Investigating Volatile Organic Compound Emissions from Ozonolysis of Phytoplankton Cultures

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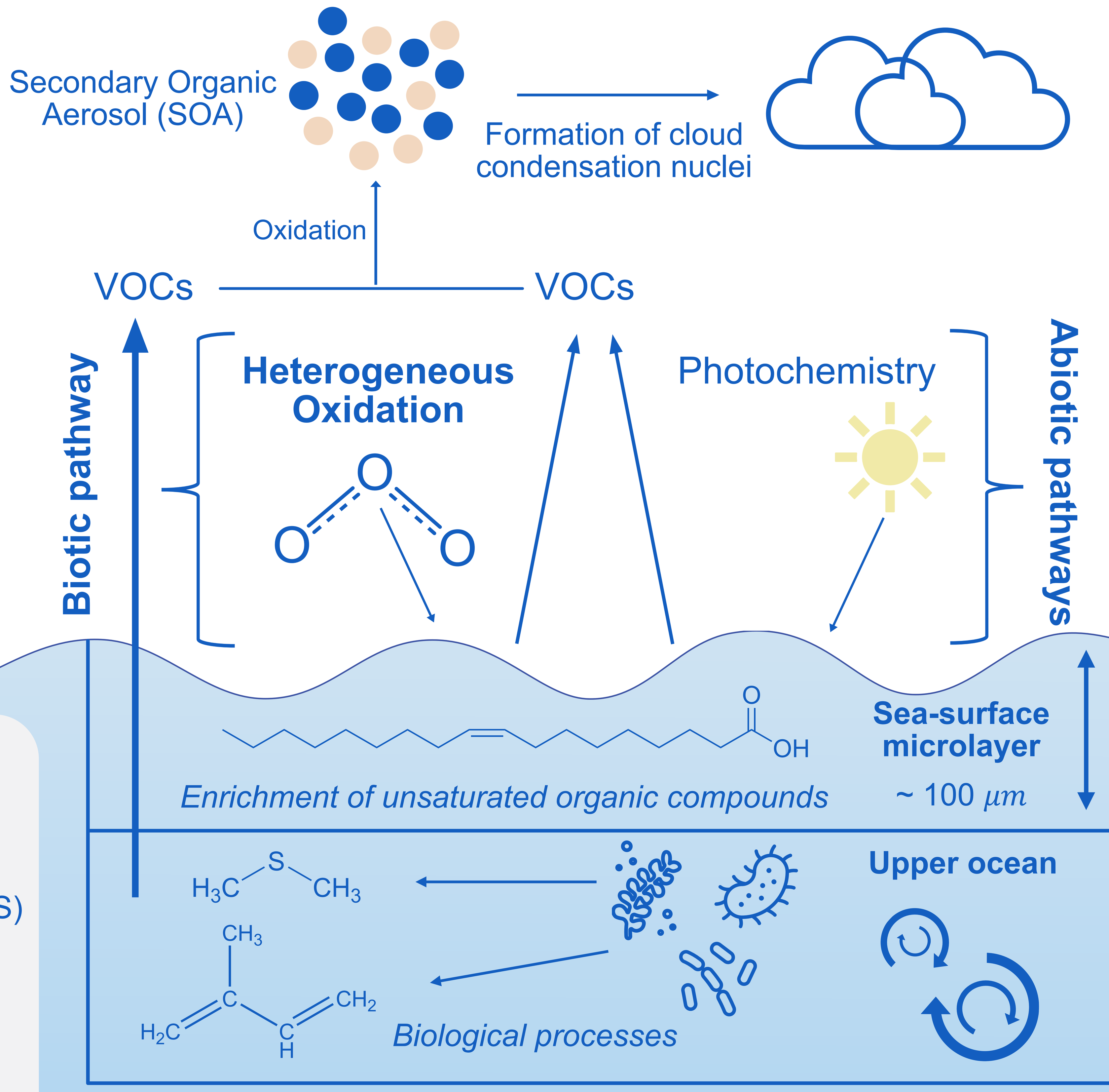
Motivation

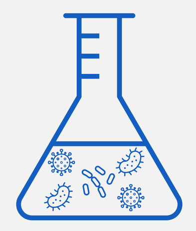
- The ocean's surface is covered by the sea-surface microlayer (SML), a unique interface efficient at mediating the air-sea exchange of atmospheric trace gases
- Emissions from the ocean are a significant source of volatile organic compounds (VOCs) into the marine boundary layer. Marine VOCs can be emitted via biotic and abiotic (photochemical and oxidation) pathways[1,2]
- VOCs produced via abiotic pathways have particular climatic importance, but their representation in global climate models is poorly quantified[3]

Aim: Explore the abiotic emission of VOCs from heterogenous oxidation of phytoplankton cultures under varying environmental circumstances

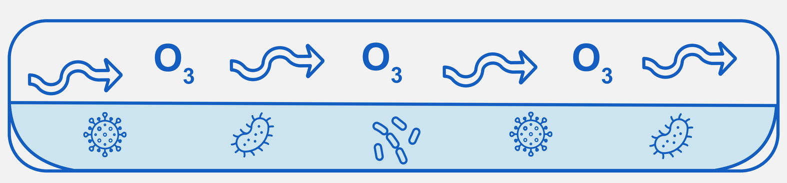


Experimental Approach

1. Growth and characterisation of culture medium
2. Degas and ozonolysis of sample solution (~ 85 ppb)
3. VOC detection using proton transfer reaction time-of-flight mass spectrometry (PTR-ToF-MS)

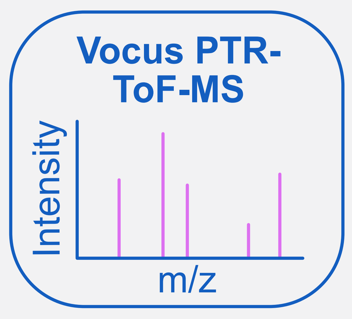


P. tricornutum monoculture and *P. tricornutum-Yoonia* coculture selected to represent the SML



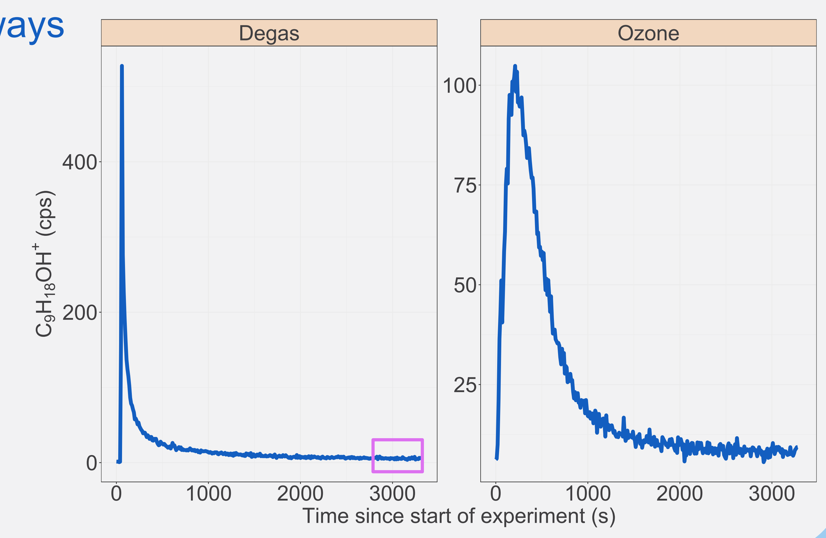
Heterogenous flow reactor

Degas process required to volatilise in-water VOCs produced via biotic pathways



Data Processing

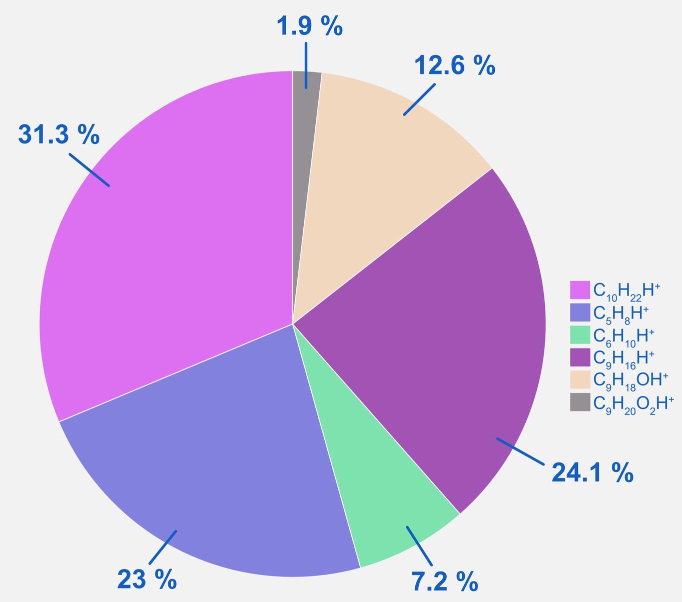
- VOC ozonolysis response determined as the increase from the degassing baseline
- f/2 growth media experiments taken as the blank
- PTR-ToF-MS calibration to determine the sensitivity according to Kilgour et al. (2024)[4] scaling factor



Results

Major Ion Emissions

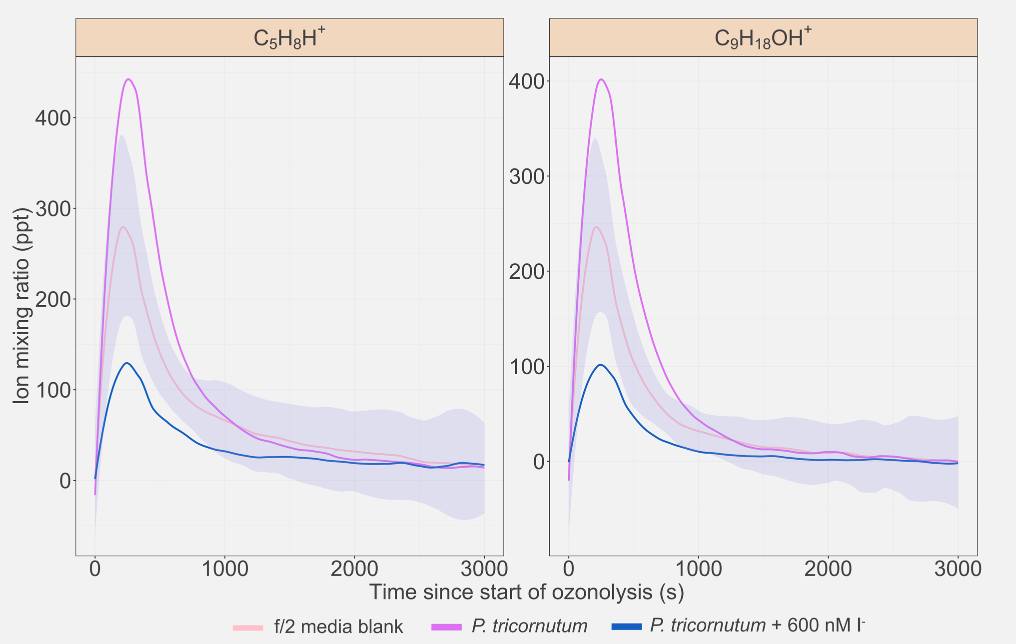
Set of criteria similar to Kilgour et al. (2024)[4] applied to determine those ions showing a significant response to ozonolysis



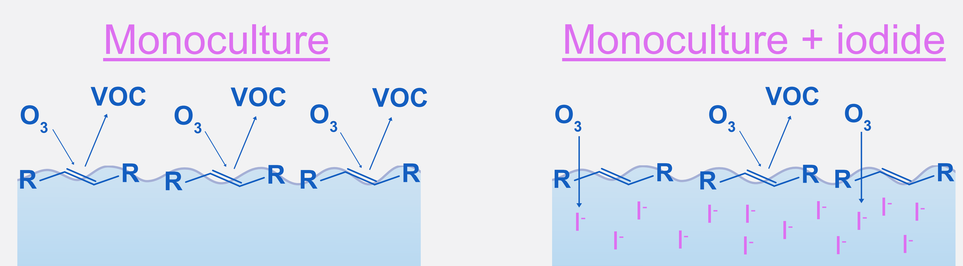
- $C_5H_8H^+$ peak likely arising from fragmentation of higher molecular weight aldehydes. Specific ion attribution requires separation prior to analysis on the PTR-ToF-MS
- $C_9H_{18}OH^+$ peak likely nonanal - a common product of the ozone + oleic acid reaction in the SML

Addition of Iodide

- The reaction of ozone with iodide facilitating oceanic ozone deposition is well understood[5]

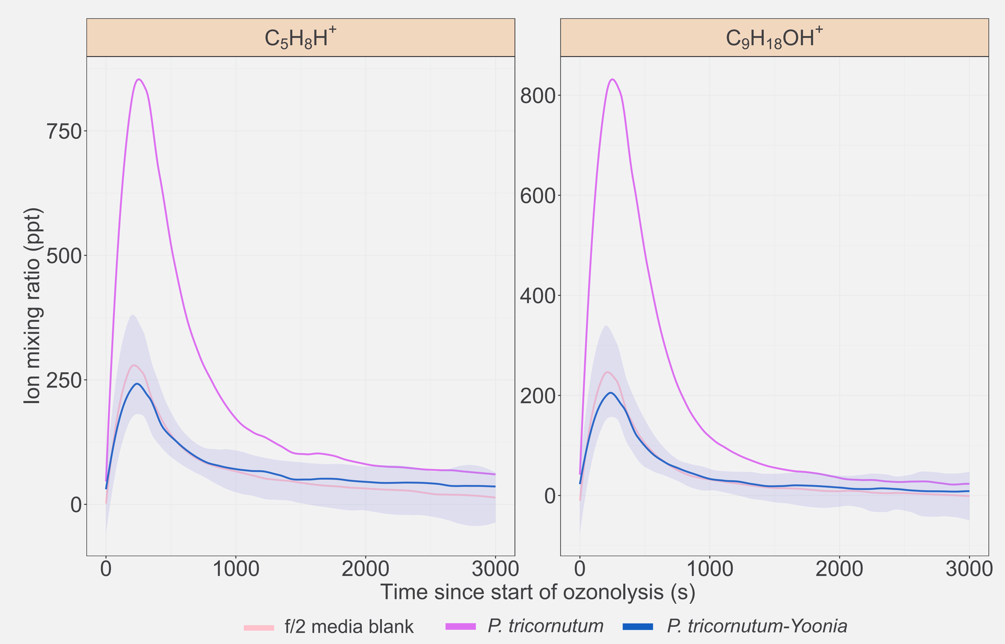


- Addition of iodide to the monoculture reduced VOC emissions, showing that the reaction of ozone with iodide at the air-water interface is in competition with that of organics in these experiments

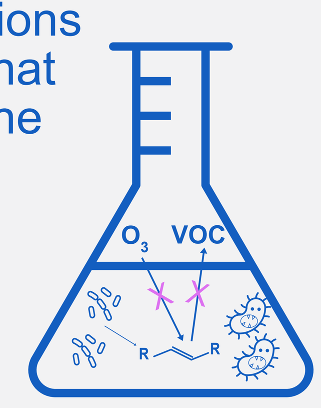


Monoculture vs Coculture

- Does the presence of bacteria impact abiotic VOC emissions in the exponential phase?

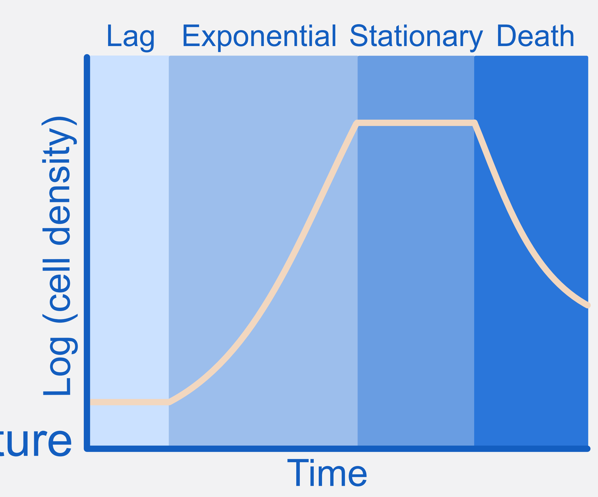


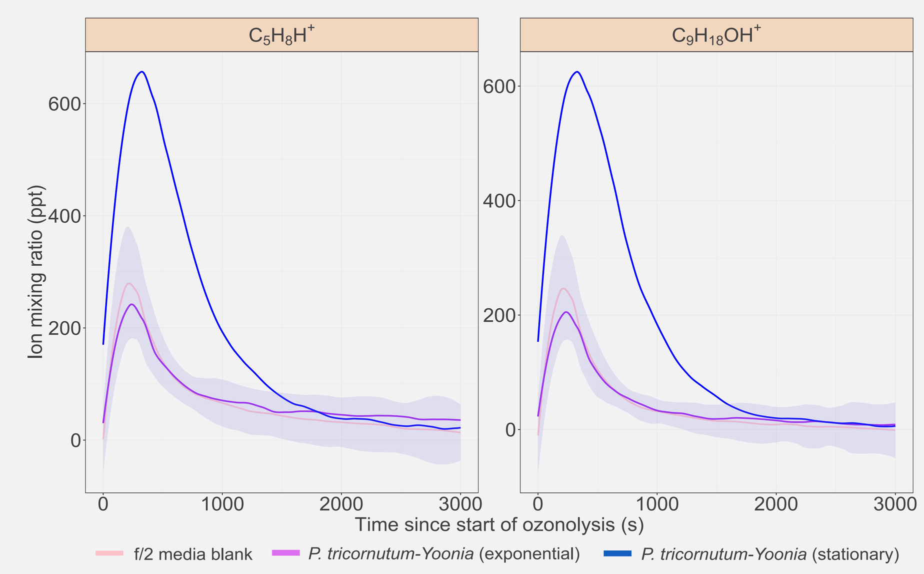
- Reduction in abiotic VOC emissions from the coculture, suggesting that the bacteria are consuming ozone reactive precursor compounds
- Padaki et al. (2024)[6] observed a reduction of the in-water VOCs of the coculture compared to the monoculture



Culture Growth Phase

- Cultures can be classified by their growth cycle which represents their cell density
- An increase in emissions were observed in the stationary vs exponential phase for the coculture





- Additional experiments are required to determine the repeatability of the presented observations

Future Work

- Simultaneous measurement of ozone uptake to better constrain the chemical drivers
- Couple gas chromatography to the system to enable separation of the ions contributing to $C_5H_8H^+$ signal
- Expand the study to perform mesocosm experiments to investigate the VOC response to changes in ocean variability
- **Overall project aim:** parameterise marine VOC emissions using satellite remote sensing observations

This presentation participates in OSPP
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References

[1] Novak and Bertram **2020** *Reactive VOC Production from Photochemical and Heterogeneous Reactions Occuring at the Air-Sea Interface*
[2] Schneider et al. **2019** *Formation of Secondary Organic Aerosol from the Heterogenous Oxidation by Ozone of a Phytoplankton Culture*
[3] Schneider et al. **2024** *Abiotic Emission of Volatile Organic Compounds from the Ocean Surface: Relationship to Seawater Composition*
[4] Kilgour et al. **2024** *Production of Oxygenated Volatile Organic Compounds from the Ozonoylsis of Coastal Seawater*
[5] Carpenter et al. **2021** *Marine Iodine Emissions in a Changing World*
[6] Padaki et al. **2024** *Bacterial Volatile Organic Compound Specialists in the Phycosphere*

Acknowledgements

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