

Investigation of the SOA formation potential of particulate photosensitized oxidation processes

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Introduction

- Secondary organic aerosol (SOA) formation remains one of the most intensively but also most poorly understood topic in atmospheric science
- SOA masses underestimated by atmospheric chemistry models compared to observed SOA masses from field studies^[1] because of unknown SOA sources and formation processes
- Photosensitized particulate-phase chemistry was identified as a potential SOA source^[2-5]
- Absorption of solar radiation by photosensitizers (PS) generating an excited triplet state (³PS*) which transfers its excess energy to other compounds such as oxygen,^[6] halogenides,^[7] or organic compounds^[8]
- Photosensitized reactions either within or at the interface of the aerosol particles may impact SOA formation, growth, and processing (Fig. 1)

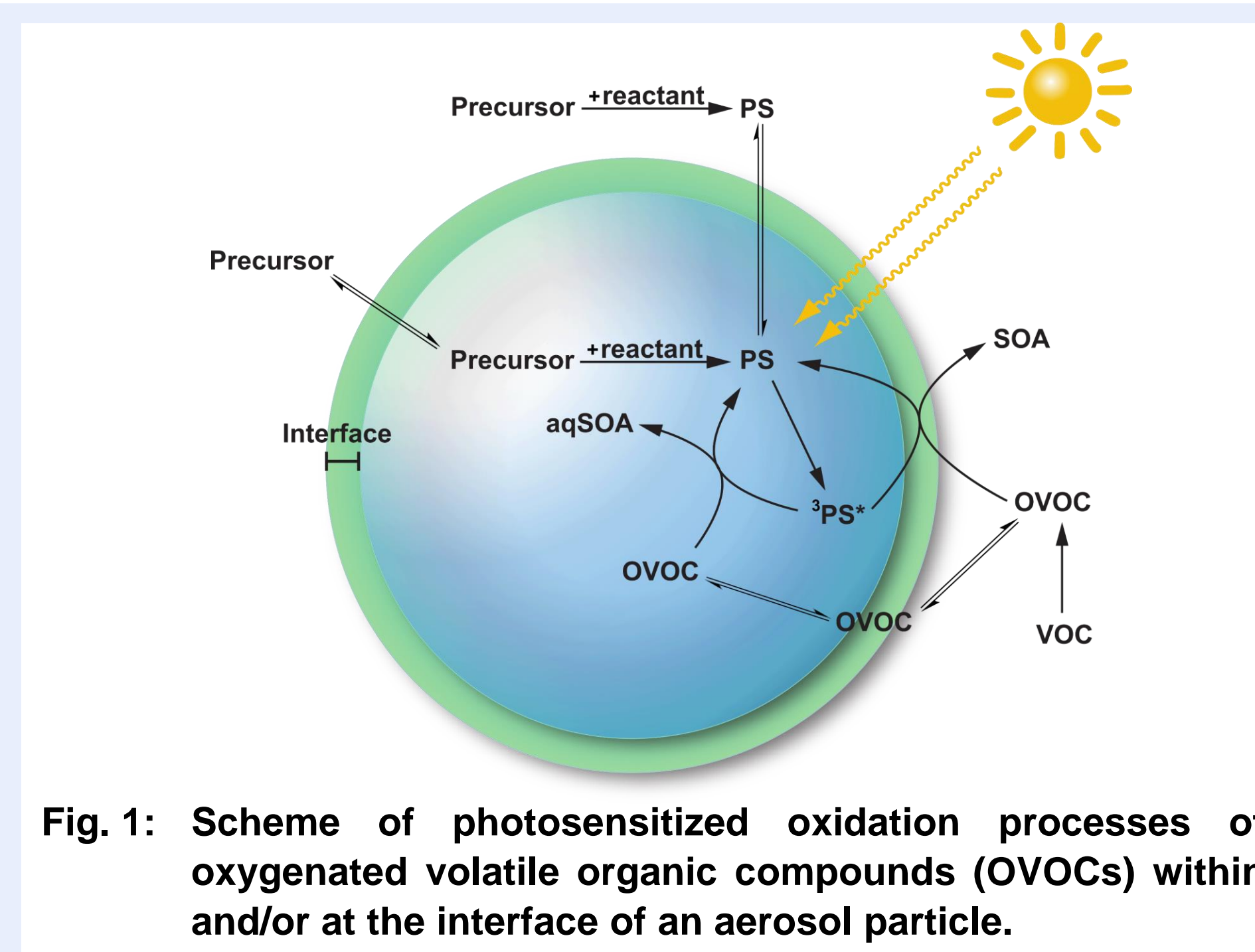


Fig. 1: Scheme of photosensitized oxidation processes of oxygenated volatile organic compounds (OVOCs) within and/or at the interface of an aerosol particle.

Experimental

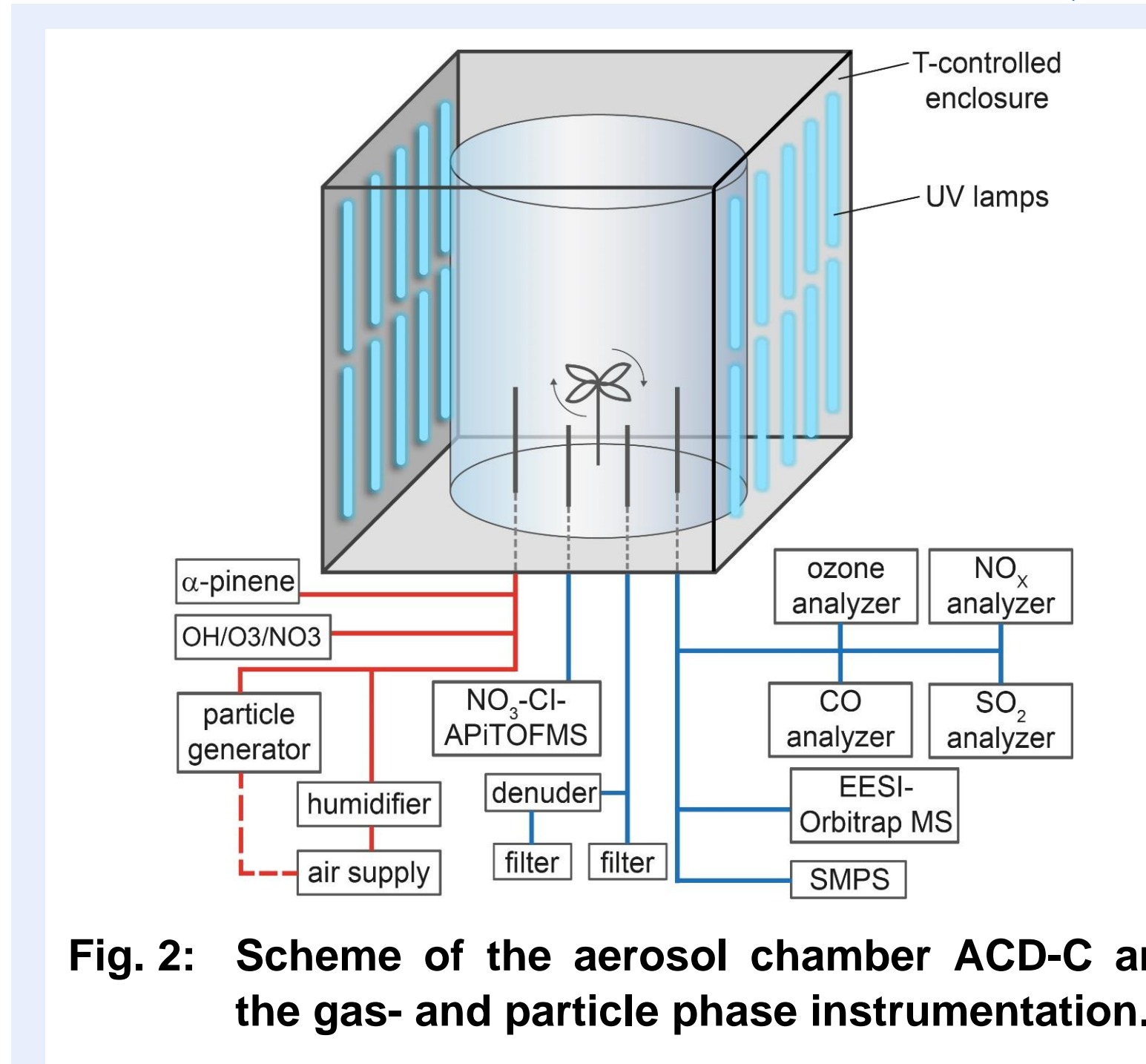


Fig. 2: Scheme of the aerosol chamber ACD-C and the gas- and particle phase instrumentation.

- 19 m³ Teflon chamber
- UV-VIS lights: 300 <math>< \lambda < 550 \text{ nm}</math>
- Relative Humidity: 80%
- pH = 4
- [PS] = 1 × 10⁻³ mol L⁻¹
- [Limonene] = 125 ppb
- [Butanol-d9] = 75 ppb (•OH scavenger)
- Two different lamp configurations
 - Group I+III: 2x 42.4 W m⁻²
 - Group I+II+III: 2x 62.7W m⁻²
- Intensity measured via an optical fiber connected to a gated ICCD camera coupled to a grating spectrograph

First Results

Spectra of radiation sources and PS

- Excitation of the ground state PS into its excited triplet state with UV-VIS light

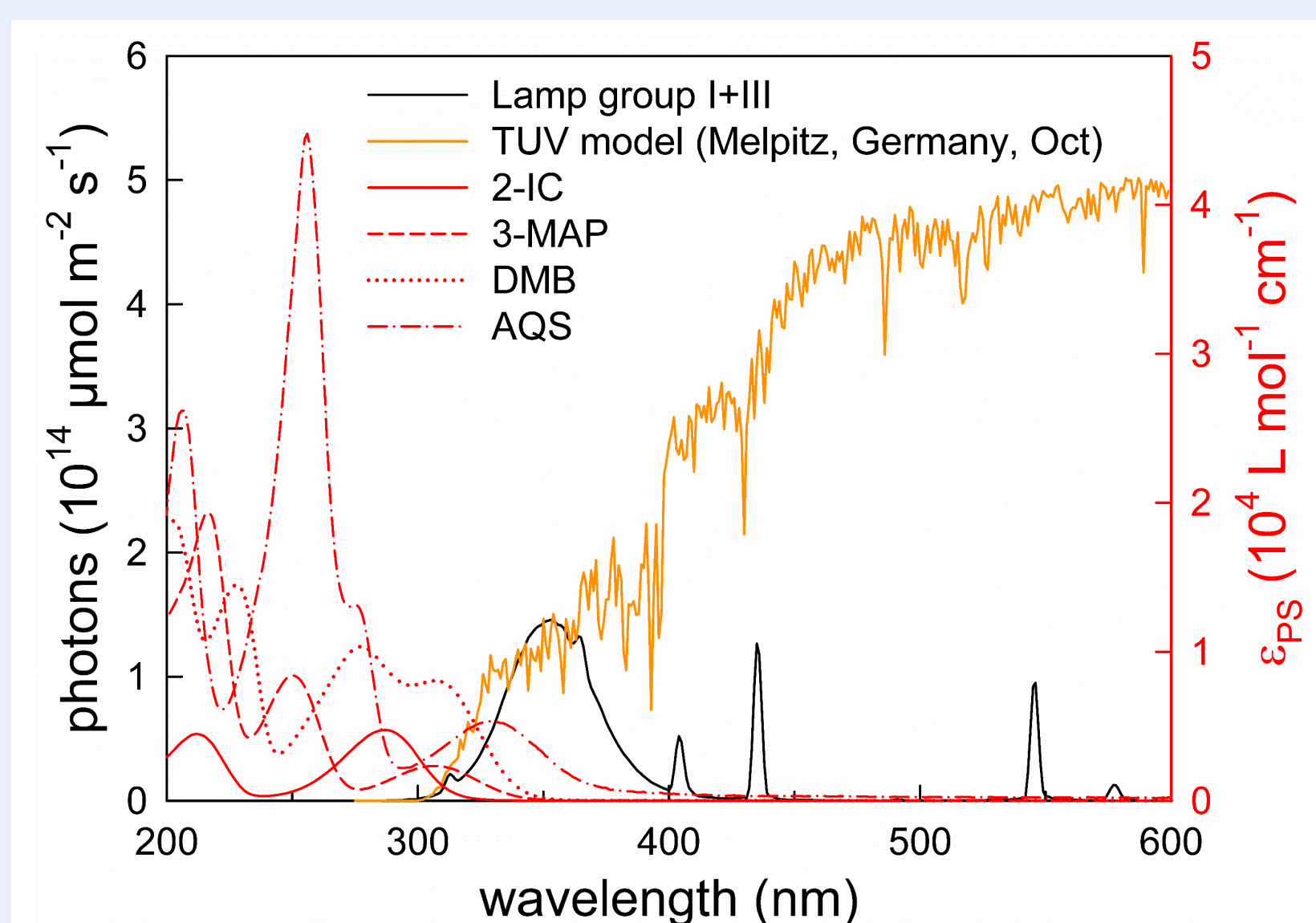


Fig. 3: Lamp spectra of the UV-lamps I-III of the aerosol chamber (black line), TUV model of the solar radiation (orange line) and molar attenuation coefficients of the photosensitizers (red).

Henry constant^[9] & vapor pressure^[10]

PS	Vapor pressure (atm)	Henry constant (mol L ⁻¹ atm ⁻¹)
2-IC	9.89 × 10 ⁻⁶	1.74 × 10 ⁶
3-MAP	2.57 × 10 ⁻⁵	9.42 × 10 ²
DMB	1.04 × 10 ⁻⁶	7.29 × 10 ³
AQS [†]	1.16 × 10 ⁻⁷	3.14 × 10 ⁵

[†]Values for anthraquinone

- 3-MAP and DMB more likely to be in the gas phase
→ loss of particulate PS due to gas-to-particulate phase partitioning
- 2-IC & AQS in the gas- and aqueous phase

2-IC: Imidazole-2-carboxaldehyde
3-MAP: 3-Methoxyacetophenone
DMB: 3,4-Dimethoxybenzaldehyde
AQS: Anthraquinone-2-sulfonate

Experiments of AQS with limonene

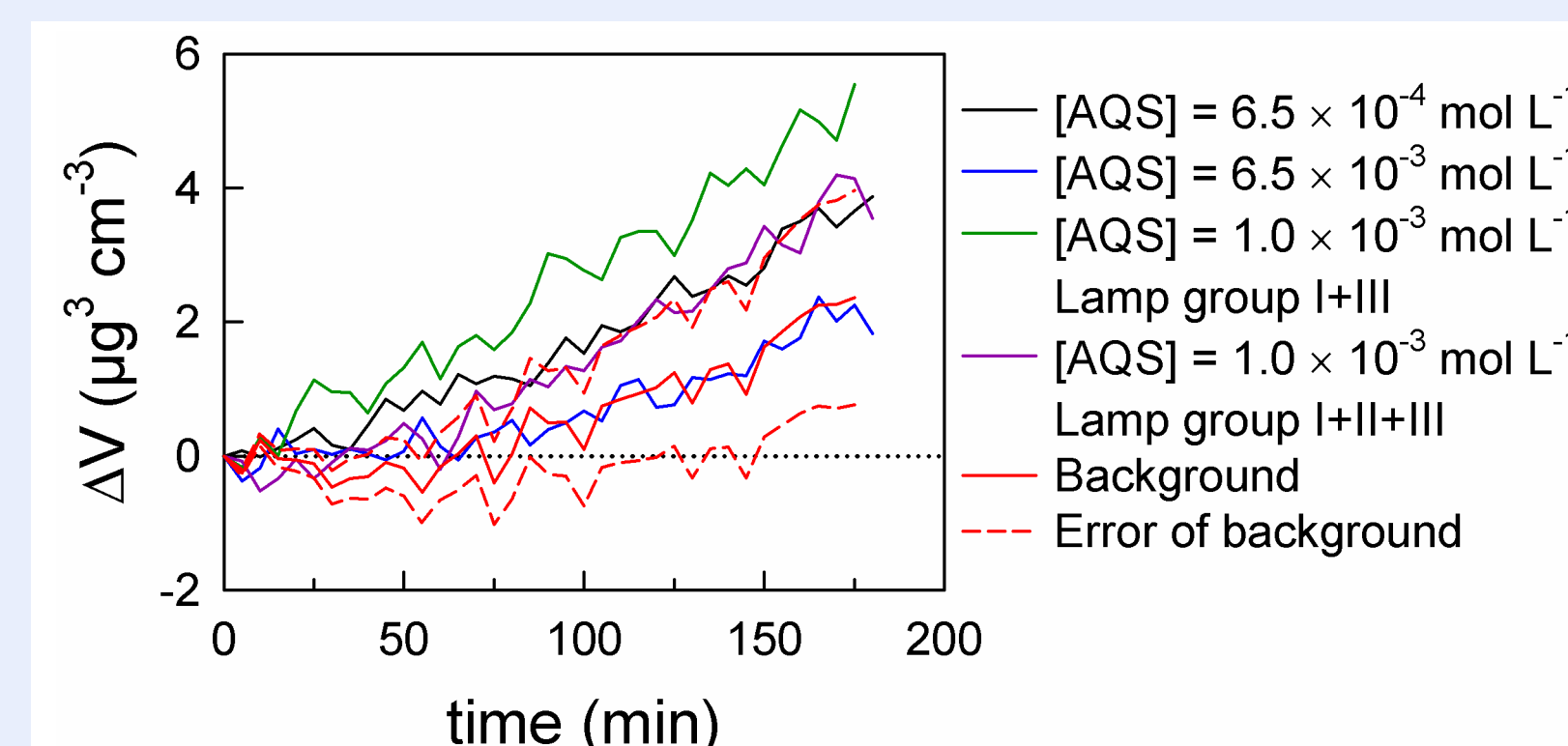


Fig. 4: Particle growth as a function of time observed for different AQS concentration and light intensities.

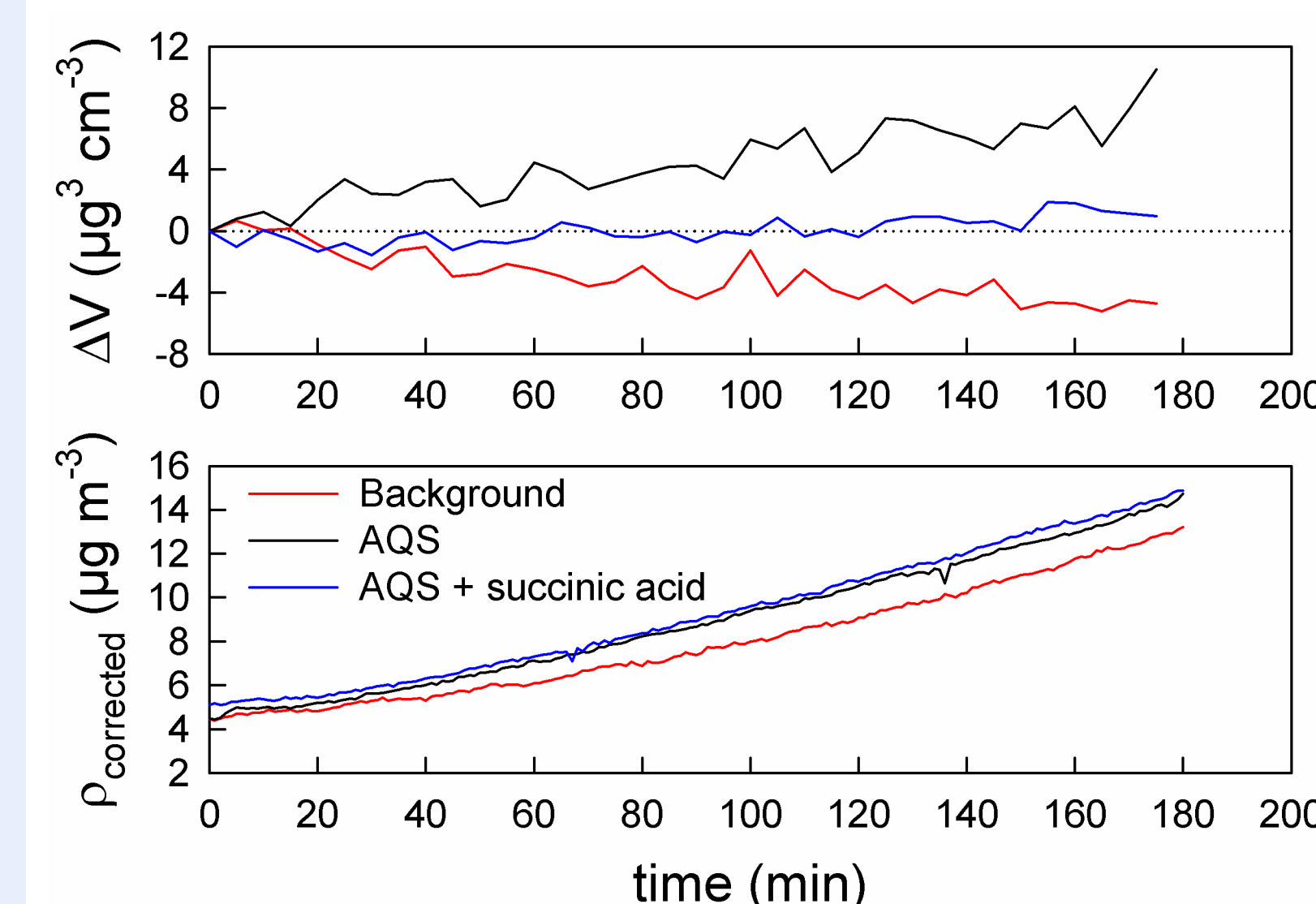


Fig. 5: Upper graph: Particle growth, lower graph: Corrected mass concentration of organics. Red line: Background, black line: AQS + limonene, blue line: AQS + succinic acid + limonene.

1.) Low number of particles

- Initial seed particle concentration: ~2.2 × 10⁴ cm⁻³
- Particle growth was observed without AQS indicating background oxidation processes of limonene with other reagents like O₃, NO_x, HONO (wall-loss considered^[11])
- No significant change of the particle growth by the variation of AQS concentration and light intensity
- Measured particle growth of the photosensitized oxidation process within the range of the background oxidation processes

2.) High number of particles

- Initial seed particle concentration: ~15 × 10⁴ cm⁻³
- Photosensitized oxidation of limonene resulting in particle growth (Figure 5 upper graph)
- But no significant effect on the mass concentration of organic matter was observed (Figure 5 lower graph)
- Addition of succinic acid into the seed (c = 2.0 × 10⁻³ mol L⁻¹) shows similar results

Summary & Outlook

Summary

- 3-MAP and DMB partition most likely into the gas phase → Cannot be considered as particulate PS
- Background oxidation processes interfere with the photosensitized oxidation process
- No particle growth and increase of mass concentration observable under the used experimental conditions

Outlook

- Experiments with other PS
- Variation of relative humidity and seed matrix (e.g. chemical composition)
- Evaluation of gas- and particulate-phase products measured by PTR-MS and offline filter analysis techniques like HPLC-Orbitrap MS

References and Funding

- [1] Hallquist et al. (2009) *Atmos. Chem. Phys.* **9**, 5155-5236.
 [2] Monge et al. (2012) *Proc. Natl. Acad. Sci.* **109**, 6840-6844.
 [3] Aregahegn et al. (2013) *Faraday Discuss.* **165**, 123-134.
 [4] Rossignol et al. (2014) *Environ. Sci. Technol.* **48**, 3218-3227.
 [5] Wang et al. (2020) *Environ. Sci. Technol.* **54**, 3114-3120.
 [6] Gorman and Rodgers (1986) *J. Am. Chem. Soc.* **108**, 5074-5078.
 [7] Tinel et al. (2014) *C. R. Chimie* **17**, 801-807.
 [8] Li et al. (2016) *J. Phys. Chem.* **120**, 9042-9048.
 [9] Chemspider (2007) Royal Society of Chemistry <http://www.chemspider.com>, 11th Aug 2020.
 [10] Pankow and Asher (2008) *Atmos. Chem. Phys.* **8**, 2773-2796.
 [11] Wang et al. (2018) *Atmos. Meas. Tech.* **11**, 6577-6588
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