Light-mediated chemistry at the surface of urban road dust: implications for air quality and health

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Dust in the atmosphere: over one billion tons are emitted annually



https://gmao.gsfc.nasa.gov/research/aerosol/modeling/nr1_movie/

Dust catalyzes a wide variety of atmospheric transformations



Local dust emission



different composition ... different reactivity?

Loganathan et al., Crit. Rev. Environ. Sci. Tech. 2012; Chen et al., Chem. Rev. 2012 http://www.thedailystar.net/city/take-steps-control-dhaka-road-dust-pollution-winter-dry-season-activists-1482997

Road dust makes a significant fraction of atmospheric particulate matter (PM)



https://extranet.gov.ab.ca/env/infocentre/info/library/8862.pdf; http://www.health.utah.gov/utahair/pollutants/PM/

Road dust makes a significant fraction of atmospheric particulate matter (PM)



http://www.healthyenvironmentforkids.ca/sites/healthyenvironmentforkids.ca/files/No_Breathing_Room.pdf

Road dust photochemistry: experimental strategy





nine-compartment, temperature-controlled, stirred photochemical reactor

Dust-catalyzed singlet oxygen production



Appiani et al., Env. Sci. Process. Impact 2017; Haag et al., Chemosphere 1984

Comparative reactivity studies



Surface area-scaled $[^{I}O_{2}]_{ss}$

Road dust is more reactive than desert dust

The smallest road dust fraction is the most reactive



Organic matter contributions



Appiani et al., Env. Sci. Process. Impact 2017; Haag et al., Chemosphere 1984

Effect of season/location on road dust reactivity

1.6x10⁻¹³ 1.4 1.2 $[^{1}O_{2}]_{ss}$ / M 1.0 -0.8 0.6 0.4 0.2 0.0 Urban Fall 2016) 2017) 2017) 2017) Urban Fall 2016) Urban Fall 2016) Urban Fall 2017) Esteet Sweet Sweet Suburban Losidential Dan Barry Suburban Losidential Suburban Losidentia Suburban Losidential

[¹O₂]_{ss} relatively similar for the sample set studied

Contributions from carbon



no obvious correlations with total carbon or UV-Vis absorbance of sample extracts

Imaging and elemental analysis of road dust



Elemental composition of road dusts

| | Urban (Fall 2016) | Urban (Spring 2017) | Urban (Fall 2017) | Street Sweepings | Suburban (residential) | Suburban (park) | | | |
|----------|----------------------|------------------------|----------------------|------------------|---------------------------|--------------------|--|--|--|
| Na | 1.63 | 5.57 | 1.95 | 0.94 | 1.11 | 0.9 | | | |
| Mg | 1.63 | 1.27 | 1.41 | 2.03 | 1.5 | 1.22 | | | |
| Al | 9.43 | 6.01 | 8.66 | 7.87 | 9.56 | 8.94 | | | |
| Si | 60.23 | 54.06 | 62.95 | 57.35 | 63.5 | 66.86 | | | |
| к | 4.02 | 3.26 | 3.84 | 3.39 | 4.86 | 4.42 | | | |
| Ca | 8.54 | 9.59 | 6.36 | 16.08 | 6.14 | 3.42 | | | |
| Mn | | | | 0.63 | | | | | |
| Ti | 0.88 | | | | 0.77 | 0.82 | | | |
| Fe | 11.07 | 8.74 | 12.58 | 11.03 | 11.27 | 12.93 | | | |
| тс | 3.93 | 4.27 | 5.36 | 5.66 | 5.57 | 2.80 | | | |
| OC (est) | | 2.87 | 4.15 | 3.41 | 4.29 | 2.15 | | | |

Current work and future goals

- Redesign the reaction chamber to be more robust, and allow for increased sample throughput
- Determine surface area-scaled [¹O₂]_{ss} for the different road dust samples
- Collect and analyze more road dust samples from additional locations during different seasons

Photochemical uptake of ozone onto road dust



Does ozone react with road dust?

Does irradiation affect the reaction?

Does humidity affect the reaction?



How do we study ozone uptake onto road dust?



Coated-wall flow

Gas flow into movable injector



Schematic of coated-wall flow tube set-up



Size fractionation of dust



Preparation of coated tubes







Reaction profile of road dust and ozone



Road dust is much more reactive than desert dust!



Rate of reaction increases with mass



Enhanced reactivity at increasing relative humidity



Future outlook

What is responsible for road dust reactivity?

 Further analysis of composition and comparison of different samples Can road dust influence local air quality?

 Use calculated uptake coefficients for atmospheric modeling





With thanks to ...





Edmonton

Machine/glassblowing shop photochemical reaction chamber Department of Chemistry / Faculty of Science start-up funding





Equations



 γ_{geo} = geometric uptake coefficient k = pseudo first order rate constant r = radius of Pyrex tube c = mean molecular speed of ozone $\boldsymbol{\gamma}_{BET} = \frac{\boldsymbol{\gamma}_{geo} * S_{geo}}{m * BET}$

 γ_{BET} = BET uptake coefficient γ_{geo} = geometric uptake coefficient S_{geo} = geometric surface area m = mass of dust BET = surface area

$[O_3] = [O_3]_0 e^{-kt}$

[O₃] = concentration of ozone at time t
[O₃]₀ = concentration of ozone at time 0
k = pseudo first order rate constant
t = residence time inside tube

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