Urban grime photochemistry and its interaction with the air pollutants NO and NO_2

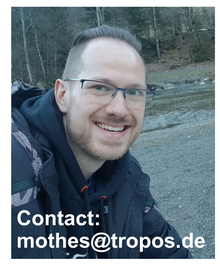
Falk Mothes and Hartmut Herrmann

Leibniz Institute for Tropospheric Research, Leipzig, Germany

DFG Deutsche Forschungsgemeinschaft German Research Foundation

TROPOS Leibniz Institute for Tropospheric Research

Leibniz Association

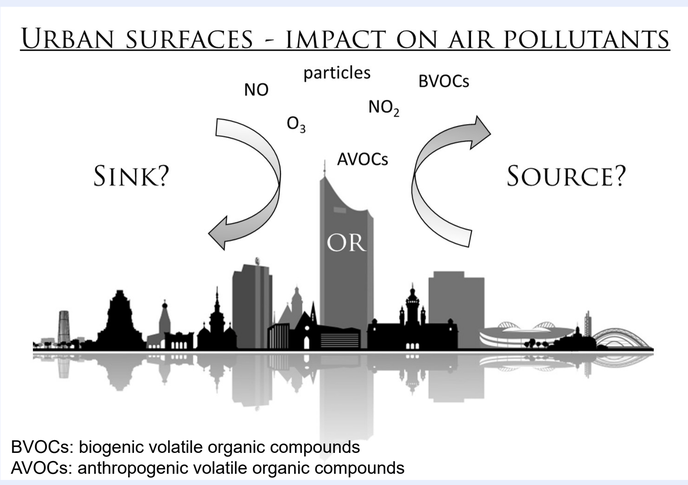


Introduction / Motivation

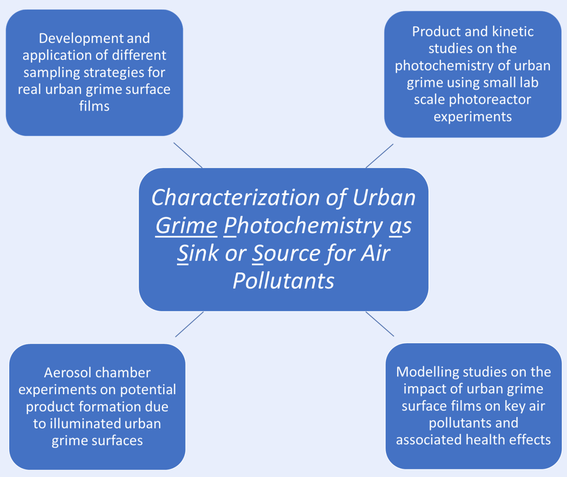
What is urban grime and how can urban grime impact local air quality?

- 1998 Law and Diamond (1) hypothesized the first time the development of an organic film on impervious surfaces when they are exposed to the atmosphere for a certain time
- Film development via direct condensation of semi-volatile chemicals and/or deposition of secondary organic aerosol (SOA)
- Follow up studies (2-8) sampled urban surfaces (window glass) and determined the chemical composition: 1) inorganic anions and cations (nitrate, sulfate, carbonate, ammonium, sodium, calcium) and 2) up to 25% organics (fatty acids, long chain aliphatic compounds, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs)
- Lab studies (9-13) exist on its chemical reactivity, however merely on proxies for urban grime, like 1-octanol, pyrene or humic acid
- Only a few studies (14-20) exist on real urban grime investigating if…

"Urban grime acts as a separate environmental compartment!"

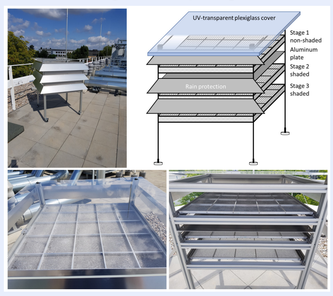


Project „GrimePaSS"



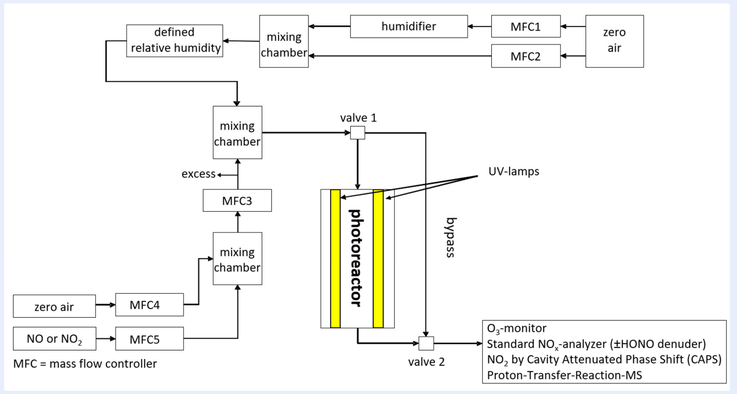
Sampling procedure

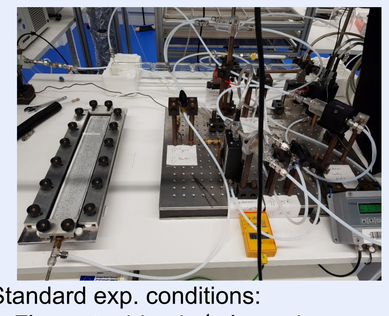
Sampling on glass beads (Ø 3mm) using a custom built 3 stage sampling device



- Samples protected from rain
- Shaded and non-shaded sampling
- Sampler placed on the roof of the lab building (urban background)
- 12 weeks sampling time

Small scale photoreactor setup





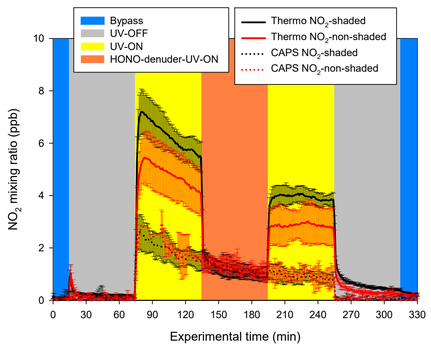
Standard exp. conditions:

- Flow rate 4 L min^{-1} clean air
- Relative humidity (RH) 70%
- Light intensity (21 W m^{-2}, 300-400 nm)

1) Clean air experiments on urban grime surface films – shaded vs. non-shaded glass beads
2) Impact of the experimental conditions, relative humidity and light intensity / source
3) Interaction of target pollutants with urban grime surface films – results for NO and NO_2

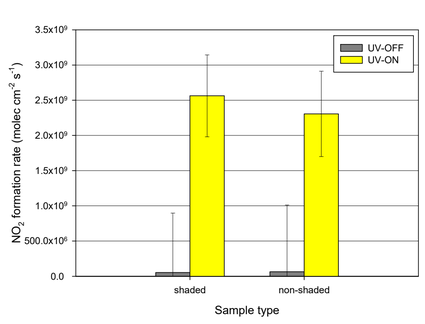
Results

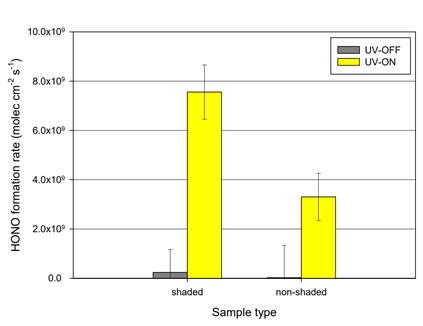
1) Clean air experiments on urban grime surface films – shaded vs. non-shaded glass beads



- O_3 and NO negligible (not shown)
- NO_2 from blank exp. < 0.2ppb
- Small NO_2- signal for UV OFF
- Increase NO_2-signal if UV-ON
- Clear change for NO_2- signal if HONO denuder is active
- Steady state after 2hrs irradiation

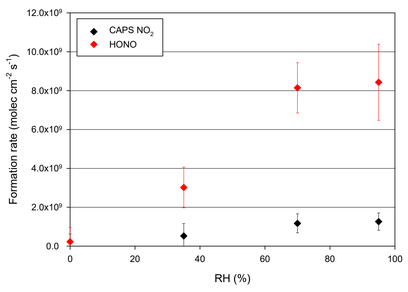
➢ Differences observed depending on the sampling conditions

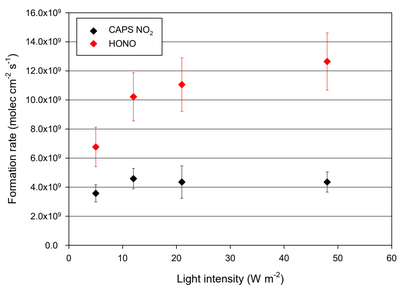




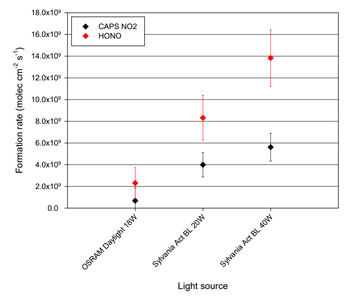
- ➢ In general formation observed for NO_2 and HONO if UV-ON
- ➢ Formation rate ~ 10^9 molecules cm^{-2} s^{-1}
- ➢ HONO formation on shaded glass beads 2.5 times higher compared to NO_2
- ➢ NO_2 formation independent on the sampling conditions
- ➢ HONO formation higher for shaded compared to non-shaded samples

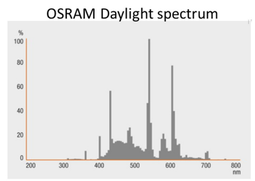
2) Impact of the experimental conditions relative humidity and light intensity / source

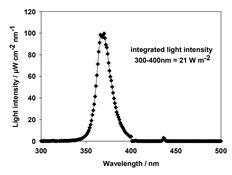




- Clear impact of RH and light intensity, with in general higher values with increasing humidity and light intensity
- Important: Almost no formation observed for experiments with dry air (<1% RH)
- Clear increase up to 70% RH and approx. 20 W m^{-2} , but no further impact for higher values → levelling off again / saturation effect
- Clear impact of light source on the formation rates, dependence on the UV part of the light, product formation only below 400 nm

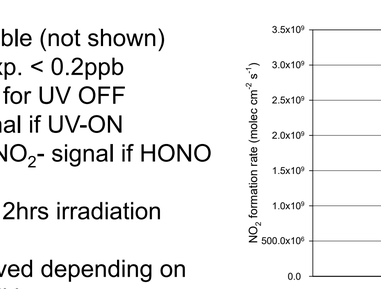


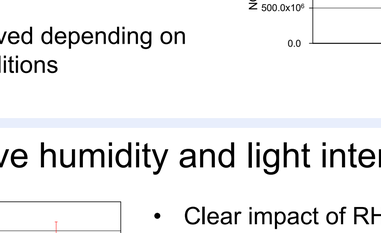




3) Interaction of NO and NO_2 with urban grime surface films @ 70% RH

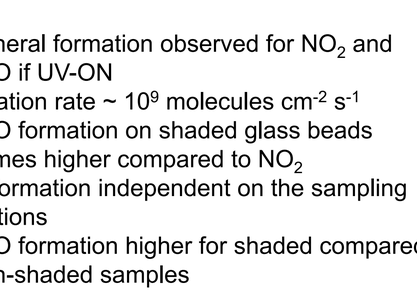
a) NO

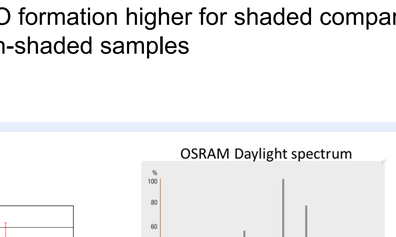




- No uptake of NO on urban grime surface films observed
- No clear impact of NO- addition on the formation of NO_2 and HONO
- Only slightly negative impact on the formation of NO_2 for shaded glass beads

b) NO_2





- No reactive uptake of NO_2 on urban grime surface films observed, in contrast to references 18-20
- Formation of NO_2 suppressed if NO_2 is added, slightly higher impact on shaded glass beads
- No clear impact of added NO_2 on HONO formation (Δ<0.3ppb), also no difference shaded vs. non-shaded glass beads

References

1) Law and Diamond **1998**, *Chemosphere*, *36* (12), 2607-2620. 2) Diamond et al. **2000**, *Environmental Science & Technology*, *34* (14), 2900-2908. 3) Gingrich et al. **2001**, *Environmental Science & Technology*, *35* (20), 4031-4037. 4) Liu et al. **2003**, *Environmental Science & Technology*, *37* (11), 2340-2349. 5) Butt et al. **2004**, *Environmental Science & Technology*, *38* (3), 724-731. 6) Lam et al. **2005**, *Atmospheric Environment*, *39* (35), 6578-6586. 7) Wu et al. **2008**, *Atmospheric Environment*, *42* (24), 6131-6143. 8) Kroptavich et al. **2020**, *ACS Earth and Space Chemistry*, *4* (10), 1813-1822. 9) Stemmler et al. **2006**, *Nature Letters*, *440* (7081), 195-198. 10) Handley et al. **2007**, *Environmental Science & Technology, 41* (11), 3898-3903. 11) Brigante et al. **2008**, *The Journal of Physical Chemistry A, 112* (39), 9503-9508. 12) Ammar et al. **2010**, *ChemPhysChem, 11* (18), 3956-3961. 13) Liu et al. **2020**, Environmental Science & Technology Letters, *54* (18), 11079-11086. 14) Baergen and Donaldson **2013**, *Environmental Science & Technology*, *47* (2), 815-820. 15) Baergen et al. **2015**, *Environmental Science & Technology*, *49* (21), 12688-12696. 16) Baergen and Donaldson **2016**, *Atmospheric Chemistry and Physics*, *16)* (10), 6355-6363. 17) Styler et al. **2018**, *ACS Earth and Space Chemistry*, 2 (9), 935-345. 18) Liu et al. **2019**, Environmental Science & Technology Letters, 6 (7), 413-417. 19) Yu et al. **2021**, *Journal of Environmental Sciences, 106*, 124-135. 20) Yu et al. **2022**, *ACS Earth and Space Chemistry*, *6* (8), 1960-1968.

Funding and contact

This work was funded by the German Research Foundation (Deutsche Forschungsgemeinschaft (DFG) - project number 415705351).

Dr. Falk Mothes (mothes@tropos.de)

Prof. Hartmut Herrmann (herrmann@tropos.de)