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A model system to mimic environmentally active surface film roughness and hydrophobicity

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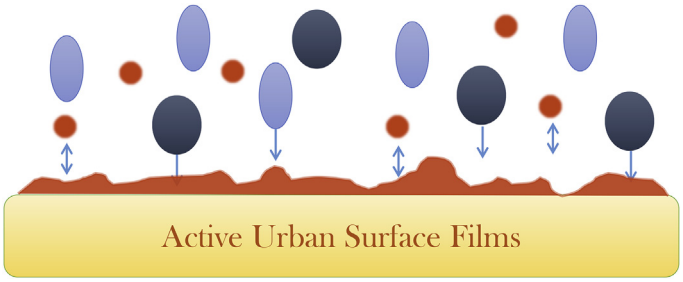
HIGHLIGHTS

- Developed novel model to simulate urban film morphology and hydrophobicity.
- Characterized surface morphology of model compared to native films.
- Oxidized film to investigate changes in composition and hydrophobicity.
- Quantified water sorption and diffusion with model.
- Model functions as platform to investigate organic pollutant fate and transport.

GRAPHICAL ABSTRACT



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ABSTRACT

This work presents the development and initial assessment of a laboratory platform to allow quantitative studies on model urban films. The platform consists of stearic acid and eicosane mixtures that are solution deposited from hexanes onto smooth, solid substrates. We show that this model has distinctive capabilities to better mimic a naturally occurring film's morphology and hydrophobicity, two important parameters that have not previously been incorporated into model film systems. The physical and chemical properties of the model films are assessed using a variety of analytical instruments. The film thickness and roughness are probed via atomic force microscopy while the film composition, wettability, and water uptake are analyzed by Fourier transform infrared spectroscopy, contact angle goniometry, and quartz crystal microbalance, respectively. Simulated environmental maturation is achieved by exposing the film to regulated amounts of UV/ozone. Ultimately, oxidation of the film is monitored by the analytical techniques mentioned above and proceeds as expected to produce a utile model film system. Including variable roughness and tunable surface coverage results in several key advantages over prior model systems, and will more accurately represent native urban film behavior.

1. Introduction

Solid environmental surfaces represent ubiquitous substrates for the deposition of particulate matter and reaction of atmospheric persistent organic pollutants (POP). These surface films cover thousands of square kilometers of human-made structures and natural surfaces. While significant previous research has focused on the behavior of particulate matter and their surface chemistry (Al-Abadleh and Grassian, 2003; Barsanti et al., 2017; Gentner et al., 2017), the notion that urban films are active contributors to the fate and transport of airborne chemical species is a relatively young and exciting area of environmental research (Butt et al., 2004; Diamond et al., 2000; Diamond and Hodge, 2007; Gingrich et al.,

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2001; Law and Diamond, 1998; Liu et al., 2003; Wu et al., 2008). Given the immense film surface area and volume, and its' propensity to absorb POP, it is clear that these surfaces provide heterogeneous reaction sites relevant to environmental and human health. This research focuses on developing improved laboratory model systems to replicate principle aspects of the dynamic chemistry and morphology found in native 'urban grime' surfaces.

The urban grime surface has complex physical and chemical properties that depend on several environmental and geographic factors. These are thought to include: geographic location and proximity to emission sources (Butt et al., 2004; Diamond et al., 2000; Gingrich et al., 2001; Law and Diamond, 1998; Melymuk et al., 2011; Lam et al., 2005; Simpson et al., 2006), exposure to sunlight (Asad et al., 2004; Baergen and Donaldson, 2013, 2016), exposure to rainfall and wind (Csiszar et al., 2012), and the presence of bacteria, molds, or fungi (Oldham et al., 2016). Due to the complex nature of these factors, the chemical composition and physical morphology of urban films are both highly variable and poorly defined. However, investigating the films' roles as mediators of environmental chemistry is essential to elucidating the fate and transport of POP and volatile organic compounds (VOC). While both are important to environmental chemistry, POP can have variable volatility and are present in the atmosphere and urban films due to their resistance to environmental degradation. VOC are organic species that have significant vapor pressures and thus are present in the atmosphere as vapors or gases.

The chemical composition of the films is highly dependent on geographic location (Gingrich et al., 2001). In several literature reports, naturally occurring films are reported to be comprised of 5–50% organics (of which roughly one-third is carbohydrates, another third is aliphatics, and a remaining third is aromatics and carbonyls). The remaining inorganic fraction is reported to be 7% nitrates, 8% sulfates, and ca. 18% metals (49% calcium, 13% iron, 13% sodium, 13% magnesium, 6% aluminum, 2% potassium, and 4% other trace metals), all by mass. Unclassified residual mass is attributed to inorganic components, likely including silicates (Lam et al., 2005; Simpson et al., 2006; Donaldson et al., 2009; McBride, 1994).

Prior research has shown that urban films can often build to thicknesses of hundreds of nanometers, and the resulting volume can contain hundreds of nanograms of POP species per square meter (Wu et al., 2008). Over the weeks and months that urban grime films persist, they are known to accumulate significant amounts of POP. Specific examples include ab/adsorption of polychlorinated biphenyls (PCB) (Diamond and Hodge, 2007; Cotham and Bidleman, 1995; Helm and Bidleman, 2003), polycyclic aromatic hydrocarbons (PAH) (Unger and Gustafsson, 2008), and polybrominated diphenyl ethers (PBDE) (Butt et al., 2004) (see Fig. 1). A simple calculation of urban film volume multiplied by observed loading rates (Diamond and Hodge, 2007; Cotham and Bidleman, 1995; Helm and Bidleman, 2003) indicates that a single high-rise building could support a film that contains approximately 6 g of PCBs. Large-scale models, like one for the downtown area of Toronto, Canada (19.6 km^2), have estimated that an average 1 g/day of five PCB congeners is transported from the air into the film, and subsequently washed into the groundwater (Csiszar et al., 2012). Further, a fugacity model considering rainfall intensity, wind speed and direction, and the octanol-air partition coefficients (K_{oa}) of various compounds, suggests urban films' mass accumulation is influenced by two major factors: 1) wind exposing the film to more or less particulates, and 2) by partitioning (semi)volatile organic species into the film (Csiszar et al., 2012; Diamond et al., 2001).

The POP uptake of an urban film has been shown to be correlated with the fraction of organic species within the film. One report highlights the trend that POP mass increases by a factor of one hundred for every tenfold increase in organic matter mass (Liu et al., 2003). To examine this environmentally important aspect of urban films, our work focuses on the organic phase of a model urban film as a highly active stationary phase for POP species. This model of native urban films will capture the important contributions of the organic phase, and allow a platform for incorporation of other significant inorganics, amorphous carbon species, and saccharides into subsequent, more complex iterations of the urban film model that will mimic their naturally occurring physical and chemical properties. Film mass is lost during rain events as wash-off, which is proposed to be the source of significant spikes in groundwater concentration seen immediately after rain events (Csiszar et al., 2012; Diamond et al., 2001).

While few laboratory experiments have been carried out on native urban films that developed naturally in the environment, it is clear that urban films provide a significant reservoir of POP species and a transport pathway from the atmosphere into groundwater. Recently, the Donaldson group has characterized the photochemistry (Baergen and Donaldson, 2013, 2016) of urban films along with composition and reactivity relative to atmospheric particles (Baergen et al., 2015), further highlighting important reactive sites for atmospheric species undergoing photochemical

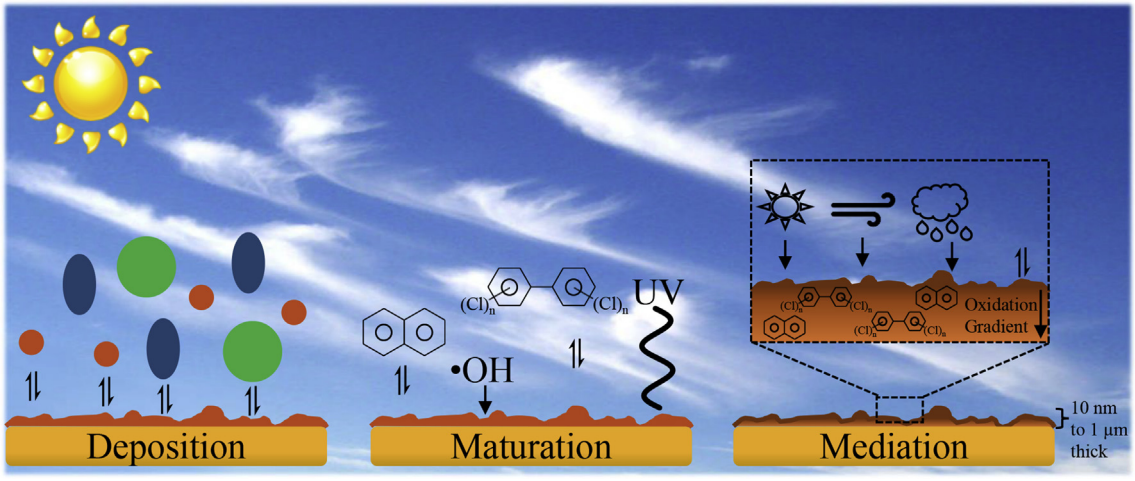

Fig. 1. Schematic illustrating from left to right: urban film formation via settling of biogenic and anthropogenic emissions; film interactions with UV radiation, atmospheric oxidizers and radicals, and POP ad/desorption; and a matured film that has experienced POP loading, degradation and oxidation, and climatological maturation processes.