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New Particle Formation and Aerosol Growth due to Surfactant Photochemistry at the Air/Water Interface

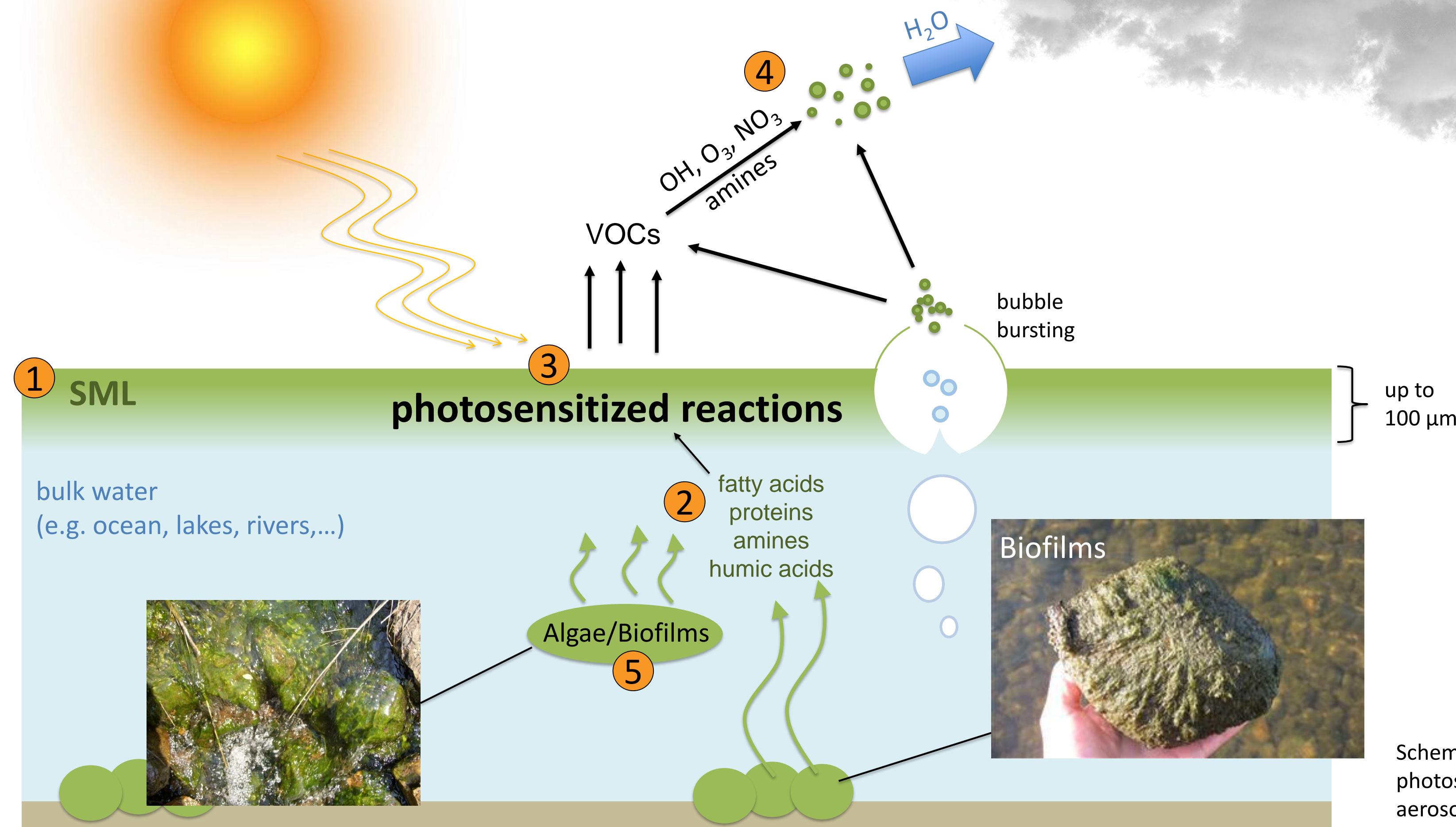
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Objective



Summary

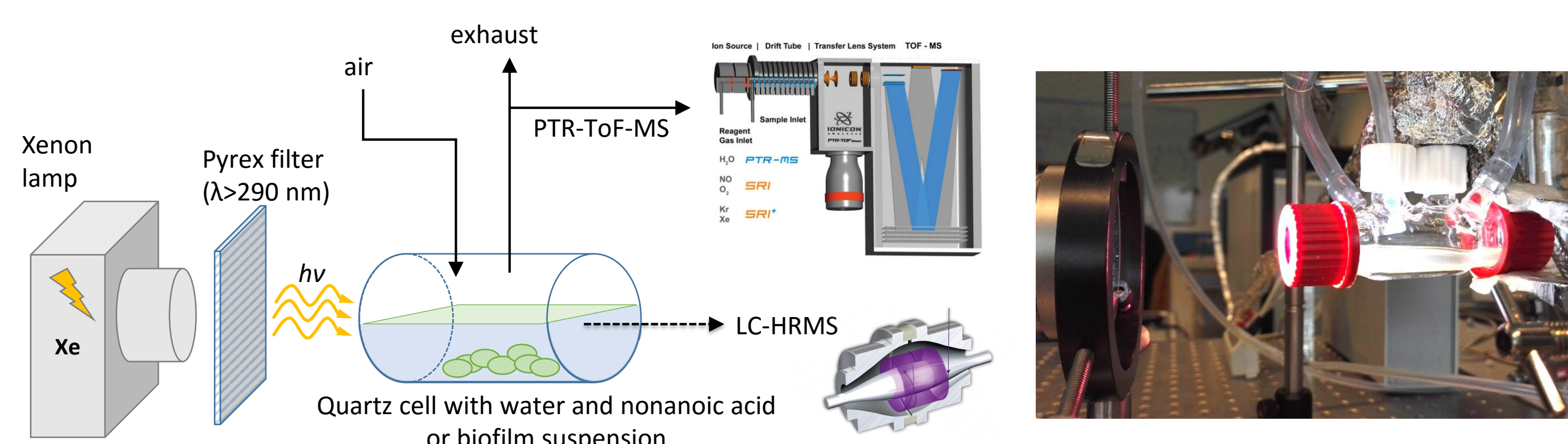
- 1 thin films of organic compounds, i.e. surface microlayers (SML), are ubiquitously found on aqueous surfaces such as freshwater systems and the ocean [1]
- 2 these microlayers host countless biogenic amphiphilic compounds which are concentrated there with respect to the bulk water (i.e. surfactants) [2]
- 3 photosensitized reactions in biogenic SMLs lead to the production of volatile organic compounds (VOCs) [3,4]
- 4 the resulting VOCs react with atmospheric oxidants, eventually leading to the formation of organic aerosol particles which affect cloud formation and lifetime
- 5 here we present evidence for the abiotic formation of such VOCs by photochemical processes in SMLs produced by riverine biofilms

Scheme 1: Algae and Biofilms (5) produce surfactants (2) which will form a surface microlayer (SML, 1). Due to photosensitized reactions (3), volatile organic compounds (VOCs) are formed which can act as secondary organic aerosol precursors (4).

Methods

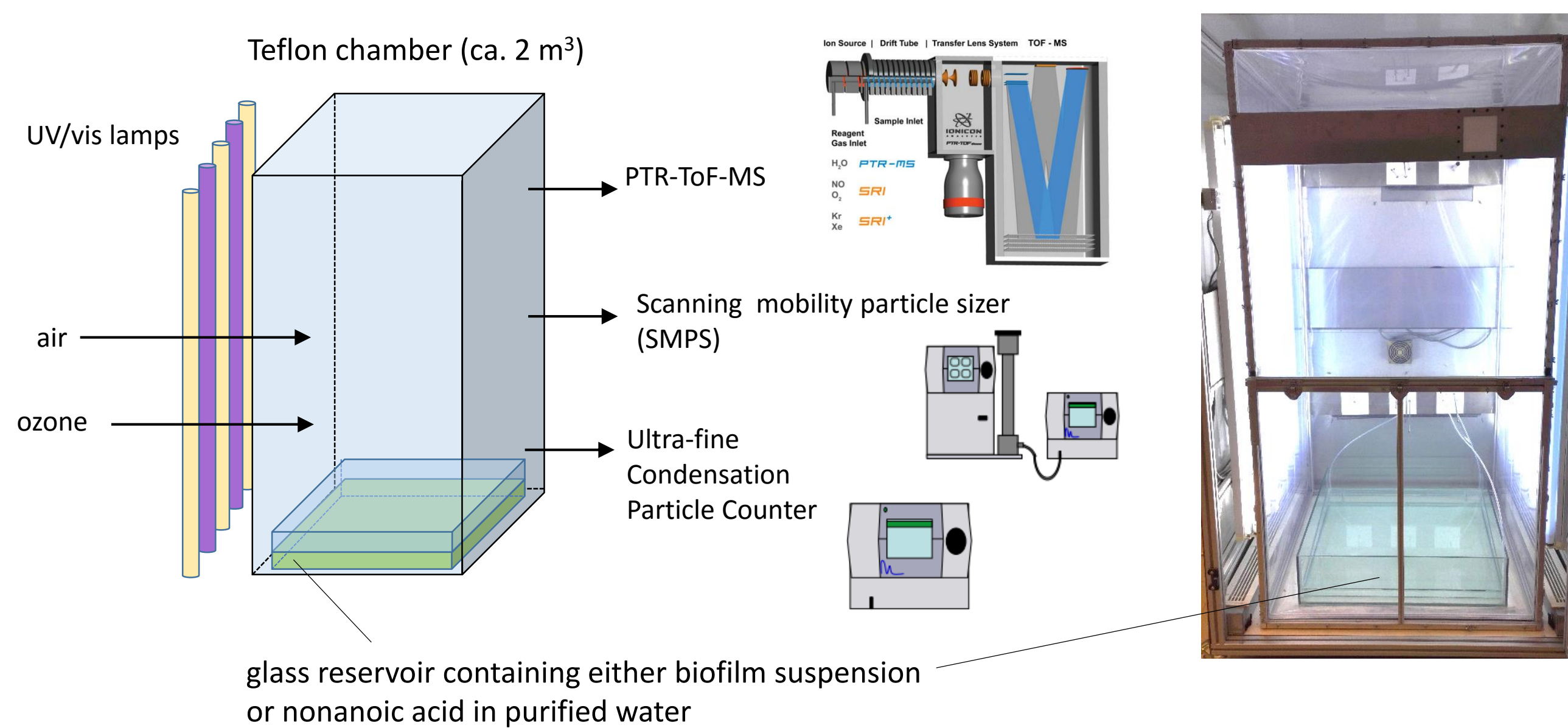
Investigation of 1, 2 & 3 using a quartz cell

Riverine biofilms were grown under controlled conditions and suspended in water. The resulting suspensions were investigated with regard to VOC production upon irradiation. Potential aerosol formation from these VOCs upon oxidation was investigated using an atmospheric simulation chamber.



Scheme 2: Experimental setup for measuring gas-phase and liquid-phase products upon UV/vis irradiation of biogenic SML samples. A xenon lamp is used to produce actinic radiation ($\lambda > 290$ nm). Liquid samples are analyzed by liquid chromatography-mass spectrometry (LC-HRMS, Orbitrap). Gas-phase VOCs are detected by proton transfer reaction-time of flight-mass spectrometry (PTR-ToF-MS).

Investigation of 3 & 4 using an atmospheric simulation chamber



Scheme 3: Experimental setup for measuring the formation of VOCs and their corresponding particle formation potential upon oxidation. A scanning particle mobility sizer (SMPS) and a condensation particle counter (CPC) are applied for particle characterization, while gas-phase compounds are measured by a PTR-MS.

Photosensitizers & surfactants present in the SML

LC-MS analysis proofed presence and formation of known surfactants and photosensitizers:

negative mode:

- saturated fatty acids detected in all samples (C2-C10)
- formation of sat. & unsat. dicarboxylic acids with irradiation (C2-C12)
- formation of sat. & unsat. oxo-fatty acids with irradiation (C3-C18)
- formation of sat. hydroxy fatty acids with irradiation (C3-C8)

pos. mode:

- acetone detected
- trimethylamine (and other sat. amines) detected

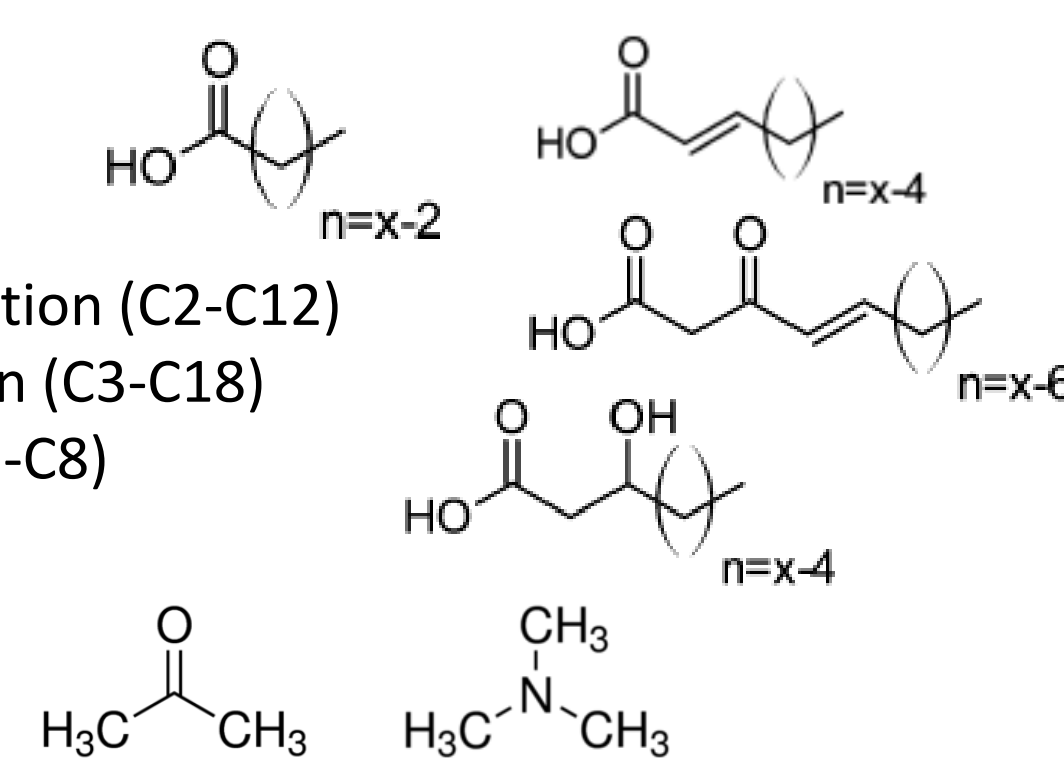


Photo-induced production of VOCs

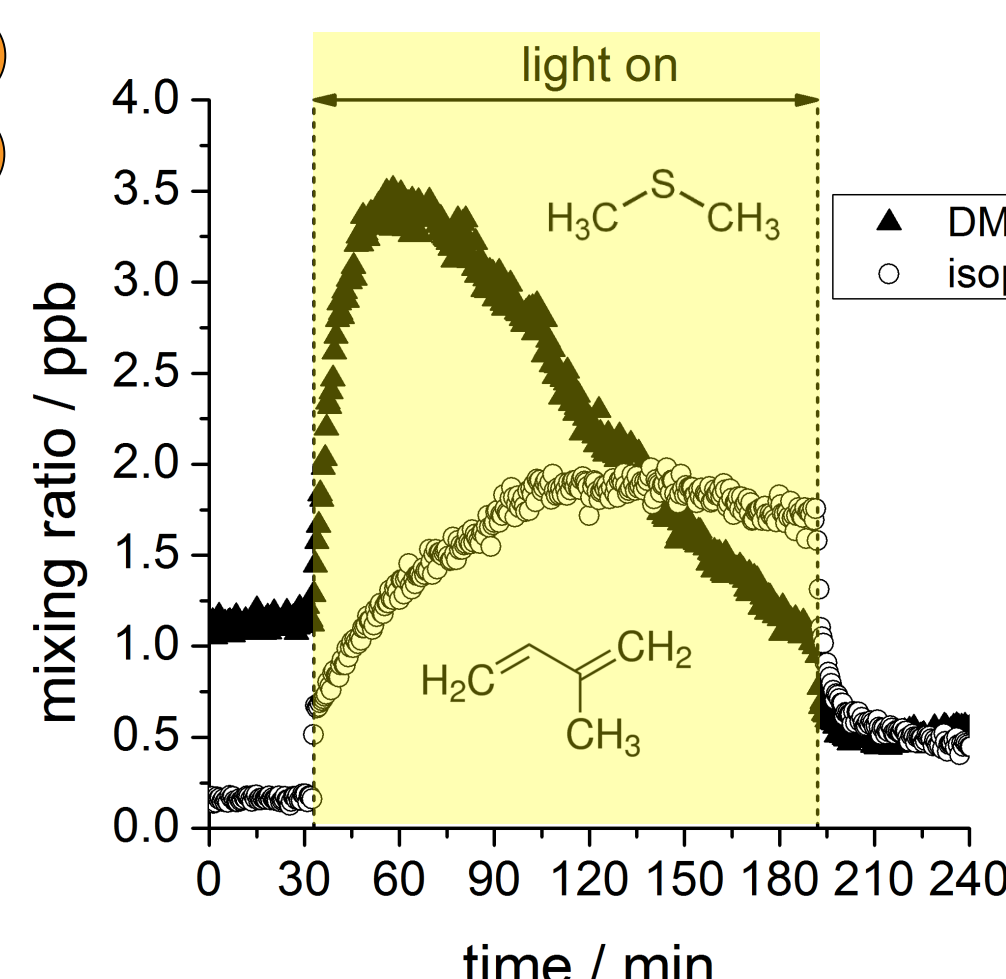


Figure 1: change in mixing ratios of dimethylsulfide and isoprene (measured by PTR-MS) during an irradiation experiment.

Table 1: tentatively identified VOCs generated by photochemical processes.

m/z	assigned compound	Δ mixing ratio / ppb _v	Production / 10 ⁹ molec mW ⁻¹	Flux* / 10 ⁹ molec cm ⁻² s ⁻¹
33.03278	MeOH	0.756	0.729	15.3
45.03188	Acetaldehyde	0.819	0.789	16.6
47.04715	EtOH	1.123	1.08	22.7
59.04620	Acetone	2.747	2.65	55.6
60.04697		0.158	0.152	3.20
69.06540	Isoprene	0.232	0.223	4.69
70.06384		0.084	0.081	1.71
71.04555	MVK/MACR	0.103	0.100	2.09
71.08130		0.089	0.086	1.80

* calculated for a mean solar flux of 21 mW cm⁻²

Experiments using the quartz cell setup with PTR-MS:

- Immediate formation and release of VOCs was observed upon irradiation of the SML samples (Fig. 1)
- among the photochemically generated VOCs, known aerosol precursors were identified (e.g. isoprene, dimethylsulfide, Table 1)
- biologically-produced compounds such as DMS decrease after a certain irradiation time while the abiotic photochemical products, e.g. isoprene, reach a steady state after a certain time (Fig. 1)

The observed differences in mixing ratios for abiotically-produced compounds were converted to fluxes according to:

$$flux = \frac{c \cdot f}{A \cdot L}$$

c: concentration of the compound (1 ppb=2.46·10¹⁰ molec/cm³),
f: flow through the cell (5 cm³/s), A: water surface area (16 cm²),
L: light intensity (8 mW/cm²)

→ The observed flux for isoprene is in good agreement with results from laboratory and field measurements, where fluxes of 0.02–17·10⁹ molec cm⁻² s⁻¹ were found [3]

New particle formation due to oxidation of VOCs

- after UV irradiation of biofilm-containing water, ozone was introduced into the chamber in order to simulate atmospheric oxidation
- new particle formation (homogeneous nucleation) was observed due to formation of low volatile organic compounds (LVOCs) from VOCs
- initial low particle growth rates suggest the presence of stable clusters (e.g. acid-base), forming first particles in the sub-20 nm range

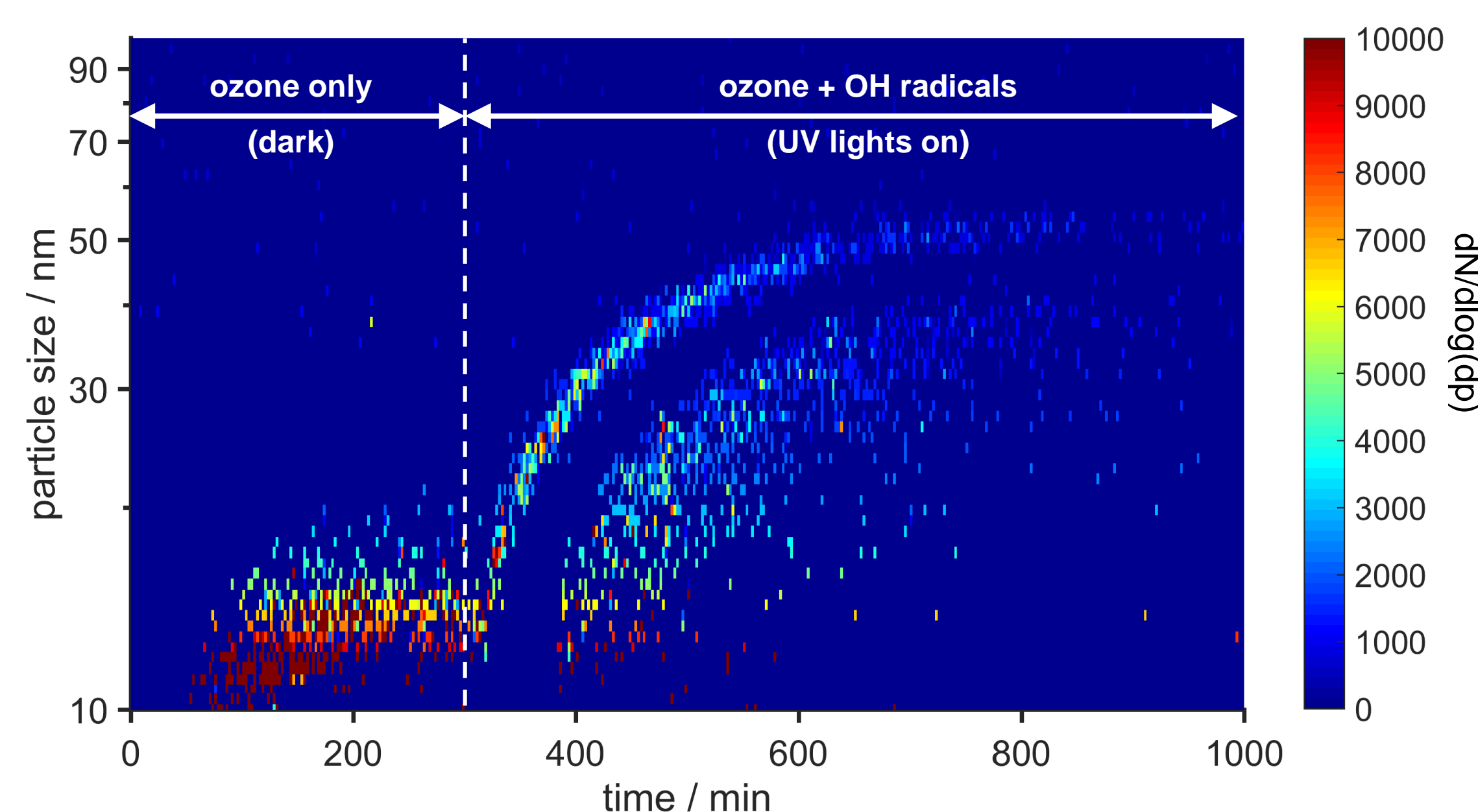


Figure 2: Particle number size distribution measured by a scanning mobility particle sizer (SMPS). At t=0 min, ozone was injected for 3.5 min into the chamber (reaching ~600 ppb). At t=300 min, another ozone injection was conducted under UV irradiation, producing additional OH radicals for oxidation of VOCs.

Implications and Perspectives

- production of VOCs was observed upon UV/vis irradiation of biogenic freshwater SML samples due to photochemical reactions
- detected VOCs are reactive towards atmospheric oxidants, such as ozone and OH radicals
- photochemical processes in biogenic SMLs affect atmospheric chemistry and aerosol formation processes directly and indirectly, thereby influencing climatic relevant processes, such as cloud formation and lifetime