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Modeling urban films using a dynamic multimedia fugacity model

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ABSTRACT

A thin film coats impervious urban surfaces that can act as a source or sink of organic pollutants to the greater environment. We review recent developments in the understanding of film and film-associated pollutant behavior and incorporate them into an unsteady-state version of the fugacity based Multimedia Urban Model (MUM), focusing on detailed considerations of surface film dynamics. The model is used to explore the conditions under which these atmospherically-derived films act as a temporary source of chemicals to the air and/or storm water. Assuming film growth of 2.1 nm d^{-1} (Wu et al., 2008a), PCB congeners 28 and 180 reach air–film equilibrium within hours and days, respectively. The model results suggest that the film acts as a temporary sink of chemicals from air during dry and cool weather, as a source to air in warmer weather, and as a source to storm water and soil during rain events. Using the downtown area of the City of Toronto Canada, as a case study, the model estimates that nearly 1 g d^{-1} of $\sum_5$PCBs are transferred from air to film to storm water.

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1. Introduction

Diamond and co-workers found that a thin film accumulates on impervious surfaces in urban and rural areas which is derived from atmospherically deposited and condensed species (Law and Diamond, 1998; Diamond et al., 2000a). Semi-volatile organic compounds (SVOCs) such as polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), and polycyclic aromatic hydrocarbons (PAHs) have all been detected in films (Gingrich et al., 2001; Butt et al., 2004; Unger and Gustafsson, 2008). The film is significant as it alters the surface characteristics of impervious surfaces and as a consequence it can mediate contaminant dynamics (e.g. Lam et al., 2005). This phenomena is especially important in urban areas where chemical emissions are numerous and impervious surfaces can cover up to 98% of dense urban areas with an even larger area on a 3-dimensional basis (Diamond et al., 2001; Diamond and Hodge, 2007).

The Multimedia Urban Model (MUM) of Diamond et al. (2001) and the models of Foster et al. (2006), Prevedouros et al. (2008), and Ashley et al. (2009) have included surface films. These models considered the film as a static compartment whereas the research of Wu et al. (2008a) has shown that films are dynamic as they grow thicker during dry periods and are washed off during rain events. In this paper, we review empirical information gathered on the nature and dynamics of films and chemicals associated with films. This information is incorporated into an unsteady-state extension of MUM (Diamond et al., 2010a) to investigate the source/sink nature of films in an urban area using PCBs in downtown Toronto, Canada as a case study.

1.1. Film properties and processes

Film thicknesses and growth rates are ~5 to ~12–20 times greater in urban than rural areas, respectively. Film thickness is on the order of nm's on urban glass windows and growth rates on glass beads deployed at an urban site in Toronto were on the order of a few nm d^{-1} (Diamond et al., 2000b; Gingrich et al., 2001; Wu et al., 2008a). Film mass is dynamic as it grows with time but it also decreases during rain events via wash-off. The mechanism of film wash-off is presumed to be physical detachment of particles by the mechanical action of raindrops and secondarily by solubilization (Diamond et al., 2000b; Wu et al., 2008a). For example, Vaze and Chiew (2003) noted that rain intensity plays a larger factor in pollutant wash-off loads than total rain volume as the impact energy of rain drops is responsible for the amount of particles that can be dislodged from a surface. Furthermore, particle wash-off from urban surfaces is greatest during initial rainfall (Vaze and Chiew, 2003; Egodawatta et al., 2009). This is consistent with the findings of Eckley et al. (2008) who found that 52% of particle associated mercury was washed off within a 2 mm simulated rain event, Labencki et al. (in preparation) who reported that average wash-off rates for PAHs were 59% based on a 0.75 mm

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simulated rain event, and Diamond et al. (2000b) who reported that 72% of PCBs were washed off based on a simulated rain event of 0.45 mm.

The chemical composition of films reflects that of the atmosphere. Semi-volatile organic compounds such as PCBs, PBDEs, PAHs, OC pesticides, and PFCs have been measured in urban window films in North America, Europe, and Australia (Gingrich et al., 2001; Butt et al., 2004; Unger and Gustafsson, 2008; Duigu et al., 2009; Gewurtz et al., 2009). Following an urban–rural trend, PCB, PAH, and OC pesticide concentrations were 50, 30, and 11 times higher, respectively, in urban compared to rural films (Gingrich et al., 2001). The congener profiles of each compound class closely resembled that of atmospheric particles from which the film is derived.

Semi-volatile organic compounds, however, contribute to a minor fraction of the total organic composition of the film. Lam et al. (2005) and Simpson et al. (2006) studied the composition of films in Toronto and found them to contain ~5% organic carbon which, in turn, was comprised of 35%, 35%, 20%, and 10% carbohydrates, aliphatics, aromatics, and carbonyls, respectively. This is significant for film modeling as the organic carbon content of a material provides the sorptive capacity for partitioning characteristics with gas-phase compounds in air. These compounds are also "stickier" than inorganic compounds and as such could increase film growth due to the dry deposition of particles (by minimizing particle rebound). Lam et al. (2005) found that the non-organic constituents were 8%, 7%, and 18% sulfate, nitrate, and metals, respectively, and Duigu et al. (2009) also found that metals accounted for a significant mass of film in Brisbane, Australia.

Assuming that all organic compounds are available to partition between gas and condensed phases such as particles and film, we can then assume that chemical concentrations in films can be described by equilibrium partitioning between the gas phase in air and the organic fraction of the film (Diamond et al., 2001), similarly to that assumed for particulate matter (Harner and Bidleman, 1998). Wu et al. (2008b) derived an empirical relationship for the bulk film–air partition coefficient, K_{fa} based on empirical studies with PCBs, as $\log(K_{fa}) = 1.1\log(K_{EVA-air}) - 1.2$ where $K_{EVA-air}$ is the EVA–air partition coefficient (EVA represents an ethylene vinyl acetate film). Using the average relationship based on four studies (as reported in Wu et al. (2008b)) between the octanol–air partition coefficient, K_{oa}, and $K_{EVA-air}$ yields the following relationship between K_{fa} and K_{oa}

$$\log(K_{fa}) = 1.1\log(K_{oa}) - 0.54. \tag{1}$$

The partition coefficient between the film organic fraction and air is equal to K_{fa} divided by the organic matter fraction of film (f_{OM}) (Wu et al., 2008b).

Limited information is available on chemical reaction rate constants on or in film, however, several studies have examined reactions on surrogate surface films (e.g. Isidorov et al., 1997; Kwamena et al., 2007b; Finlayson-Pitts, 2009; Shiraiwa et al., 2009). Donaldson et al. (2005) and Kahan et al. (2006) found that reactions of PAH with ozone in pure films made of oleic acid and squalene; and octanol or decanol on grease coated glass slides, respectively, can be a significant loss process, however film-associated reaction rate constants of PAH can be slower than on particles (Kwamena et al., 2004, 2007a; Kahan et al., 2006). Using measured rates, Kwamena et al. (2007a) modeled PAHs in order to explore the significance of degradation in film as a loss process compared to air advection and particle-associated degradation. They found that air advection was by far the dominant removal process from a highly urbanized (high impervious surface coverage) environment. However, reaction losses from films exceeded that from particles for higher mass, lower volatility PAHs by virtue of the chemical mass that partitioned into the film and because of the higher surface area of the film compartment compared to particle surfaces. Minimal information is available on reaction rate constants of PCBs associated with surface film. Atkinson (1996) reported that particle-phase PCB reaction rates were not significant compared to gas-phase reaction with OH radicals.

Further details about film properties and processes can be found in Diamond and Thibodeaux (2010).

2. Model development

MUM (Diamond et al., 2001, 2010a) is a steady-state version of a fugacity based model which divides the environment into seven compartments (upper and lower air, water, soil, sediment, vegetation, and surface film). The film compartment was previously represented in MUM as a 100 nm thick layer that coats the 3-dimensional impervious surface area of the system. Film growth was not taken into account and rain wash-off was considered to be constant. Chemical that was washed off with the film was entirely transferred to the water compartment with no transfer to storm water or soil. These latter issues are addressed in the updated unsteady-state version of MUM that is presented here.

2.1. Film inter-compartmental interactions

The film compartment interacts with the air (bi-directional gas diffusion and wet and dry particle-phase deposition) and soil (one-way chemical transfer via film wash-off) compartments; and with storm water (one-way chemical transfer via film wash-off).

The transport processes between film and air are described by Diamond et al. (2001) as wet and dry particle deposition, wet gas deposition, and gas diffusion. The D-value for gas diffusion is given by

$$D_v = \left[\frac{1}{k_{af}A_fZ_a} + \frac{1}{k_{ff}A_fZ_f}\right]^{-1} \tag{2}$$

where k_{af} and k_{ff} are the air- and film-side mass transfer coefficients (m s^{-1}), respectively, A_f (m^2) is the film area, and Z_a and Z_f are the Z-values (mol m^{-3} Pa^{-3}) for air and dissolved phase of the film, respectively. Priemer and Diamond (2002) expressed k_{af} as the ratio of the diffusivity and boundary layer thickness, δ^{bl} (m), which depends on wind speed, as such

$$\delta^{bl} = \beta\sqrt{\frac{l}{v}} \tag{3}$$

where v is wind speed (m s^{-1}), l (m) is the mean surface length in the wind direction, and β is given a value of 6 mm s$^{-1/2}$.

As discussed above, chemical wash-off is a bulk removal process. Wash-off studies suggest that the process can be modeled using a simple wash-off efficiency, W_E, such that W_E% of chemical and film are washed off for any given rain event (see Eq. (11) below). The next factor to consider is the fraction of rain water delivered to storm water which has been well studied for the purpose of municipal hydrological planning (e.g. Chen and Adams, 2007; Goldshleger et al., 2009; Mueller and Thompson, 2009). Goldshleger et al. (2009) studied 800 rain events on three continents to derive a relationship to describe the runoff ratio, R, which is defined as the ratio of the volume of urban runoff to the water volume of the rain event. The relationship is based on fraction of two-dimensional impervious surface area, x, such that

$$\begin{aligned} &R = 0;\ x < 0.2 \\ &R = 2x - 0.4;\ 0.2 \leqslant x \leqslant 0.4 \\ &R = x;\ x > 0.4. \end{aligned} \tag{4}$$

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