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ScienceDirect
Atmospheric Environment 41 (2007) 37–50
ATMOSPHERIC ENVIRONMENT
www.elsevier.com/locate/atmosenv

Assessing the importance of heterogeneous reactions of polycyclic aromatic hydrocarbons in the urban atmosphere using the Multimedia Urban Model

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Received 14 April 2006; received in revised form 9 August 2006; accepted 11 August 2006

Abstract

The Multimedia Urban Model (MUM-Fate) of Diamond, M.L., Priemer, D.A., Law, N.L., 2001. Developing a multimedia model of chemical dynamics in an urban area. Chemosphere 44, 1655–1667 was used to evaluate the contribution of heterogeneous reactions of polycyclic aromatic hydrocarbons (PAHs) with gas-phase ozone to the total loss of these compounds in an illustrative urban environment. Recent laboratory studies by Kahan, T.F., Kwamena, N.-O.A., Donaldson, D.J., 2006. Heterogeneous ozonation kinetics of polycyclic aromatic hydrocarbons on organic films. Atmospheric Environment 40, 3448–3459 and Kwamena, N.-O.A., Thornton, J.A., Abbatt, J.P.D., 2004. Kinetics of surface-bound benzo[*a*] pyrene and ozone on solid organic and salt aerosols. Journal of Physical Chemistry A 108, 11626–11634 provided half-lives for these heterogeneous reactions on surface films and atmospheric particulate matter, respectively. Two model scenarios were studied, representing urban environments with varying amounts of impervious surface coverage. We investigated six PAHs spanning a wide range of physical and chemical properties; results for anthracene, pyrene and benzo[*a*]pyrene are presented here. Advection from air was the dominant loss process for all PAHs investigated. Heterogeneous reactions primarily on surface films but also on atmospheric particulate matter accounted for up to 75% of the reactive losses of lower volatility PAHs, which accumulate in condensed phases. The results suggest that surface films can be efficient reactive sinks for lower volatility PAHs.

Keywords: Surface film; Particulate matter; Heterogeneous reactions; Urban air pollution; Mass balance model

1. Introduction

Numerous adverse health effects have been attributed to exposure via inhalation of polycyclic aromatic hydrocarbons (PAHs), which are products of incomplete combustion. These health effects include allergic responses, cancer and impaired foetal development (Perera et al., 2004; Pope III et al., 2002; WHO, 1998). In addition, the oxidised and nitrated reaction products of these compounds have been found to be more potent carcinogens and mutagens than their parent PAHs (Pitts Jr et al.,

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doi:10.1016/j.atmosenv.2006.08.016

1980). Since atmospheric concentrations of PAHs are highest in urban environments (Cotham and Bidleman, 1995; Prevedouros et al., 2004; Tsapakis and Stephanou 2005), there is an incentive to identify the factors, such as reactive losses, that determine their ambient air concentrations and transport out of the urban airshed.

Gas-phase reactions with OH are believed to be the dominant loss process for volatile PAHs like anthracene and pyrene (Atkinson and Arey, 1994; Finlayson-Pitts and Pitts, 2000). On the other hand, for heavier PAHs like benzo[*a*]pyrene (BaP), loss via heterogeneous ozonation and nitration reactions on condensed phases is believed to dominate (Finlayson-Pitts and Pitts, 2000). In fact, recent evidence shows that heterogeneous reactions of PAHs on atmospheric particulate matter (PM) (Kwamena et al., 2004; Poschl et al., 2001) and at the air–aqueous interface (Mmereki and Donaldson, 2003a; Mmereki et al., 2004) may be more important than the corresponding gas-phase reactions as an atmospheric sink for these heavier PAHs.

One potential reactive sink for PAHs that has been overlooked is the thin film that coats impervious surfaces in urban areas. Surface films are thought to develop by direct deposition of primary gas-phase and particulate emissions and through the deposition of secondary reaction products of primary pollutants (Law and Diamond, 1998). The film determines the functionality of impervious surfaces, acting as both a sink and source of chemical compounds to the atmosphere. As a sink, the film can accumulate gas-phase compounds as well as particles and their associated components via deposition and condensation processes. Some of these compounds can then undergo reactions, which may be promoted by the large surface area-to-volume ratio of $\sim 10^7$ provided by the films (Diamond et al., 2001). Acting as a source, compounds such as PAHs and their reaction products may re-volatilise and contribute to atmospheric concentrations (Gustafson and Dickhut, 1997). Further, compounds that accumulate in the film can be transferred to surface waters by precipitation events that wash away the film's constituents (Labencki et al., resubmitted).

Although surface films are in part formed by deposition of particulate emissions, atmospheric PM and surface films from the same environment have been found to differ in their composition. For example, Lam et al. (2005) noted that whereas $PM_{2.5}$ in Toronto is composed of 30–40% organic carbon (Lee et al., 2003), surface films in the same area consisted of only ~5% organic carbon. The film was composed of 94% inorganic species, including 16% sulphate and nitrate (Lam et al., 2005). PAHs constituted $<0.05\%$ by mass of the organic fraction of the film. The lower fraction of organic carbon (f_{OC}) in the films compared with $PM_{2.5}$ was hypothesised to be either due to the preferential deposition of large, soil-derived particles and/or greater losses via reaction of organic compounds in the film. Evidence in support of the latter explanation was the observation of low abundances of reactive PAHs (i.e., benz[*a*]anthracene, BaP and perylene) compared to the more unreactive PAHs (i.e., chrysene and benzo[*b*]fluoranthene) in films sampled in downtown Toronto (Gingrich et al., 2001).

Results from laboratory studies of the heterogeneous ozonation of PAHs provide additional evidence that these reactions may account for the lower f_{OC} in films. Recently, Mmereki et al. (2003b) demonstrated that heterogeneous reactions of PAHs with ozone are increased on aqueous surfaces coated with an organic film (Mmereki and Donaldson, 2003a; Mmereki et al., 2004). Kahan et al. (2006) expanded these studies by measuring the rates of reaction of six PAHs (naphthalene, fluoranthene, anthracene, phenanthrene, pyrene, and BaP) with ozone on 1-octanol (a proxy for surface film) in the presence of several additional organic species.

The present study set out to test the hypothesis that reactions of PAHs on surface films and atmospheric PM are important sinks for PAHs in a typical urban environment. We hypothesise that reactive losses of certain PAHs on surface films (deposited on impervious surfaces and PM) are more important than gas-phase reactions. To test this hypothesis, we used the Multimedia Urban Model or MUM-Fate, which is a level III fugacity model, to quantitatively determine the importance of heterogeneous reactions on surface films in the urban environment. The model is unique in that it includes films on impervious surfaces as one of its compartments (Clarke, 2006; Diamond et al., 2001). Multimedia models have proven useful for evaluating the environmental behaviour of chemicals, to the extent that they have been adopted by several jurisdications as tools for screening potential chemical hazards (e.g., Cowan et al., 1995).