Field and Laboratory Investigations of Organic Photochemistry on Urban Surfaces

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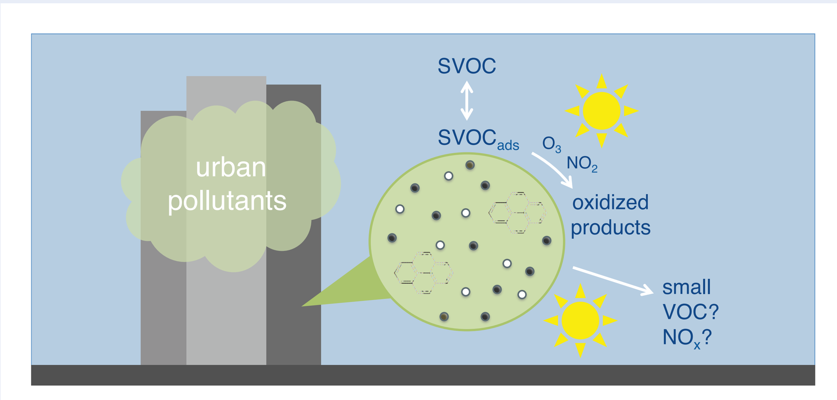
Urban Film: a Complex Reaction Medium



Urban surfaces are coated with a complex mixture of chemicals, both inorganic and organic:

- ions and metals[1]
- alcohols, alkenes, esters, acids, and carbohydrates[1]
- trace toxic species, including polycyclic aromatic hydrocarbons (PAH)[2]

To date, nearly all studies of urban film have focused on its composition—only one study has explored its role as a substrate for photochemistry.[3]

Research Questions

1. Does urban film composition evolve with time?
2. How does urban film composition differ from aerosol composition?
3. Does urban film promote the photooxidative processing of organic and inorganic species contained within it?
4. Does urban film act as a photochemical source of reactive gas-phase species, including NO_X and small organic molecules?
5. Are PAH contained within urban film subject to rapid oxidation by light and/or ozone?

Field Sampling Strategy and Analytical Methods

Sampling Details

Sampling was conducted from September 19 to October 25, 2014 at the Leipzig-Mitte air quality monitoring station, which is located in a high-traffic area opposite the main train station.

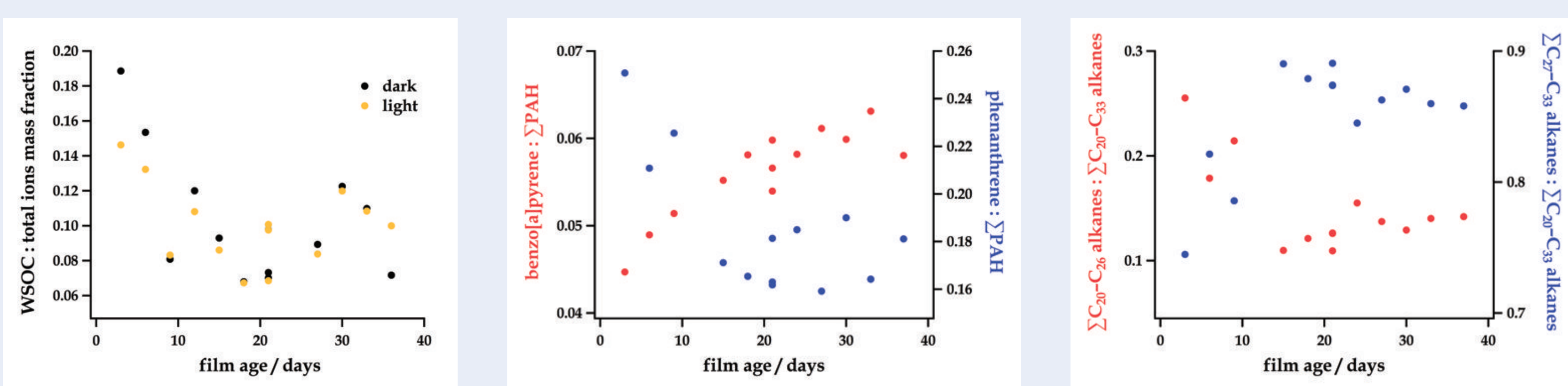
Film was collected using a home-built three-stage sampler. The top stage is exposed to sunlight, while the two lower stages are light-shielded. Small glass beads were used as surrogate window surfaces. Co-located PM_{10} samples were collected on quartz filters using a low-volume air sampler (17 L min^{-1}).

Analytical Methods

Aqueous bead and filter extracts were subject to routine analysis for water-soluble organic carbon (WSOC) and inorganic ions. The PAH and alkane content of bead and filter samples was determined using Curie-point pyrolysis GC-MS (CPP-GC-MS).[4]

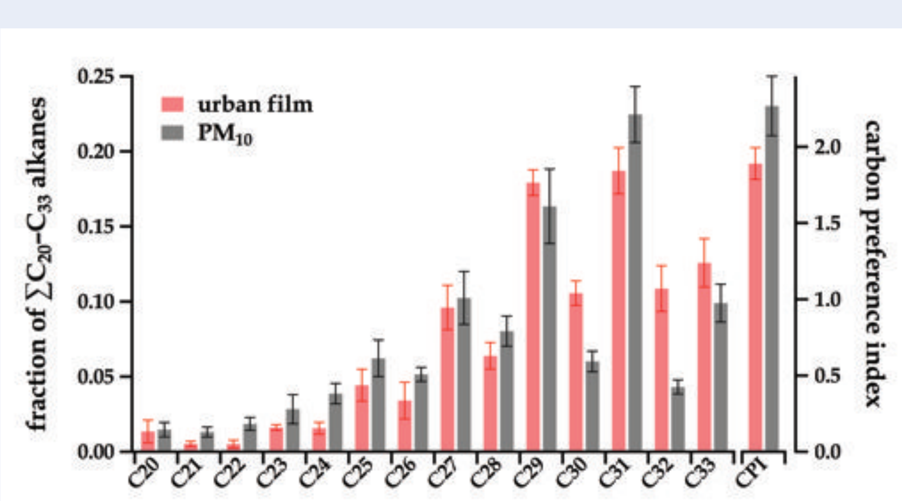
In a separate set of experiments, the PAH content of beads deployed for ~ 5 months under dark conditions was determined as a function of exposure to light and/or ozone in an atmospheric pressure flow reactor at 50% RH. The light-induced production of NO_X and gas-phase organic species by these samples was measured using a commercial NO_X analyzer and a proton-transfer reaction mass spectrometer (PTRMS), respectively.

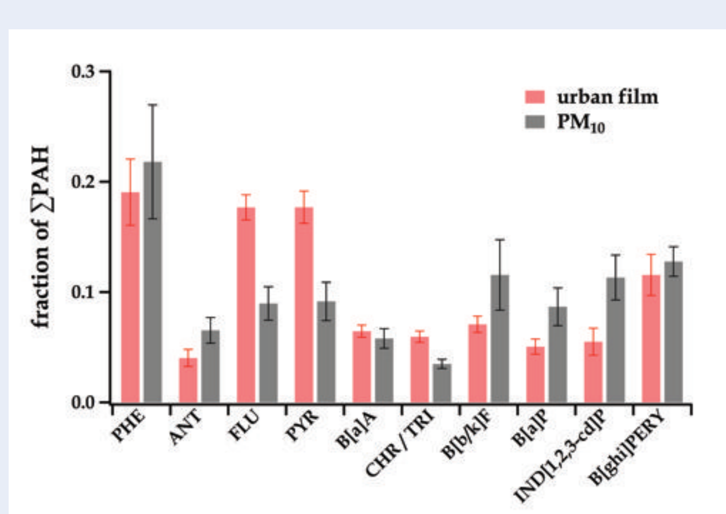
Urban Film Composition Evolves with Time

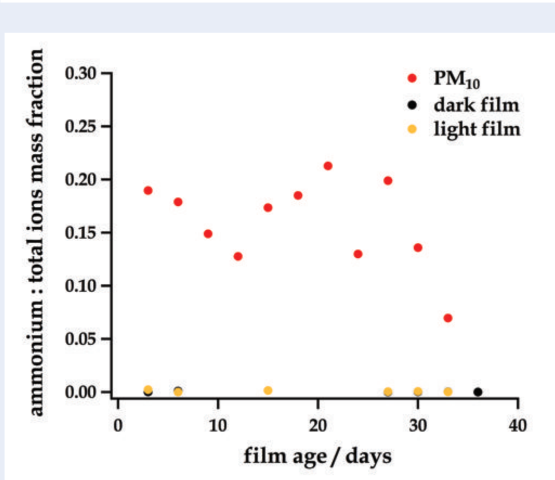


- The composition of urban film changes dramatically during the early stages of film development: the relative abundances of less-volatile, predominantly particle-associated PAH and alkanes both increase with film age, while the relative abundances of more volatile PAH and alkanes and the WSOC: total ion mass fraction all decrease with film age
- These results provide direct field evidence for previous suggestions that urban film first develops via the condensation of semivolatile organic species, and that the resultant organic coating enhances the particle capture efficiency of the surface[5,6]

Urban Film Composition Differs from PM_{10}

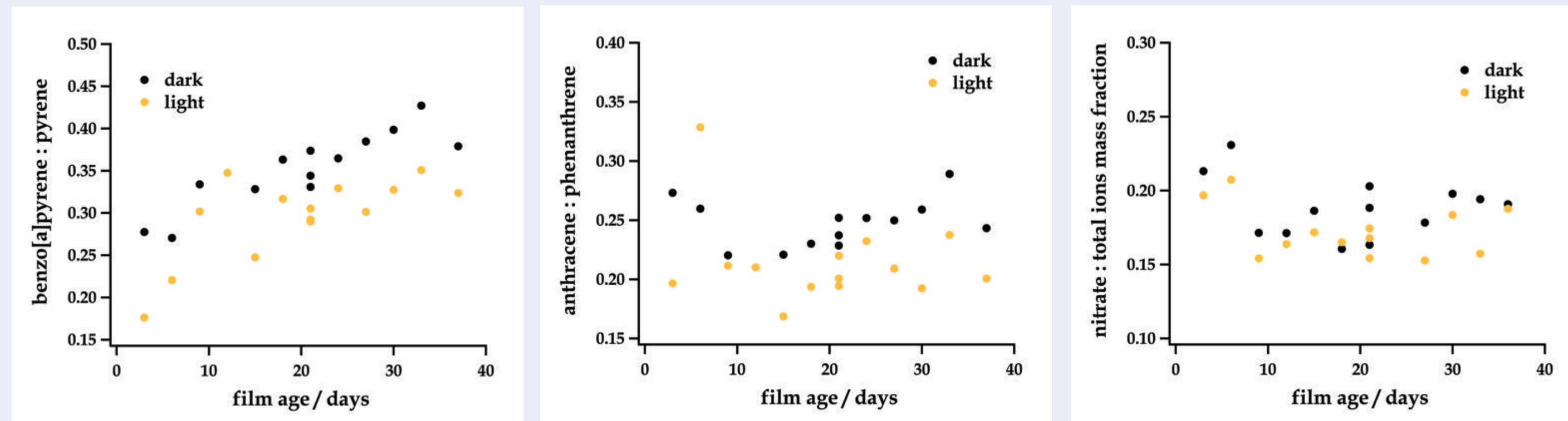






- Urban film is enriched in larger n-alkanes relative to PM_{10}; the petrogenic alkanes C_{30} and C_{32} are particularly enhanced, which may reflect contributions from coarse tire debris[7]
- Urban film is enriched in fluoranthene and pyrene, which provides further evidence that film acts as a reservoir for semivolatile species[1], and depleted in larger PAH, which likely reflects oxidative processing of these reactive PAH within the film
- Ammonium is depleted in the film relative to PM_{10}, which may reflect the contribution of coarse PM to the film, ammonium nitrate evaporation, and/or ammonium–ammonia partitioning

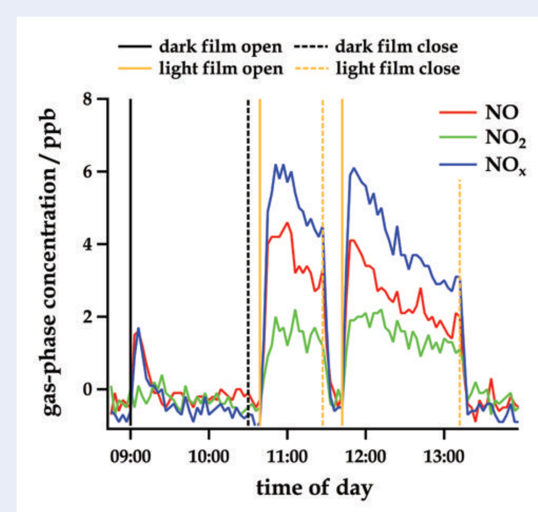
Field Evidence for Film-Phase Photochemistry

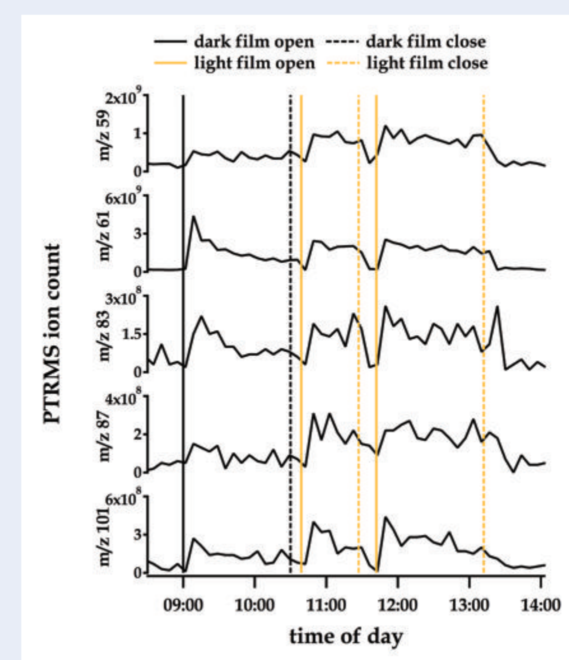


- The PAH abundance profile of urban film grown under ambient sunlight is different from film grown under light-shielded conditions: the more photochemically active PAH anthracene and benzo[a]pyrene are depleted relative to the less reactive PAH phenanthrene and pyrene
- The nitrate : total ions mass fraction of film grown under ambient sunlight is lower than that of film grown under light-shielded conditions
- Together, these results provide convincing field evidence that urban film serves as a photochemical sink for photoactive organic and inorganic species

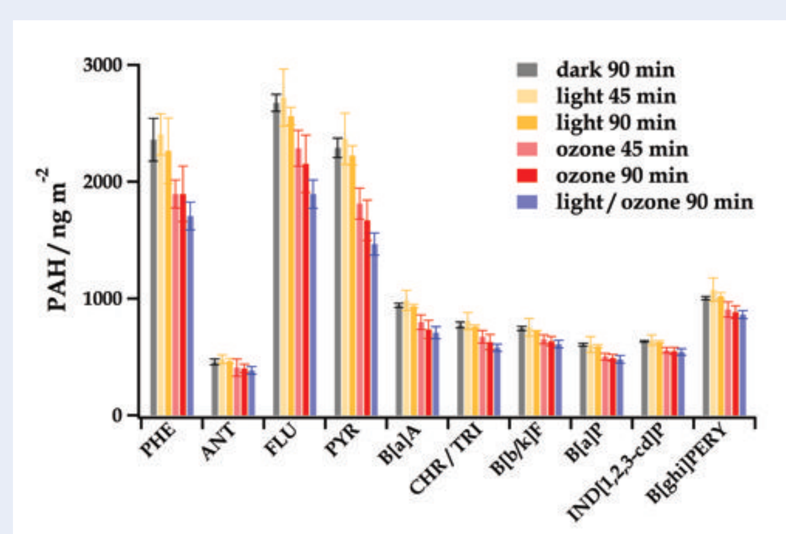
Illuminated Film Yields Reactive Gas-Phase Species

- Illumination of film samples resulted in NO_X production, which provides additional evidence that urban film serves as a temporary reservoir rather than an ultimate sink for deposited nitrate[3]
- Illumination of film samples also resulted in the production of a number of gas-phase organics, two of which were tentatively identified as acetone (m/z 59) and acetic acid (m/z 61)[8]
- These results suggest that photolysis of organic species contained within urban film has the potential to contribute to urban VOC budgets





Shielding Effects in Urban Film



- No light-induced PAH degradation was observed in collected film samples, which implies that light penetrates into only the uppermost layer of the film
- Film-phase PAH, including the highly reactive PAH benzo[a]pyrene, exhibited largely uniform, minor degradation upon exposure to ~ 17.5 ppm ozone
- These results imply that PAH reactivity with ozone is limited by ozone availability, which suggests either that ozone is depleted via its competitive reaction with unsaturated species present within the film[1] or, more compellingly, that ozone diffusion in the film is slow (i.e. that the film is solid or semi-solid)[9]

Conclusions and Outlook

- The composition of urban film rapidly evolves during the early stages of film development
- Urban film is chemically distinct from atmospheric aerosol; compositional differences reflect physical and chemical differences between the two atmospheric compartments
- Urban film serves as a photochemical sink for photochemically active inorganic and organic species, and a photochemical source of NO_X and small gas-phase organic species; further experimental and modeling work will assess the contribution of film-phase photochemistry to urban VOC budgets
- PAH contained within field-collected film samples are shielded from photolysis and reaction with ozone; further work will explore the photochemical reactivity of film-phase PAH as a function of film thickness

References

1. Lam, B.; Diamond, M.L.; Simpson, A.J.; Makar, P.A.; Truong, J.; Hernandez-Martinez, N.A. Atmos. Environ. 2005, 39, 6578–86.
2. Gingrich, S.E.; Diamond, M.L. Environ. Sci. Tech. 2001, 35, 4031–4037.
3. Baergen, A.M.; Donaldson, D.J. Environ. Sci. Tech. 2013, 47, 815–820.
4. Neusüss, C.; Pelzing, M.; Plewka, A.; Herrmann, H. J. Geophys. Res. 2000, 105, 4513–4527.
5. Law, N.L.; Diamond, M.L. Chemosphere 1998, 36, 2607–2620.
6. Liu, Q.T.; Diamond, M.L.; Gingrich, S.E.; Ondov, J.M.; Maciejczyk, P.; Stern, G.A. Environ. Poll. 2003, 122, 51–61.
7. Rogge, W.F.; Hildemann, L.M.; Mazurek, M.A.; Cass, Glen, R. Environ. Sci. Technol. 1993, 27, 1892–1904
8. de Gouw, J.; Warneke, C. Mass Spect. Rev. 2007, 26, 223–257.
9. Zhou, S.; Lee, A.K.Y.; McWhinney, R.D.; Abbatt, J.P.D. J. Phys. Chem. A. 2012, 116, 7050–7056.

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