory ($K^t_{p,OM}$, Eq. (2)):

$$K^m_{p,OM} = \frac{K^m_p}{f_{OM}} = \frac{F/M_{OM}}{A} \quad (1)$$

$$K^t_{p,OM} = \frac{RT}{10^6 \overline{MW}_{OM} \zeta_{OM} p^o_L} \quad (2)$$

where the measured G/P partitioning coefficient (K^m_p, $m^3\ \mu g^{-1}$) is normalized by the weight fraction of the absorptive OM phase (f_{OM}) in the total PM phase to obtain $K^m_{p,OM}$ (Eq. (1)); F and A are the mass concentrations (ng m^{-3}) of each SVOC associated with the particle and gas phase; and M_{OM} ($\mu g\ m^{-3}$) is the mass concentration of the particle-phase OM. In Eq. (2), R (m^3 atm K^{-1} mol^{-1}) is the ideal gas constant; T (K) is the ambient temperature; $\overline{MW}_{OM}$ (g mol^{-1}) is the mean molecular weight (MW) of the absorbing OM phase; ζ_{OM} is the mole fraction scale activity coefficient of each compound in the absorbing OM phase; and p^o_L (atm) is the vapor pressure of each pure compound. For a specific SVOC in a single OM phase at a fixed relative humidity, the G/P partitioning should be driven by ambient temperature only.

Receptor-based source apportionment of $PM_{2.5}$ usually uses particle-phase SVOCs data as inputs (Jaeckels et al., 2007; Shrivastava et al., 2007), and the resulting source/factor profile is pre-assumed to be constant over the period of ambient and source sampling (Chen et al., 2011). However, all SVOCs in ambient air are subject to G/P partitioning, and the particle-phase fraction can change with ambient temperature. As such, the output factors of receptor models are not necessarily pollution sources. Some of them also reflect the influence of G/P partitioning of SVOCs, especially those factors characterized by light SVOCs (Xie et al., 2013b). To eliminate the influences of G/P partitioning on source apportionment, Xie et al. (2013a) predicted gas-phase concentrations of SVOCs from their measured particle-phase concentrations using an absorptive partitioning theory (Eqs. (1) and (2)), and then added the gas- and particle-phase SVOCs together for source apportionment. The results showed consistent factor contributions between the full data set (32-month series) solution and temperature stratified sub-data sets solutions, suggesting that using total SVOCs (gas + particle phase) data for receptor-based source apportionment could eliminate the influences of G/P partitioning. To use this technique routinely, the prediction of gas-phase SVOCs needs to be verified by field measurements.

High volume air samplers equipped with glass fiber (GFF) or quartz fiber (QFF) filters followed by polyurethane foam (PUF) have been widely used for measuring G/P partitioning of SVOCs (Simcik et al., 1997; Chen et al., 2006; Yang et al., 2013). The sampling artifacts leading to biased G/P partitioning measurements include the re-evaporation of particle-phase SVOCs ("blow-off", negative artifact) and adsorption of gas-phase SVOCs onto filter media ("blow-on", positive artifact) (Peters et al., 2000). Schauer et al. (1999) compared different sampling equipment and found that the "blow-on" effect dominated the "blow-off" effect, resulting in elevated particulate organic carbon (OC). In addition, high breakthrough of light SVOCs (e.g., naphthalene) has been reported as a limiting factor for the application of PUF adsorbent (Hart et al., 1992; Peters et al., 2000). An XAD-coated annular denuder followed by a filter pack in the Integrated Organic Gas and Particle Sampler (IOGAPS) system has low breakthrough in collecting gas-phase per- and poly-fluorinated compounds (Ahrens et al., 2011). This sampling method can also reduce the positive artifacts in particle-phase SVOCs collection. However, considerable particle loss (10–24%) has been observed by Zhang et al. (2012) when applying the IOGAPS system for the measurements of diesel engine emissions.

In this work, a series of n-alkanes and PAHs and two oxygenated PAHs (oxy-PAHs) in gaseous and particle ($PM_{2.5}$) phases were collected using a medium volume sampler equipped with QFF and PUF/XAD-4/PUF sandwiches. The breakthrough of each target compound for gas-phase collection was then measured on selected sampling days to evaluate the performance of our sampling method. A backup QFF (bQFF) was installed to evaluate the adsorption of gas-phase organics onto filter media, which was used to correct the gas- and particle-phase concentrations of each target compound. Finally, measured $K_{p,OM}$ ($K^m_{p,OM}$) were compared to theoretically-based $K_{p,OM}$ ($K^t_{p,OM}$) for selected compounds, so as to verify the prediction of gas-phase concentrations of SVOCs using absorptive partitioning theory in Xie et al. (2013a).

2. Methods

2.1. Sampling

Details of the sampling information have been provided by Xie et al. (2014). Briefly, air samples were collected on the top of a two-story elementary school building located in a residential area of urban Denver. A medium volume sampler equipped with a 2.5 μm cut cyclone and two sampling trains, was used to collect SVOCs in gaseous and particle phases at a flow rate of 92 L min^{-1}. After the cyclone, the stream was split with 72 L min^{-1} passing through a QFF pack containing two 90 mm diameter QFFs in series, followed by a PUF (50 mm diameter and 40 mm length)/XAD-4 (5 g)/PUF (50 mm diameter and 40 mm length) sandwich. The remaining flow of 20 L min^{-1} passed through a 47 mm diameter, 2 μm pore size Teflon membrane filter (TMF), followed by another sandwich using XAD-7 resin instead of XAD-4 resin. The gaseous and particle phases of all target compounds discussed in this work were collected in the first sampling train. The top QFF (tQFF) in the filter pack was used to collect ambient particles. The bQFF was used to quantify particulate sampling artifacts due to gas sorption to QFF media. The PUF/XAD-4/PUF sandwich (PXP) was used for the analysis of all target compounds in gas-phase. Two PUF (50 mm diameter and 20 mm length)/XAD-4 (5 g)/PUF (50 mm diameter and 20 mm length) sandwiches were installed in series to measure the breakthrough of each target compound on eight sampling days. Fifty pairs of 24-h gas- and particle-phase samples were collected from August 28, 2012 to July 25, 2013. During the same study period, meteorological data (daily average temperature and relative humidity) were obtained from a nearby community monitor (CAMP, AQS ID: 080310002) operated by the Colorado Department of Public Health and Environment (CDPHE). Field blanks of QFF and PXP were collected every month to address contamination concerns. Prior to sampling, QFFs and adsorbents (PUF and XAD-4 resin) were cleaned by baking (500 °C/12 h) and solvent extraction (Soxhlet), respectively.

2.2. Sample extraction and instrumental analysis

Details of QFF extraction and analysis were provided by Dutton et al. (2009b). Prior to extraction, a half of each QFF sample was spiked with an internal standard mixture containing isotopically labeled standards, which had similar structure to our target