

Field- and Laboratory-Based Assessment of the Composition and Photoreactivity of Urban Surface Films: Development of the Leipzig Urban Film Sampling Network (LUFNS)

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Urban Film: A Complex Reaction Medium

What is Known About Urban Film?

In urban areas, surfaces are coated with a complex film of chemicals, which enhances the dry deposition of particles and the partitioning of semi-volatile organics to the surface.^{1,2}

Studies investigating the bulk composition of this atmospheric compartment—commonly referred to as “urban film”—have shown it to consist of both inorganic (sulfate, nitrate, and metals) and organic (alcohols, alkenes, esters, acids, and carbohydrates) material.³ The film also serves as a reservoir for a number of trace species of toxicological significance, including polycyclic aromatic hydrocarbons (PAH).⁴

Urban film has been postulated to promote chemical loss by wash-off, re-volatilization, and photoinduced reactions.¹ To date, however, our knowledge regarding photochemistry occurring within real urban film samples is limited to the results of a single study, which investigated nitrate photolysis at the surface of collected film samples.⁵

Research Questions

1. How does the organic composition of urban film vary with sampling location? Can urban film composition be measured in a way that limits externally induced inter-sample variability?
2. How are urban films formed? How does film composition evolve with time?
3. Does urban film promote the photo-oxidative processing of semi-volatile organic compounds present within it?
4. How does urban film interact with atmospheric oxidants, including ozone and nitrogen dioxide? Is this interaction influenced by light?
5. Does the photochemical processing of urban film release small, oxidized volatile organic compounds to the gas phase?
6. Are photochemical processes at the urban film surface promoted by photoactive minerals, including Ti, Zn, and Fe oxides?

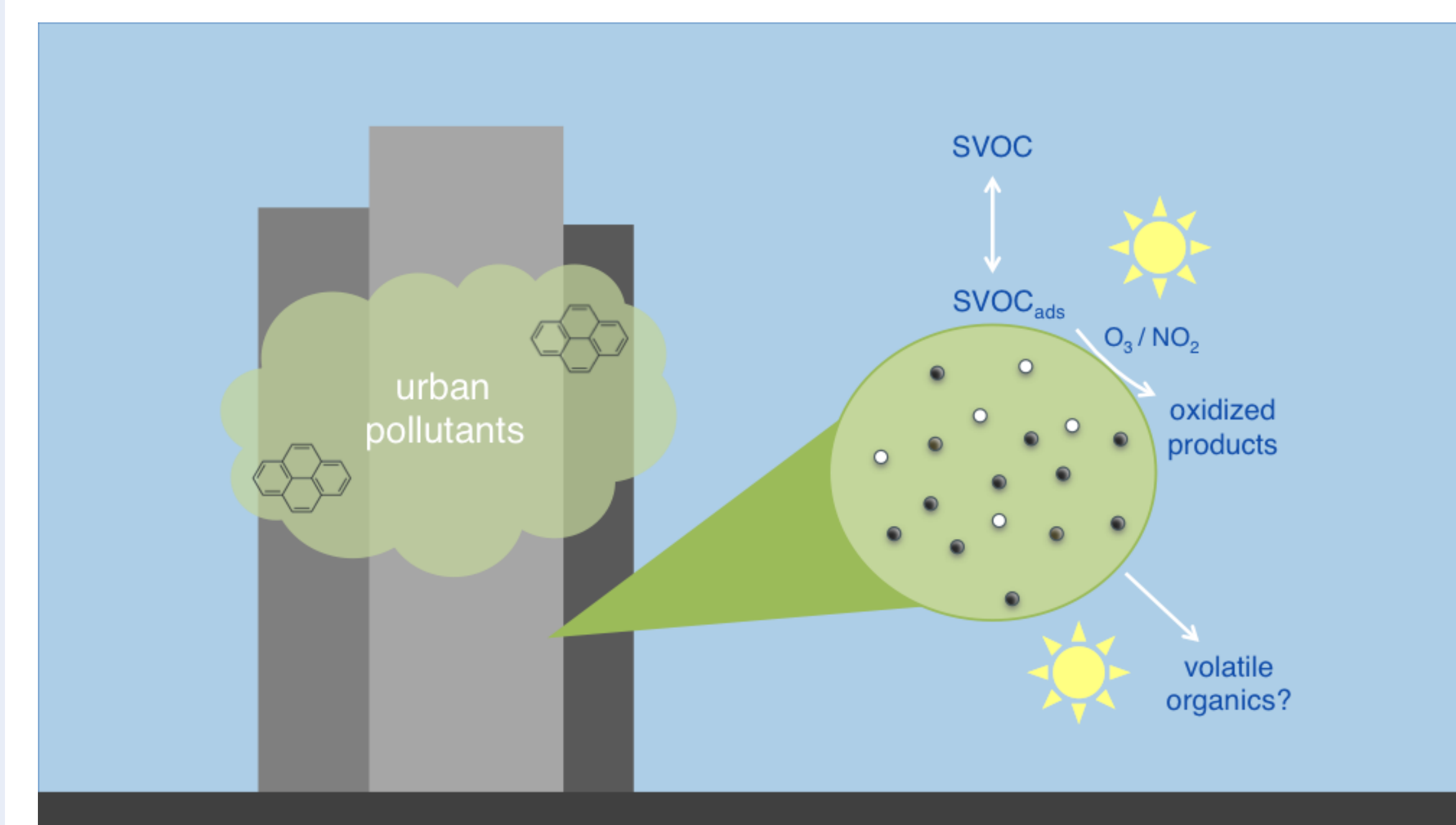


Figure 1: Urban film: a largely unexplored photochemical reaction medium.

Field Sampling Strategy and Analytical Methodologies

Field-Based Investigations of Urban Film Formation, Evolution, and Photoreactivity Under Controlled Conditions—Moving Beyond Windows

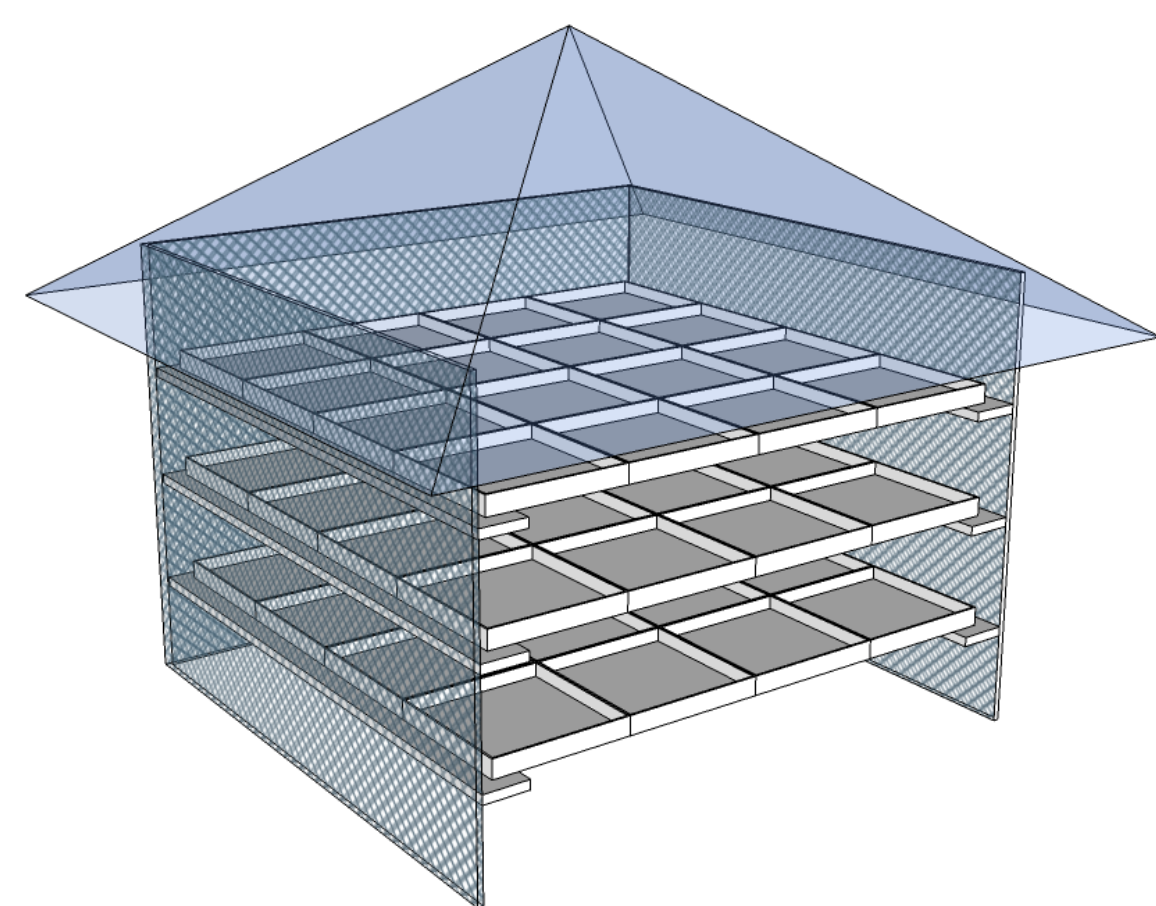


Figure 2: Urban film sampler design.

Urban film sampling in Leipzig will be conducted using newly designed rain-shielded sampler housings, which will employ small glass spheres ($d = 3$ mm) as surrogate window surfaces. The sampler housings contain three trays, each of which is subdivided into 16 individual sample compartments, and are designed such that the uppermost trays are exposed to ambient radiation while the two lower trays are light-shielded.

The formation and evolution of urban film will be studied by measuring film organic composition—initially, Σ PAH will be used as a proxy for semivolatile organics within the film—as a function of atmospheric exposure time.

In order to determine whether urban film serves as a photochemical sink for reactive organic species, film PAH composition will be measured as a function of time under both light (upper tray) and dark (middle tray) conditions. Samples from the lower tray will be used for laboratory experiments.

Samplers will be deployed at a range of urban, suburban, and rural locations in the Leipzig region.

Analytical Methods Employed

- Curie-Point Pyrolysis GC-MS (CPP-GC-MS; organic analysis)
- Scanning Transmission Electron Microscopy with Energy-Dispersive X-Ray Spectrometry (STEM-EDX; photoactive mineral analysis)

Laboratory Assessments of Urban Film Photoreactivity

PAH Photoreactivity

In these experiments, urban film samples grown under dark conditions will be exposed to atmospheric oxidants, including ozone and nitrogen dioxide, in an atmospheric-pressure flow reactor and the rate of loss of PAH within the films will be measured using CPP-GC-MS.

In order to determine the effect of light-induced chemistry upon reactions at the film surface, some experiments will be performed under illuminated conditions. In order to explore the influence of surface-sorbed water upon the interaction of film components with atmospheric oxidants, experiments will be performed at a range of relative humidities.

The primary goal of these experiments will be to improve our understanding of the heterogeneous reactivity of PAH at the surface of real urban films, with all their attendant complexity. Since the heterogeneous photooxidation of PAH occurs at different rates and via different mechanisms depending on its immediate environment,⁶ this work will contribute to our understanding of the photochemical processing of this class of chemicals in urban environments.

This work will also provide direct laboratory evidence for the role that urban films play in influencing the lifetime of semi-volatile species contained within them, and will serve as a complement to the field studies described above.

Trace Gas Uptake / Formation

The uptake of both ozone and nitrogen dioxide at a variety of atmospheric surfaces has been shown to exhibit a light enhancement. In order to determine whether this reactive pathway also occurs at the surface of urban film, the uptake of ozone and/or nitrogen dioxide by field-sourced urban film samples will be monitored under both dark and light conditions in an atmospheric-pressure flow reactor.

As mentioned previously, photolysis of nitrate has been shown to proceed efficiently at the surface of urban films.⁵ In order to determine the contribution of this pathway to measured gas-phase nitrogen dioxide concentrations, urban film samples will be illuminated in the absence of additional oxidants and the production of gas-phase nitrogen dioxide will be monitored.

Urban film contains a wide variety of organic species, some of which absorb light; its photochemistry, therefore, has the potential to result in the release of small, oxidized molecules to the gas phase (e.g. formaldehyde, acetone). To date, however, no studies have measured the production of gas-phase species from illuminated urban film. In order to assess the extent to which urban film serves as a source of reactive organic species, the production of gas-phase organics will be measured in the presence and absence of light and oxidants using proton-transfer-reaction mass spectrometry (PTR-MS).

Preliminary Measurements

Curie-Point Pyrolysis GC-MS Detection of PAH in Window Films at an Urban Background Site (TROPOS)

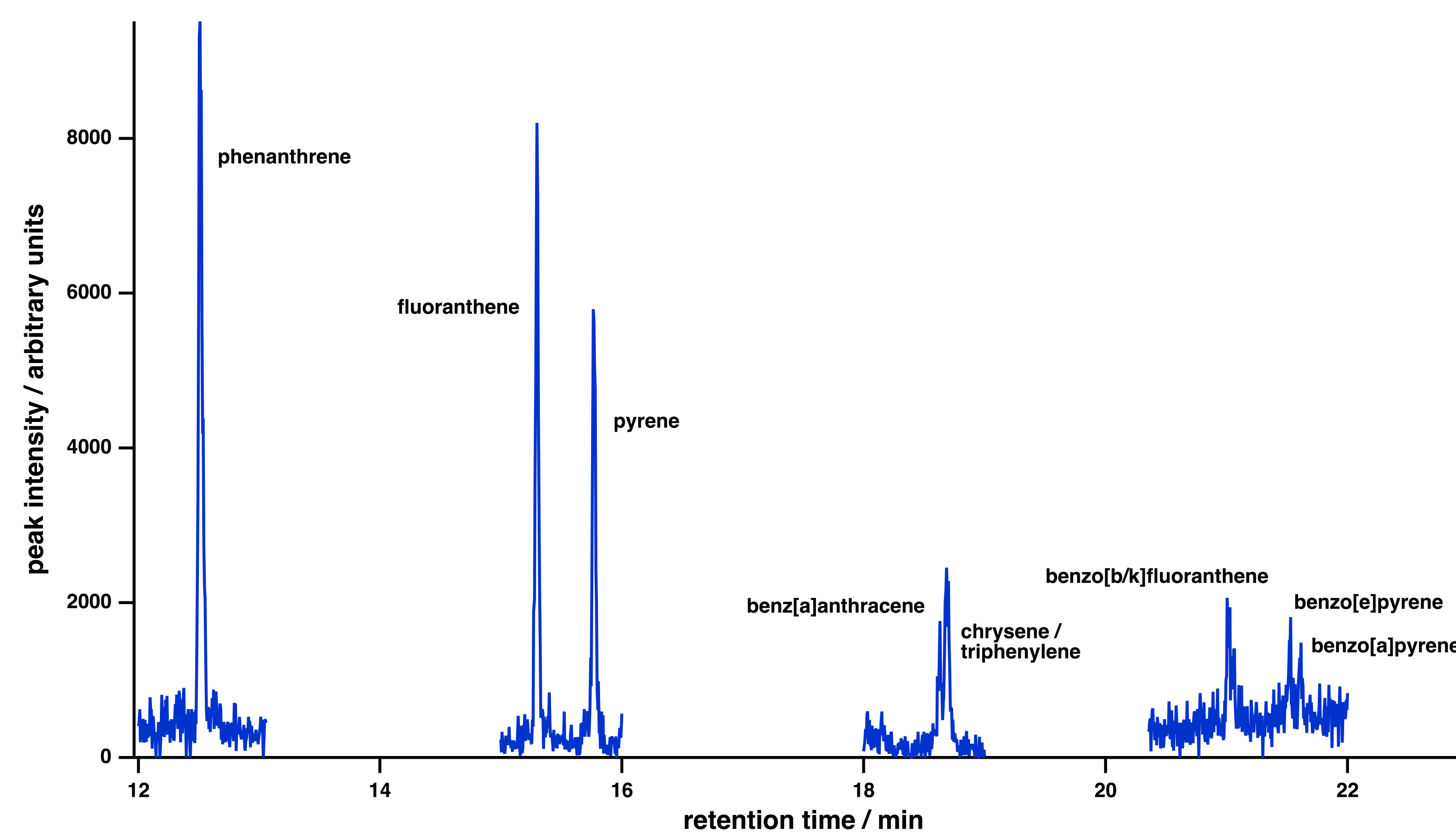


Figure 3: Extracted-ion chromatograms from CPP-GC-MS analysis of a window film extract.

The results shown above are in agreement with previous field measurements,^{1,4} which have shown that urban film contains an “aged” PAH profile: less reactive PAH such as pyrene, phenanthrene, and fluoranthene dominate while more reactive PAH such as anthracene and benzo[a]pyrene are depleted.

This abundance pattern has been attributed to the rapid photooxidation of reactive PAH within the film.⁷ The field measurements in this study, which will be performed under both light and dark conditions, will explicitly test this hypothesis.

Anticipated Contributions

This study will use a combination of analytical, field, and laboratory approaches to answer a broad range of questions regarding the composition and photochemical reactivity of urban film.

The field component of the study will provide direct insight into spatial and temporal variations in film composition, the effect of light upon the persistence and ultimate fate of PAH within the film, and the extent to which film-phase reactions contribute to the complex mixture of compounds present in urban film.

The laboratory component of the study represents the first attempt to directly study the interaction of PAH with light and atmospheric oxidants in the complex reactive environment provided by the film compartment. Comparison of the results obtained in this study with those obtained in previous laboratory studies using simple proxies for the urban film surface^{6,8} will provide insight into the extent to which inferences of reactivity obtained on these proxy surfaces correctly reflect reactivity in the real, and complex, environment.

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