Characterizing lignin as an atmospherically long-lived ice nucleating biopolymer in immersion freezing

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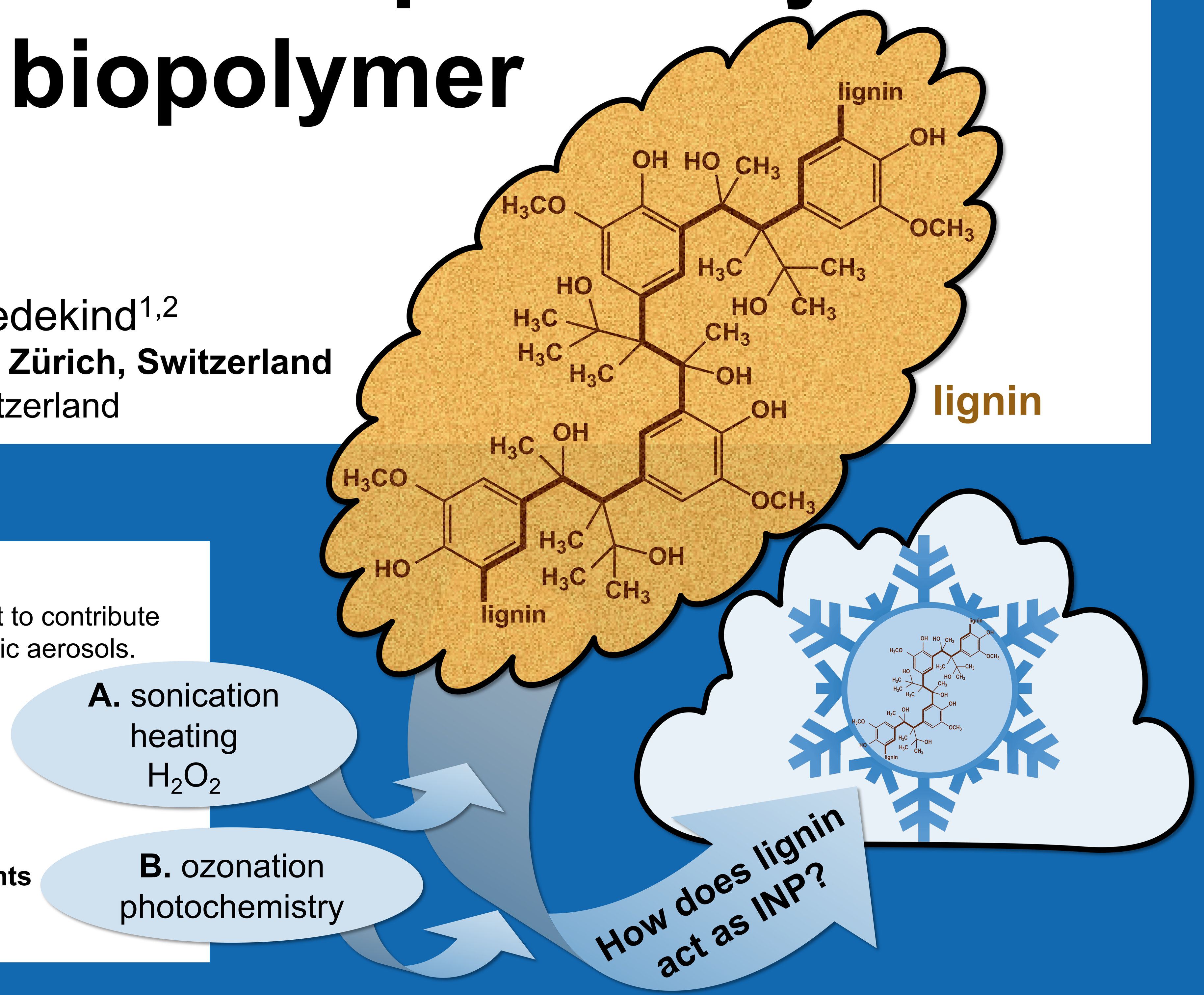


1 Introduction

Background:

- → Understanding the ice formation pathways in mixed-phase clouds remains crucial for climate models.
- → Heterogenous ice formation (> – 38 °C) relies on ice nucleating particles (INPs).
- → Organic aerosols are ubiquitous and a source of INPs, but their complexity hinders detailed IN ability (INA) characterizations.
- → The biopolymer lignin is a subcomponent of organic aerosols and serves as proxy for organic matter.

Research Questions:

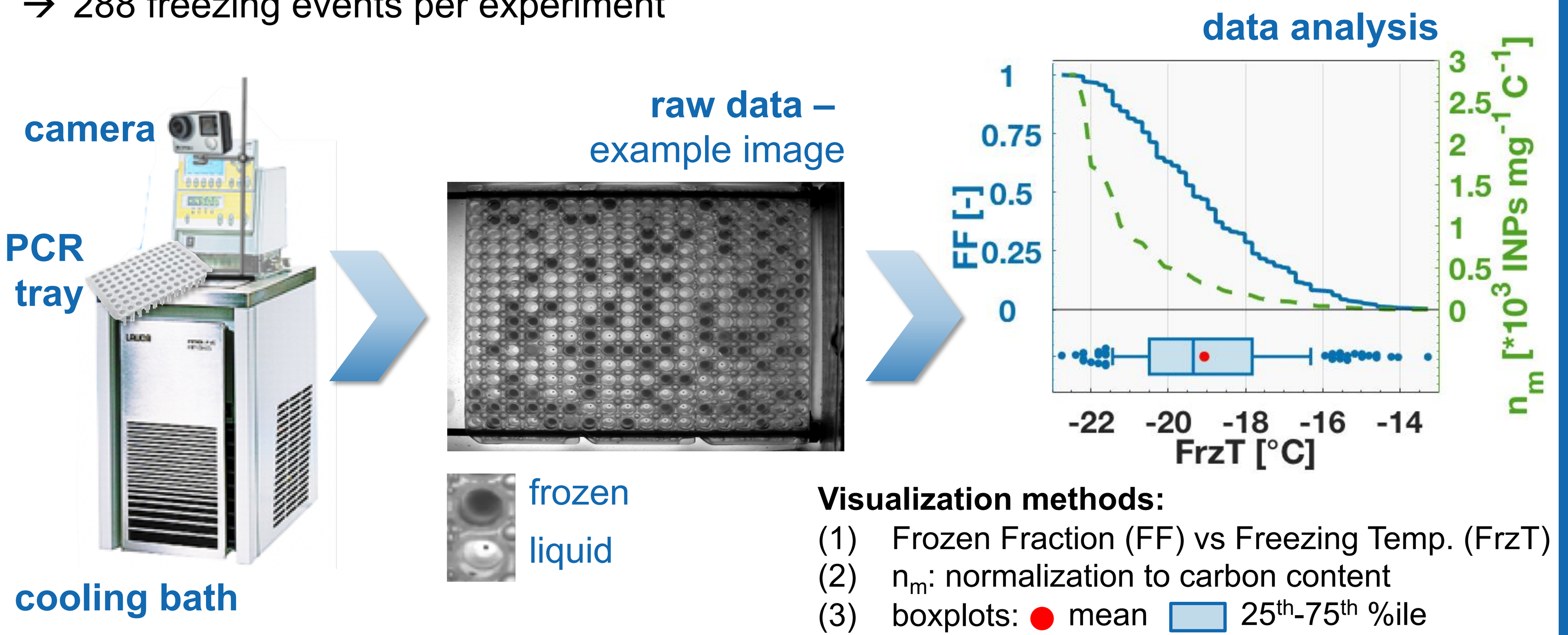
By analyzing lignin as an INP we want to contribute to the characterization of INA in organic aerosols.

What is lignin's ability to act as an ice nucleating particle in mixed-phase clouds?

What are the effects of...
A. typical IN laboratory treatments
B. atmospheric processing
... on lignin's INA?

2 Methods – Ice Nucleation Setup

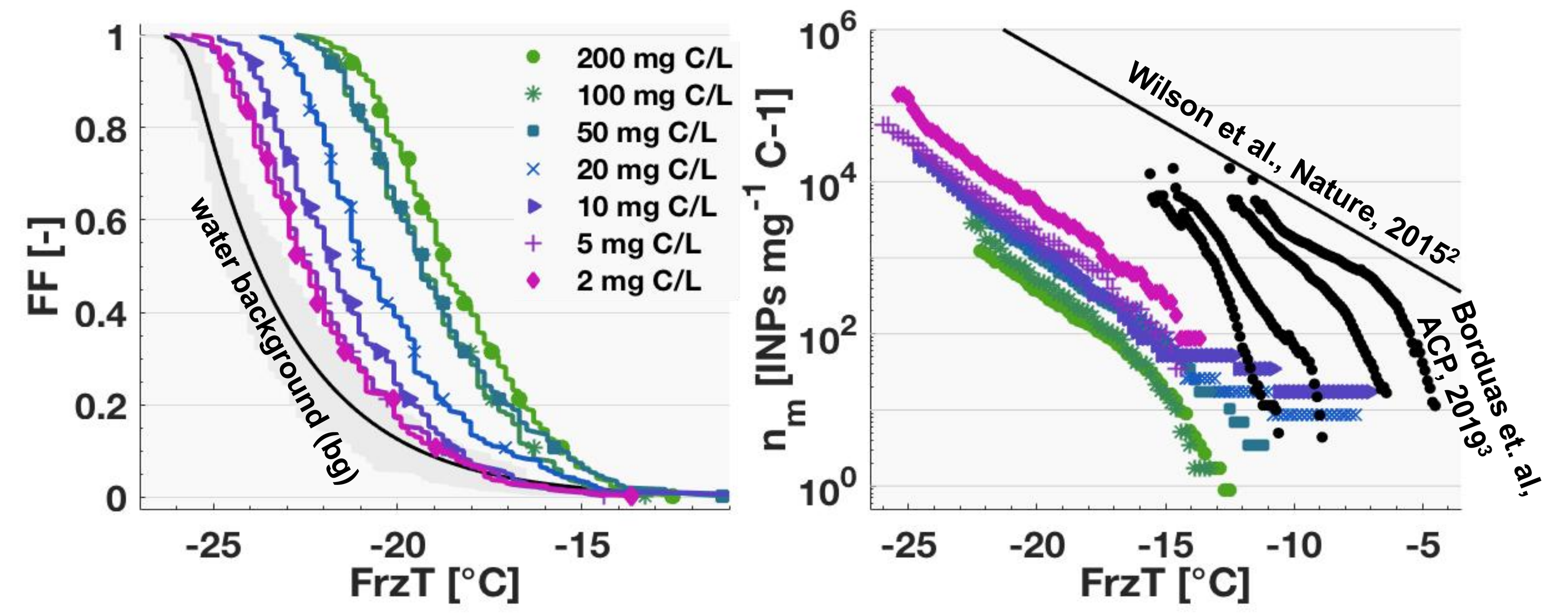
Freezing **I**ce **N**uclei **C**ounter (FINC) (Miller et al., 2020[1])
- → droplet freezing (20 µL, range 0 °C to – 26 °C)
- → 288 freezing events per experiment



Visualization methods:
(1) Frozen Fraction (FF) vs Freezing Temp. (FrzT)
(2) n_m: normalization to carbon content
(3) boxplots: ● mean ▭ 25th-75th %ile
— median ● outliers (<10th, >90th %ile)

3 Lignin's Ice Nucleating Ability

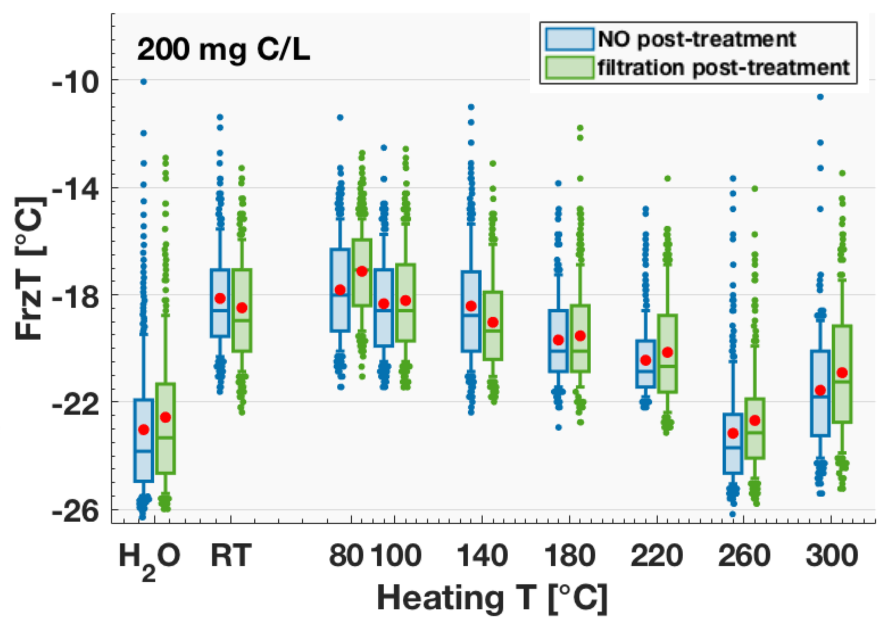
Lignin's INA is relevant for mixed-phase clouds, but lower than INA of complex dissolved organic matter (DOM)
- → **n_m range** from 1 to 10^5 INPs/mg C (– 7 °C to – 26 °C)
- → **50% FF at – 18.7 °C** for 200 mg C/L
- → **+ relative INA with – concentration, + interactions with water**



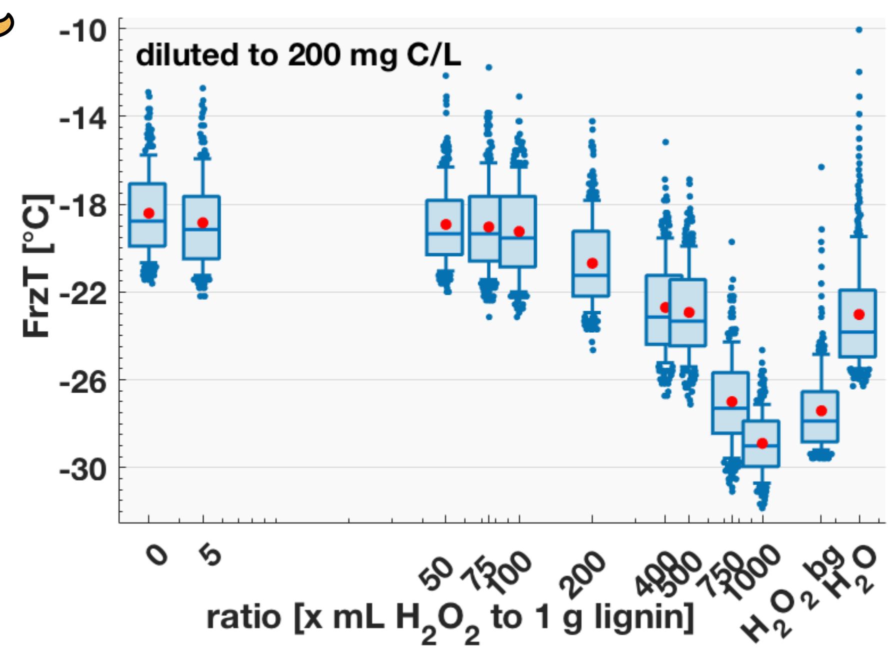
4 Laboratory Treatments

1. Sonication: no change in INA
- → extraction tool for particulates on aerosol filters, radical reactions may affect chemical structure (Miljevic et al., AS&T, 2014[4])

2. Heating: INA decrease
- → volatilization of organic material by pyrolysis
- → experiment: heating of lignin as powder, then H_2O addition to 200 mg C/L
- → **– INA with + Heating T,** FrzT of H_2O reached after heating to 260 °C
- → **+ relative INA** after removal of insoluble fraction, as **mass loss**



3. H_2O_2: INA decrease
- → oxidative removal of organic material
- → experiment: reactions with varying ratios of mL H_2O_2 (35 w%) : g lignin, then dilution with H_2O to 200 mg C/L
- → **– INA with + ratio of H_2O_2 to lignin,** FrzT of background with H_2O reached after ratio 400:1

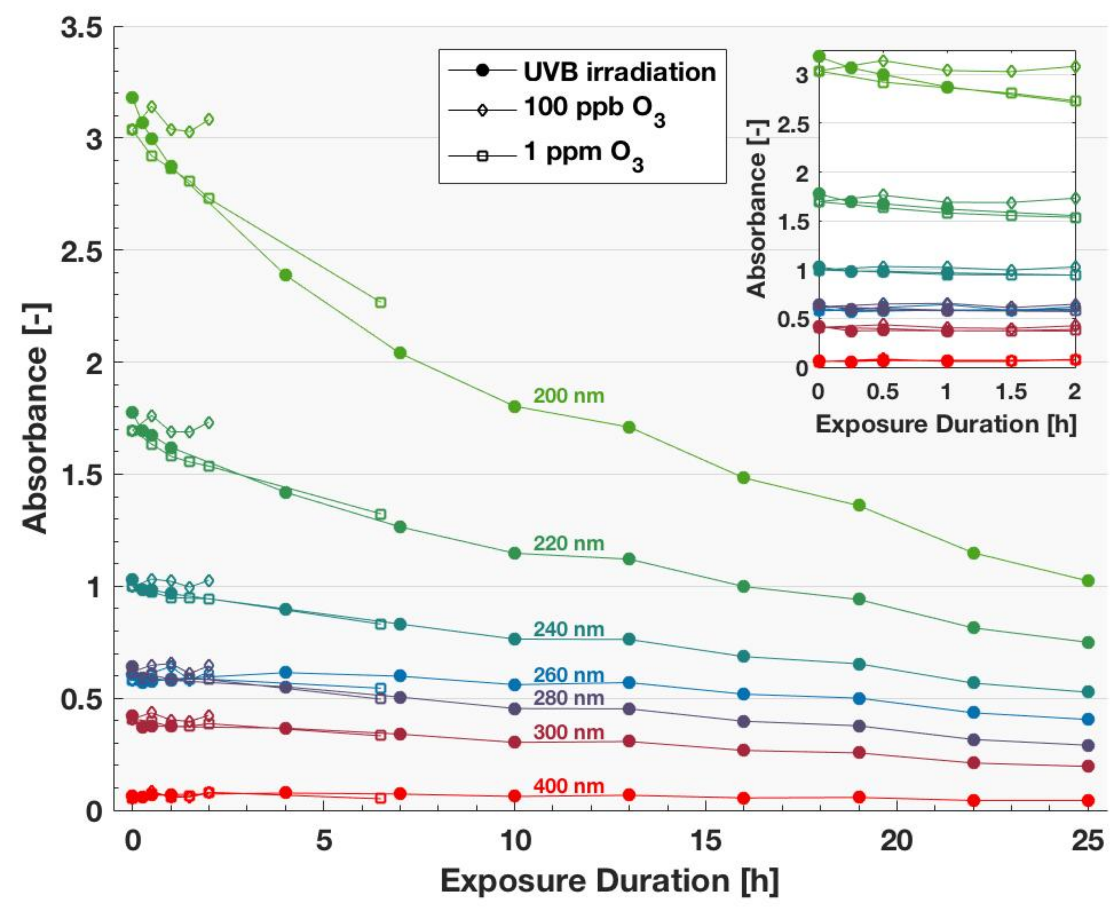


5 Atmospheric Processing

1. Ozonation: no change in INA
- → experiment: bubbling of 0.1 L/min O_3 (100 ppb – 1 ppm) through bulk solution of 20 mg C/L up to 6.5 h

2. Photochemistry: minimal INA decrease
- → experiment: up to 25 h (6.5 days atmospheric equivalent) of UVB irradiation on 20 mg C/L solution
- → **small – trend in lignin's INA** through photochemistry, however less than observed for complex DOM (Borduas et al., ACP, 2019[3])
- → **max. – 1 °C decrease at 50% FF** after 22 h compared to 0 h

Measurement of UV/Vis spectra (200 – 400 nm)
- → **– absorbance** after exposure to ozone or UVB irradiation
- → **decay of chromophoric components** in lignin's structure
- → the IN activity is mostly retained despite this decay, so these chromophores are not decisive for the biopolymer's INA



6 Conclusions

Lignin's IN ability:

1. is relevant for mixed-phase clouds
- → n_m from 1 to 10^5 INPs/mg C (– 7 to – 26 °C)

2. is robust and lasts the aerosols' lifetime
- → INA decrease to the water background requires harsh laboratory treatments (≧ 260 °C, [400:1] mL H_2O_2 : g lignin)
- → minimal change through atmospheric processing (exposed to up to 1 ppm O_3, to up to 25 h of UVB light with an atmospheric equivalent of 6.5 days sunlight)

3. is retained after structural changes in the biopolymer's chromophoric structure
- → decrease of UV/Vis absorption (200 – 400 nm) after exposure to UVB light or ozone

References:
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