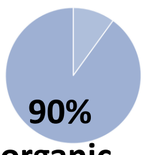
Photochemical Processing of Atmospheric Aerosols

Abigail McConnell,
School of Chemistry,
University of Leeds
pmaram@leeds.ac.uk

1. Atmospheric Aerosols

Atmospheric aerosols alter the climate by direct and indirect radiative forcing. The cooling effect of aerosols is vital for Earth's climate, however uncertainties are caused due to **aerosol ageing**, which describes the processes that alter the chemical composition and physical and optical properties of the aerosol.



- Aerosols are a liquid droplets or fine solid particles suspended in air typically in the size range of 0.001 – 10 µm in diameter.
- Can be directly emitted, primary aerosols, or formed in the atmosphere, secondary aerosols.

- **Secondary Organic Aerosols (SOAs)** represent the highest proportion of atmospheric aerosols averaged globally

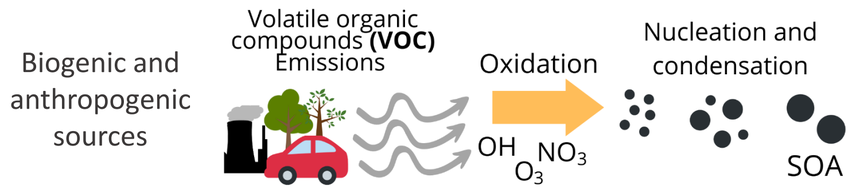


Figure 1: Formation of SOA

- SOA is a significant proportion of aerosol particles below 2.5 µm ($PM_{2.5}$)
- **$PM_{2.5}$** can penetrate deep into the lung and impair lung function, making it a global health risk attributed to millions of deaths worldwide each year.
- Aged SOA has a higher content of oxygenated species increasing its potential for inflammation and oxidative stress and thus its toxicity.

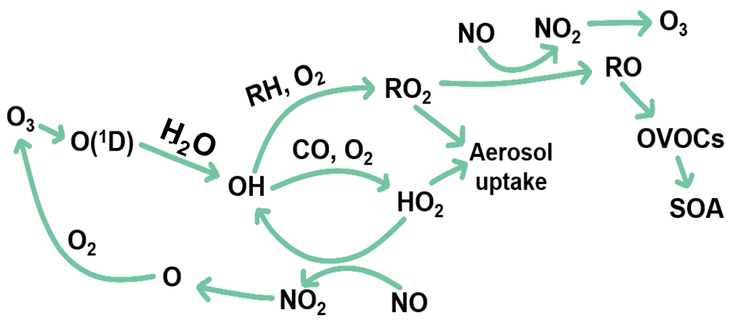


Figure 2: OH radical cycle

- The oxidising capacity of the atmosphere determined by OH
- **HO_2 and RO_2** are critical reactants in the atmosphere and are a major source of secondary pollutants, such as ozone and SOA.

4. Project Impact

- Investigations into SOAs dynamic functionality and resultant health effects guide air quality guidelines.
- Incorporation of aerosol uptake coefficients will improve the reliability of atmospheric models to predict the future climate.

Thematic Research Broadening Sabbatical: **Sensitivity of predicted SOA mass to gas-phase reaction rates**

Aim: To investigate the **sensitivity of the predicted SOA mass to gas-phase oxidation rate coefficients**, using the volatility basis set approach.

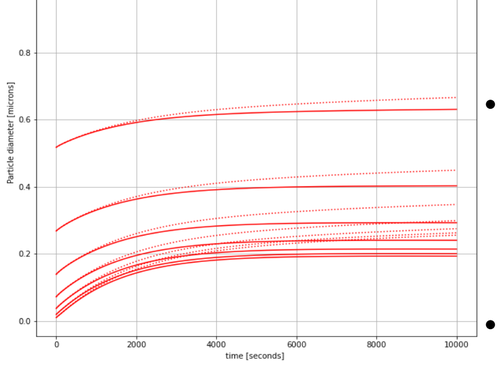


Figure 7: Evolving particle size distribution with no gas-phase reactions occurring (solid line) and when a second-order oxidation reaction of alpha-pinene with ozone is present (dashed line). *$k(O_3 + \alpha\text{-pinene}) = 9.61 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1}*

- To mitigate climate change, urban greening and biofuels are becoming more popular, **increasing the concentration of biogenic VOCs** and thus corresponding SOA mass.
- A simple theoretical model based on the volatility basis set is used to predict the SOA mass, from the oxidation of VOCs, through gas-particle partitioning, during a set time period.
- Incorporation of larger rate coefficients for the oxidation of VOCs, moves a larger mass fraction into the lower volatility bins, resulting in a larger predicted mass of SOA.
- Investigations need to be made into the current uncertainties in the VOC oxidation rate coefficients, and the following the effect this has on the sensitivity of predicted SOA mass.

2. Statement of the Problem

Few studies focus on the **photochemical processing of atmospheric aerosols** and how their chemical composition and physical properties change in the presence of sunlight.

- **SOA is photochemically active,** photochemistry on the surface or within the bulk of the aerosols initiates further oxidation leading to fragmentation of a variety of products, some of which are volatile.

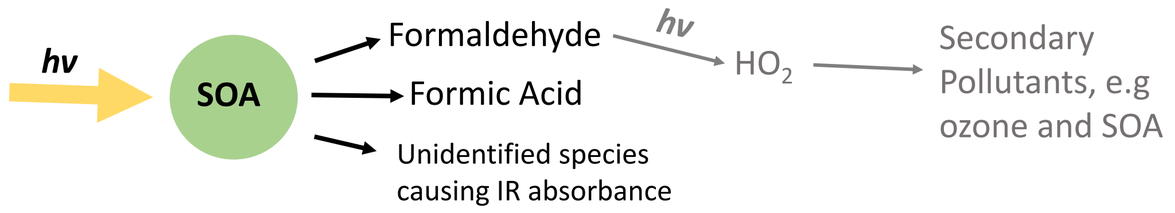


Figure 3: Schematic of the photolysis of SOA as reported by Walser et. al (1)

- Analysis of the photolysis products is needed to further understand the mechanistic pathway and predict resultant gas-phase species.
- **HOx (OH and HO_2) and RO_2 concentrations are often over predicted in models** this is due to the underestimations of the **heterogeneous uptake by aerosols.**
- Significant lack of data for uptake of HO_2 and RO_2 onto organic aerosols.
- Fractional loss of RO_2 through aerosol uptake can be predicted by atmospheric models when considering the rate coefficients for it's two main loss reactions with NO_2 and HO_2.
- In low NO_x environments uptake via aerosols becomes a significant RO_2 sink.

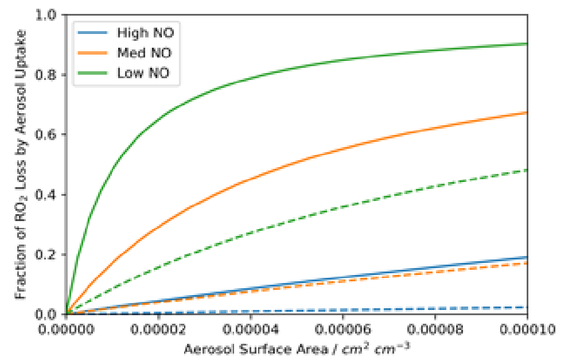


Figure 4: Predicted fractional loss of RO_2 considering reactions with NO_2 and HO_2 Assumed uptake coefficient, γ = 0.2 (solid line) and 0.02 (dashed line).

$k_{RO_2NO} = 7.7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} and $k_{RO_2HO_2} = 1.2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (2)

3. Objectives and Methodology

Investigate the heterogeneous reactions occurring on the surface and those within the bulk of an aerosol.

- Atmospherically relevant SOAs produced in **a potential aerosol mass (PAM) chamber**

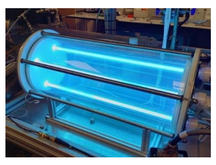


Figure 5: PAM chamber

- A **flow tube coupled to a detection cell** will investigate the gas-phase photolysis products of SOA and the uptake coefficients of RO_2 and HO_2.

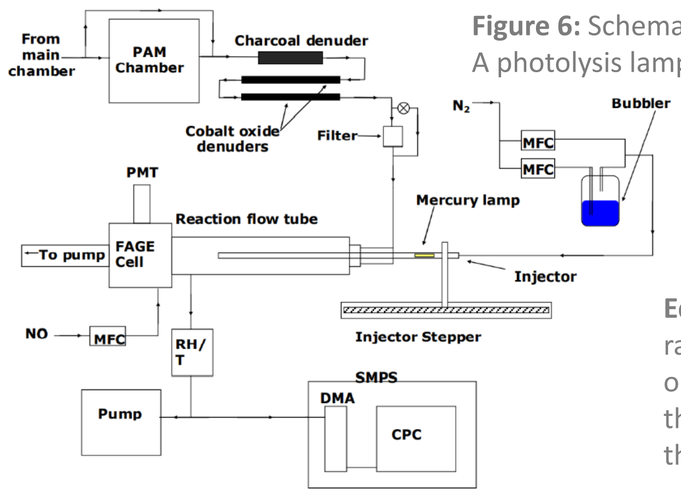


Figure 6: Schematic diagram of the flow tube set up. (3) A photolysis lamp will be placed next to the flow tube.

$$k' = s\,\frac{\gamma_{obs}\,\omega_x}{4}$$

Equation 1: Corrected pseudo-first-order rate coefficients (k'), γ_{obs} is the observed uptake coefficient, ω_x is the thermal speed of x (HO_2 or RO_2) and s is the total aerosol surface area.

- Aerosols are passed through the flow tube and illuminated with a known flux of radiation to initiate photochemical reactions.
- Uptake will be investigated by passing the radical species, via the injector, through the tube with the aerosols. Radicals are then converted to OH and the concentration is measured via Fluorescence Assay by Gas Expansion (FAGE).
- Pseudo first order rate coefficients for uptake will be calculated by **Eq. 1** and incorporated into atmospheric models.
- Parameters such as relative humidity, temperature and intensity of light can be altered in the tube, as well as composition to identify correlations with uptake.
- Chemical composition and physical properties of the aerosol will also be investigated at the University of Bristol Aerosol Research Centre.

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