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Impact of partitioning and oxidative processing of PAH in fogs and clouds on atmospheric lifetimes of PAH

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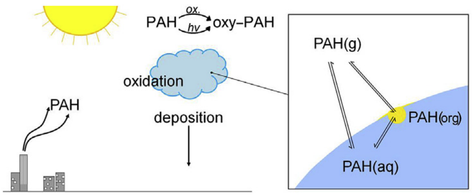
HIGHLIGHTS

- Oxy-polycyclic hydrocarbons (PAHs) can substantially partition to the aqueous phase.
- Chemical lifetimes of PAHs can be significantly shortened in the presence of fog.
- Temperature dependencies of partitioning ratios represent huge uncertainty.

GRAPHICAL ABSTRACT



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ABSTRACT

The importance of the atmospheric aqueous phase of fogs and clouds, for the processing and removal of polycyclic aromatic hydrocarbons (PAHs) is not well known. A multiphase model was developed to determine the fate and lifetime of PAHs in fogs and clouds for a limited set of daytime conditions. The model describes partitioning between three phases (aqueous, liquid organic, and gas), experimental and estimated (photo)oxidation rates. Using a limited set of microphysical and chemical input conditions, the loss rates of PAHs in the complex three-phase system are explored.

At 25 °C, PAHs with two, three and four rings are predicted to be primarily in the gas phase (fraction in the gas phase $x_g > 90\%$) while five- and six-ring PAHs partition significantly into droplets with aqueous phase fractions of 1–6% and liquid organic phase fractions of 31–91%, respectively. The predicted atmospheric chemical lifetimes of PAHs in the presence of fog or cloud droplets (<8 h) are significantly shorter than literature predictions of PAH lifetimes due to wet and dry deposition (1–14 days and 5–15 months, respectively) and shorter than or equal to predicted lifetimes due to chemical reactions in the gas and organic particulate phases (1–300 h). Even though PAH solubilities are $\leq 4 \times 10^{-2}$ g L^{-1}, the results of the current study show that often the condensed phase of fog and cloud droplets cannot be neglected as a PAH sink.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in the atmosphere. They are formed during the incomplete pyrolysis of organic matter and emitted by vehicles, cigarette smoke, wildfires, fireplaces, smoked foods, and coal power plants (*e.g.*, Rogge et al., 1993; Zhang and Tao, 2009). Many PAHs are classified as suspected human carcinogens and one (benzo[*a*]pyrene) is a known human carcinogen (U.S. EPA, 2014). The most often studied and most abundant PAHs are fluorene (FLU), acenaphthylene (ACY), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo[*a*]anthracene (BAA), benzo[*e*]pyrene (BEP), benzo[*a*]pyrene (BAP),

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perylene (PRL), dibenz[*a,h*]anthracene (DBA), and benzo[*g,h,i*]perylene (BGP) with typical atmospheric concentrations of 0.002–25 ng m^{-3} while the smallest PAH, naphthalene (NAP), has typical atmospheric concentrations of 20–500 ng m^{-3} (total of gas and particle phases; Fraser et al., 2002; Eiguren-Fernandez et al., 2004; Delgado-Saborit et al., 2013).

PAHs demonstrate semi-volatile behavior with concentrations on the order of ng m^{-3} in the atmospheric gas phase (*e.g.*, phenanthrene, PHE 0.15 ng m^{-3}; Delgado-Saborit et al., 2013). Observational studies have shown the partitioning of PAHs in the absence of fogs and clouds (*i.e.*, distribution between the gas and particulate phases) varies with temperature and the molecular weight of the PAH (Fernández et al., 2002; Eiguren-Fernandez et al., 2004; Delgado-Saborit et al., 2013). For example, Delgado-Saborit et al. (2013) reported PAHs with molecular weights of <202 Da to be >80% in the gas phase while PAHs > 250 Da were 30% or less in the gas phase. The partitioning of PAH between gas and particulate phases also varies with the composition of the particulate phase, especially the soot and organic content of particles (Lohmann and Lammel, 2004).

When fogs and clouds are present, PAHs are found in the aqueous phase (*e.g.*, BAP: 2×10^{-7} g L^{-1}; Herckes et al., 2002) despite the low water solubilities of PAHs (1.4×10^{-7} to 3.2×10^{-2} g L^{-1}; Pearlman et al., 1984). Capel et al. (1991) proposed three mechanisms to account for PAH presence in fog water: dissolved organic compounds that act as co-solvents for PAHs, organic compounds acting as surfactants at the droplet surface or in colloids, and PAHs bound to scavenged particles. It was found that filtering fog water isolated most PAHs (Leuenberger et al., 1988) which lead Capel et al. (1991) to conclude that scavenged particles were the largest reservoir of PAHs in fog. Nonetheless, Capel et al. (1990) found that the surface tension in fog water is lower than in pure water, which is a manifestation of surfactant (surface film) and/or co-solvent behavior. Valsaraj (2004, 2009) demonstrated PAH adsorption to water surfaces and to surfactant-like organic matter on water surfaces (Donaldson and Valsaraj, 2010; Chen et al., 2011).

There have been few atmospheric PAH multiphase (*i.e.*, more than two phases) studies. Lei and Wania (2004) employed partitioning ratios to predict PAH distribution in clouds. Ehrenhauser et al. (2012) compared the observed PAH distribution in fog with simple predictions using partitioning ratios. While the phase distribution and reactions within a three-phase system are not well known for PAHs, partitioning ratios have been measured and estimated for octanol-water systems (Wang et al., 1986; Hansch et al., 1995; de Maagd et al., 1998), octanol-air systems (Alaee et al., 1996; Harner and Bidleman, 1998; Bamford et al., 1999; Odabasi et al., 2006; Ma et al., 2010), and water-air systems, *i.e.*, Henry's law constants (ten Hulscher et al., 1992; Reza and Trejo, 2004; Sander, 2015). (Photo)Chemical degradation rate constants of many PAHs in the various phases have been measured or calculated (Calvert et al., 2002) and the products of PAH oxidation reactions have been reported in the gas (Helmig et al., 1992; Helmig and Harger, 1994; Lane et al., 1996; Mihele et al., 2002; Wang et al., 2007; Lee and Lane, 2010), aqueous (Sigman et al., 1996; Mallakin et al., 2000; Kong and Ferry, 2003; Woo et al., 2009; Sanches et al., 2011) and organic phases (Jang and McDow, 1997; Fioressi and Arce, 2005). To the best of the authors' knowledge, only one study has published PAH photochemical degradation rate constants in organic/aqueous liquid mixtures (Grossman et al., 2016) and this was limited to ANT and PYR. The conclusion of their study was that ANT and PYR processing in the aqueous phase is faster than in a liquid organic phase and thus chemical reactions in the aqueous phase should be considered in identifying chemical sinks of PAHs, in addition to physical deposition processes. The atmospheric oxidation of PAHs yields oxy–PAH products (PAHs with one or more oxygen atoms in carboxyl groups and/or as heteroatoms in the ring) which are more soluble than parent PAHs (Delgado-Saborit et al., 2013). This conversion affects the phase distribution of PAHs and therefore their atmospheric lifetimes.

Previously, PAH processing in the atmospheric aqueous phase was considered to be negligible (Lohmann and Lammel, 2004) due to the low solubility of PAHs. Gas phase PAH reactions and heterogeneous reactions on particulate matter surfaces were considered the main sink of PAHs where atmospheric lifetimes range from 1 to 300 h (Keyte et al., 2013). It has been suggested that dry deposition is the main physical (*i.e.*, non-chemical) loss process of PAHs and therefore their atmospheric lifetime (1–14 days) is constrained by the particle lifetime (about 7 days) (Bidleman, 1988; Škrdlíková et al., 2011). Removal by wet deposition (rain) is considered to be at least ten times less efficient than dry deposition (5–15 months) (Škrdlíková et al., 2011).

The multiphase system (organic, gas, and aqueous phases) of clouds and fogs is very complex. Multiple organic phases may exist simultaneously which are not necessarily in equilibrium with the aqueous phase. It has been shown that small PAH amounts in droplets might be associated with soot and therefore do not reside on a droplet surface (e.g., Walters and Luthy, 1984, Lohmann and Lammel, 2004; Koelmans et al., 2006; Bedjanian and Nguyen, 2010). However, given the low scavenging efficiency of soot (typically < 10%, Herckes et al., 2013) this effect can be considered minor. The incorporation of PAHs into clouds (interstitial particles or cloud droplets) strongly depends on their emission sources (co-emission with particles) and their physicochemical parameters (solubility, molecular weight etc.).

During droplet nucleation and scavenging processes, it is unknown what fraction of PAHs bound to PM (particulate matter) will dissolve into the atmospheric aqueous phase. Open questions remain as to the role of surface films on PAH uptake by fog and cloud droplets and whether PAHs incorporate into or onto atmospheric droplets. This is in part due to analytical constraints of sample size and PAH detection limits. Many studies of PAH uptake from the gas phase by surface films on water have employed planar or cylindrical surfaces which do not have the same surface area to volume ratios as cloud droplets (Moza et al., 1999; Chen et al., 2006, 2011). A few studies of PAH uptake from the gas phase have employed 92 μm droplets (Raja and Valsaraj, 2006) or modeled 1 000 μm droplets (Ma et al., 2013) which were greater than the ~5–20 μm droplets typically found in fogs and clouds (Zak, 1994). Other studies have employed concentrations of PAHs far exceeding those found in typical fogs and clouds (Kahan and Donaldson, 2007; Chen et al., 2011; Styler et al., 2011).

In the current study, we summarize partitioning ratios and oxidation rate constants of PAHs and oxy–PAHs. This data is included in a three-phase box model in order to compare the simultaneous loss rates in the gas, liquid organic and aqueous phases and to assess the role of each phase as a chemical sink of PAHs and oxy–PAHs during the daytime. We neglect possible processing during the nighttime due to the significant lack of data of corresponding (e.g., $^{\bullet}NO_3$) rate coefficients and product yields in all three phases. Simulations are performed for a limited set of fog and chemical conditions (liquid water content, initial concentrations of chemical species in the multiphase system, etc.) as we consider the current study a starting point to explore the chemical behavior of PAHs in the complex water-organic-gas system.