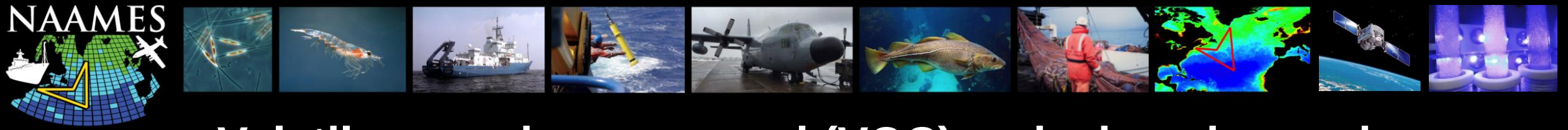
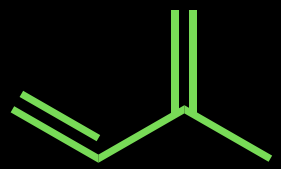
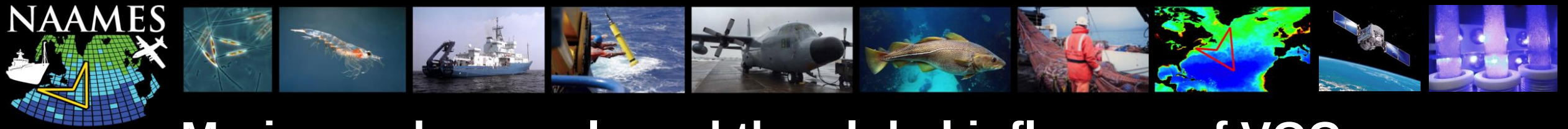


Volatile organic compound (VOC) emissions by marine plankton using proton-transfer-reaction time-of-flight mass spectrometry (PTR-ToF/MS)



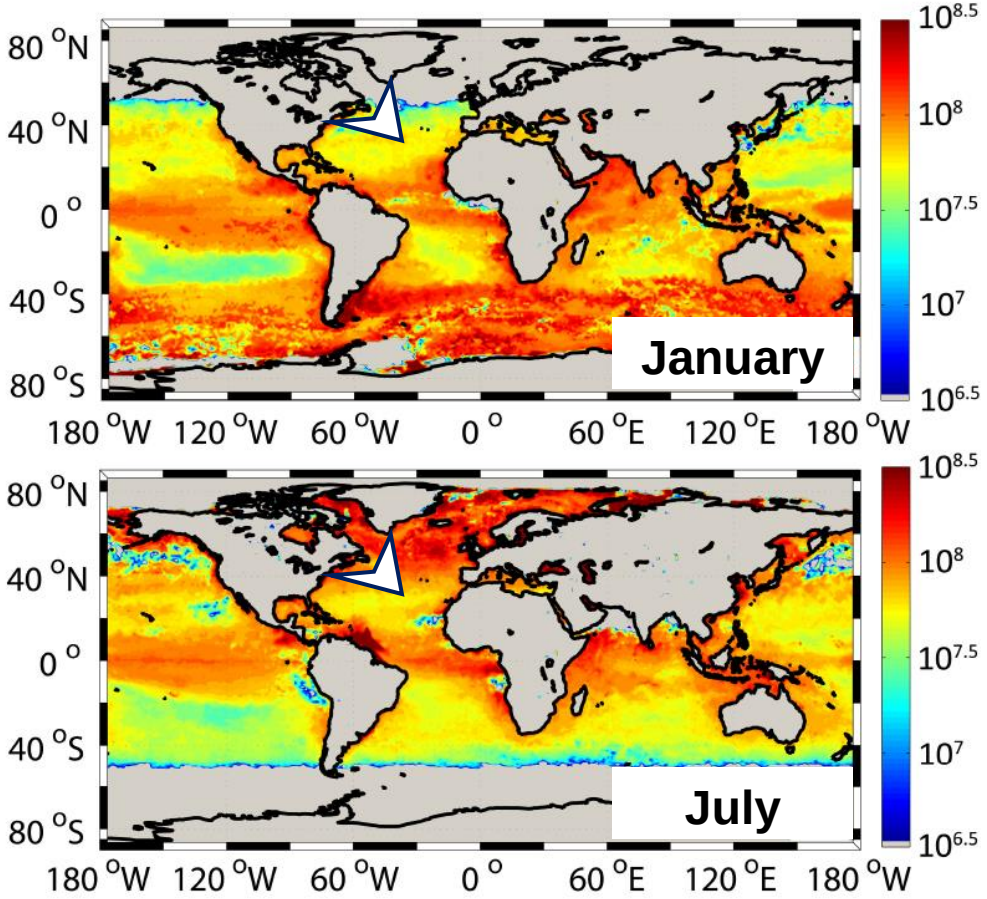

Cleo Davie-Martin, Stephen Giovannoni, and Kimberly Halsey

Department of Microbiology, Oregon State University



Marine carbon cycle and the global influence of VOCs

Estimated isoprene emission rates
(molecules cm^{-2} s^{-1})

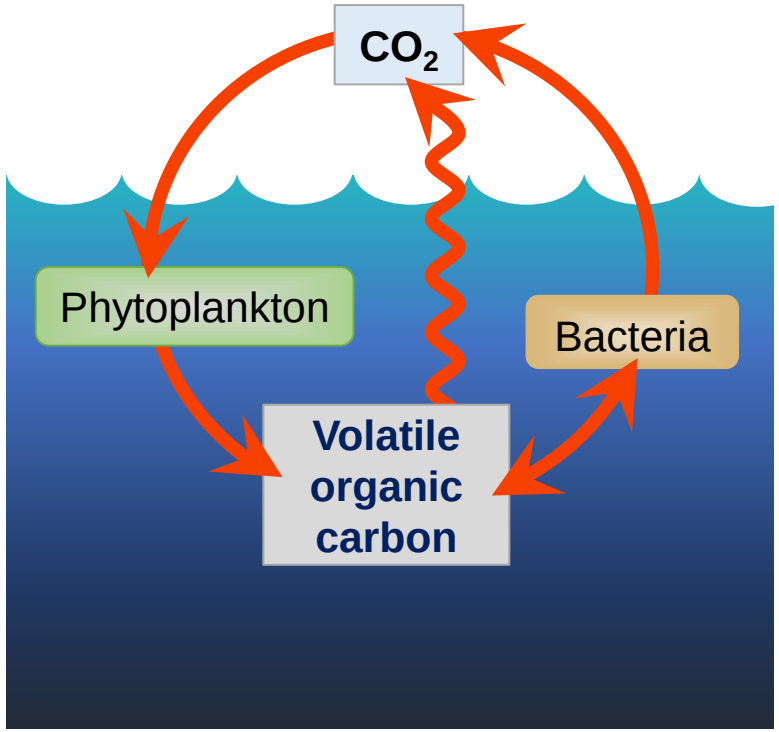


Gantt et al. **2009**, Atmos. Chem. Phys., 9, 4915-4927

What is the magnitude of this VOC cycle?

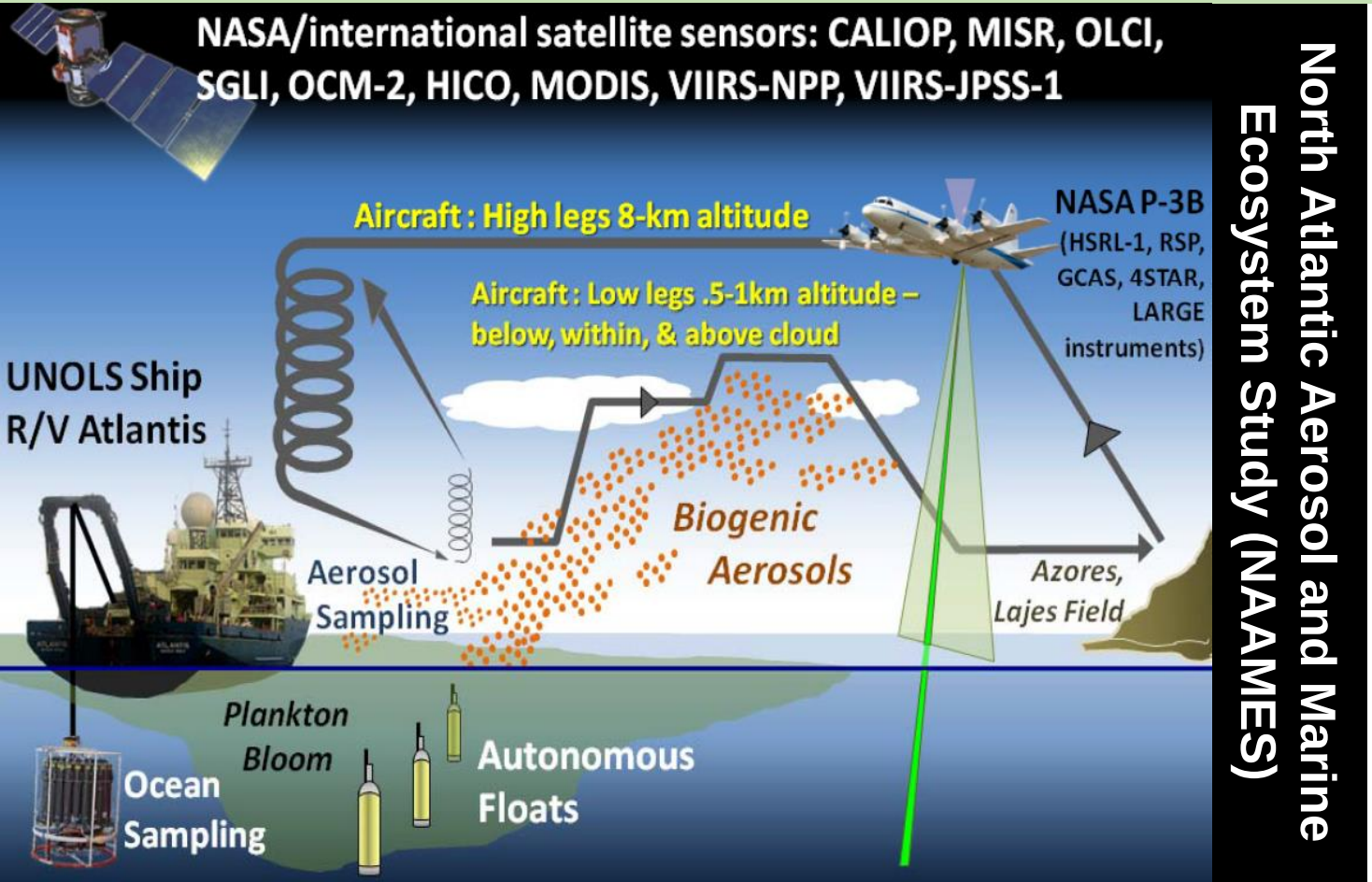
What compounds are involved?

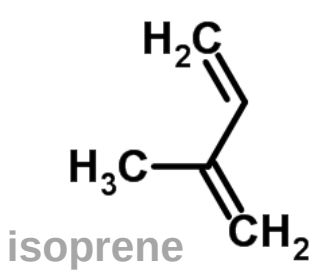
What organisms participate?



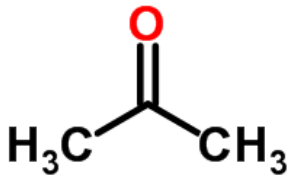
Objectives

To assess spatial and temporal patterns in the net rates of biological VOC production during different stages of the annual phytoplankton bloom

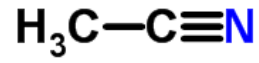




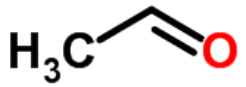
isoprene



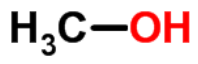
acetone



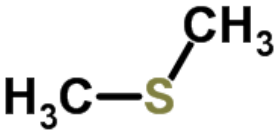
acetonitrile



acetaldehyde



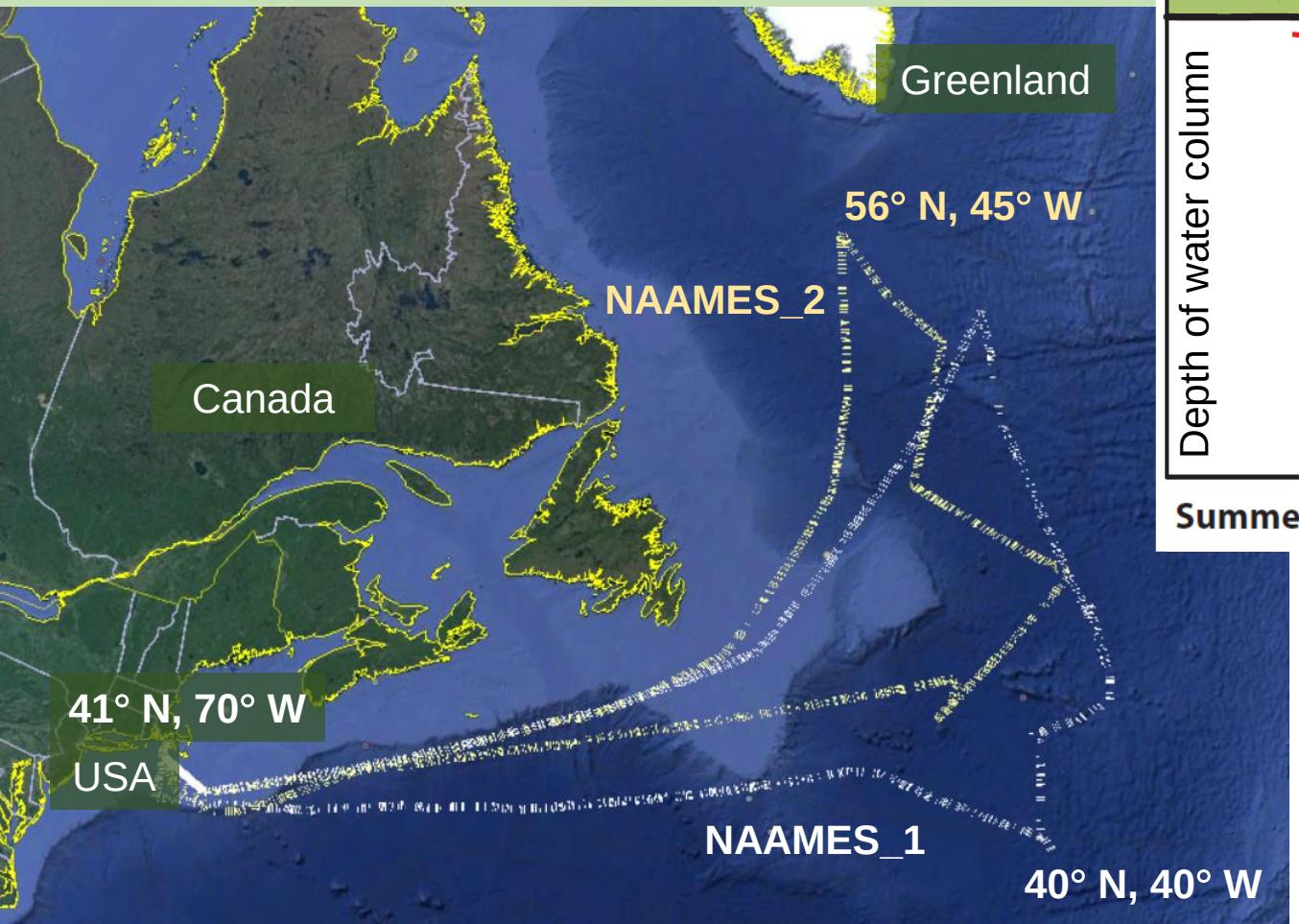
methanol

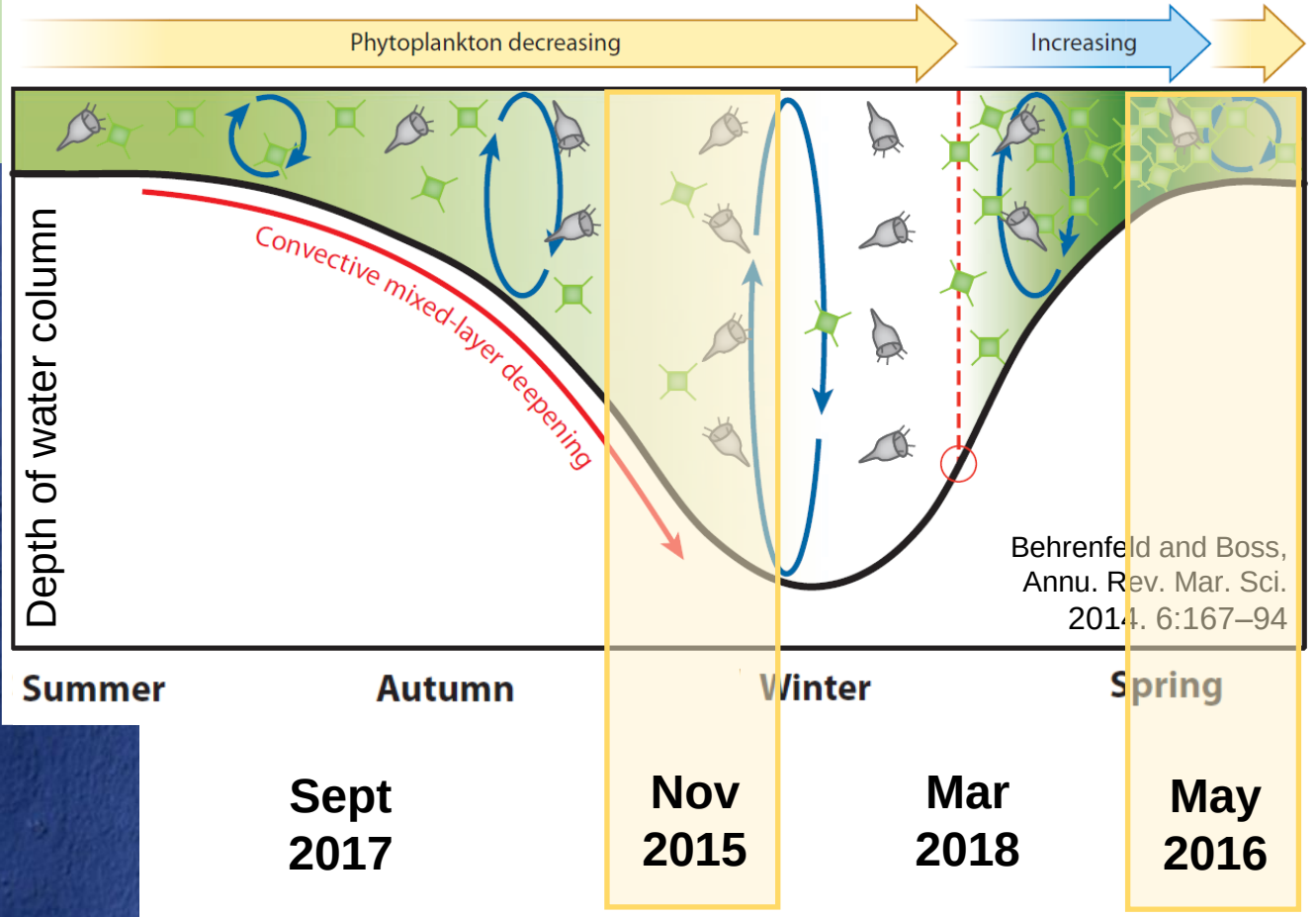


dimethylsulfide

Sampling region: North Atlantic Ocean

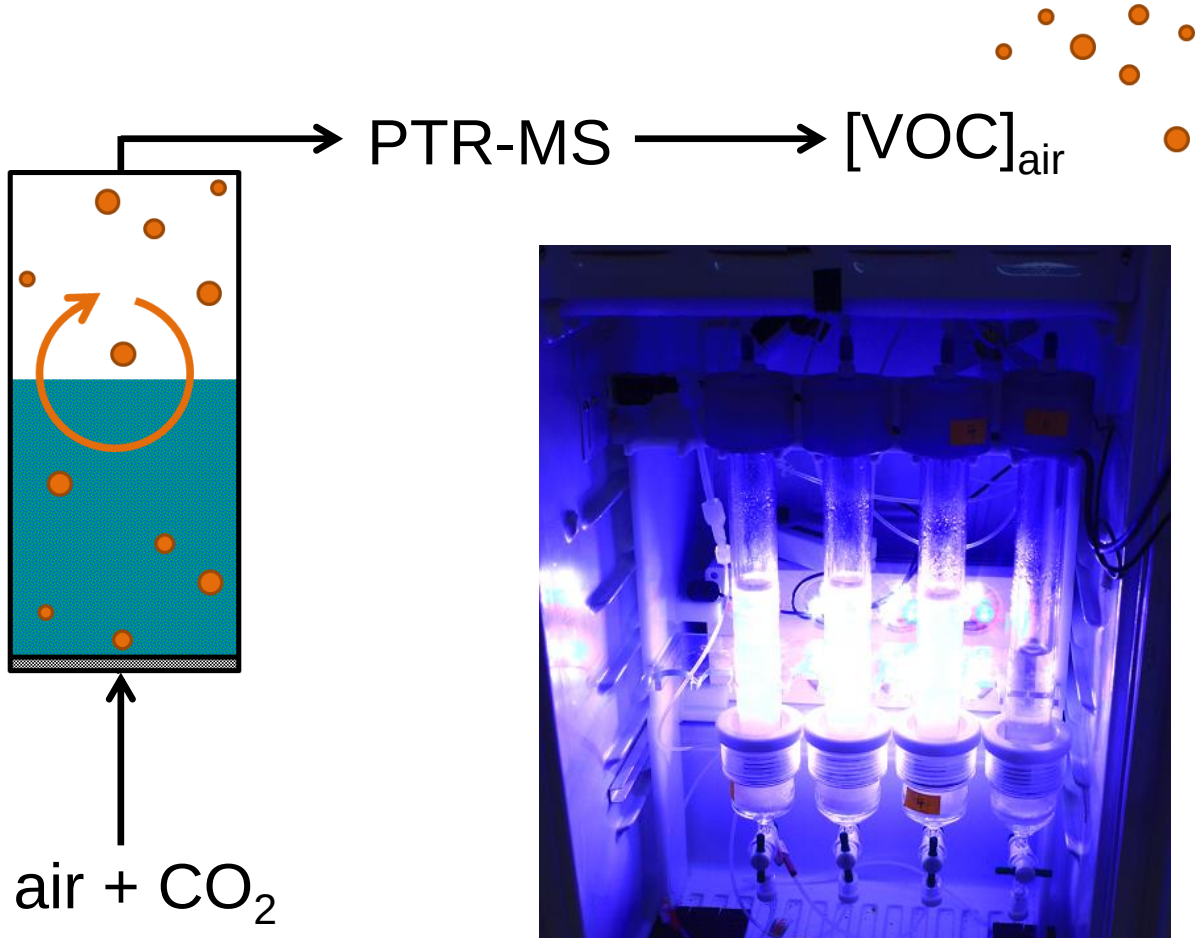
Four field campaigns target different stages of the annual phytoplankton bloom cycle





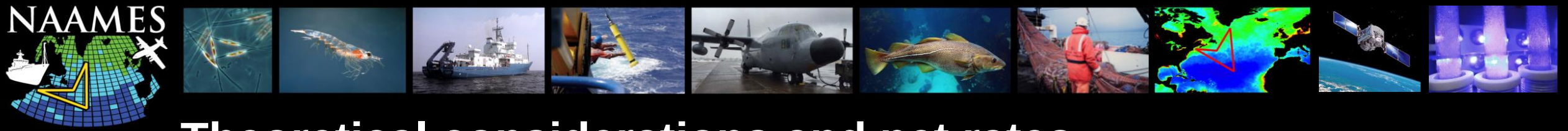
Experimental set-up: dynamic stripping chambers

New approach for understanding when the ocean acts as a net **source/sink** of VOCs

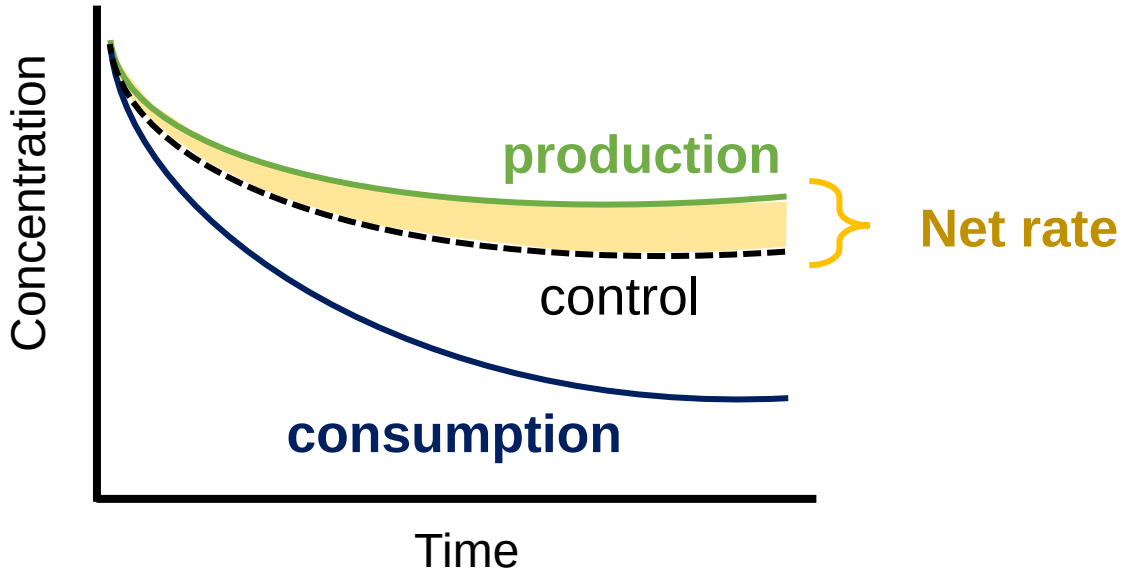


VOCs are ‘stripped’ from seawater and directed into the PTR-MS

Light and temperature-controlled



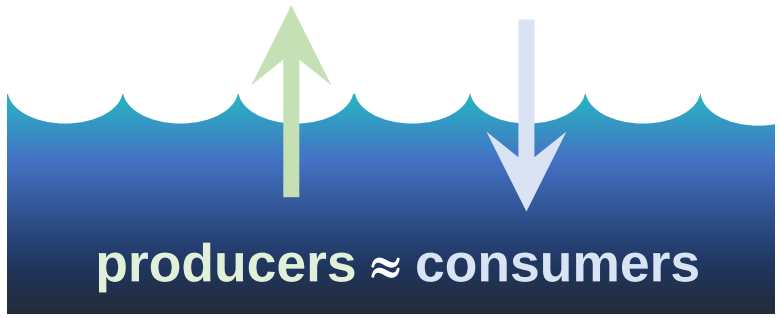
Theoretical considerations and net rates



Magnitude of the net rate ≠ indicate the magnitude of production and consumption rates

Production	Consumption	Net Rate
100	99	**1**
1.01	0.01	**1**

TIGHT COUPLING

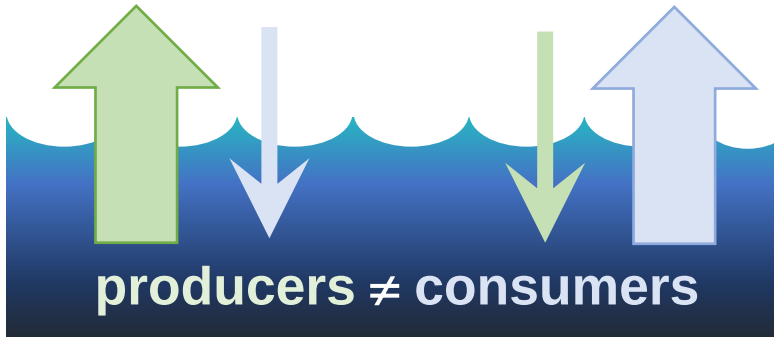


Net rates >> or <<0

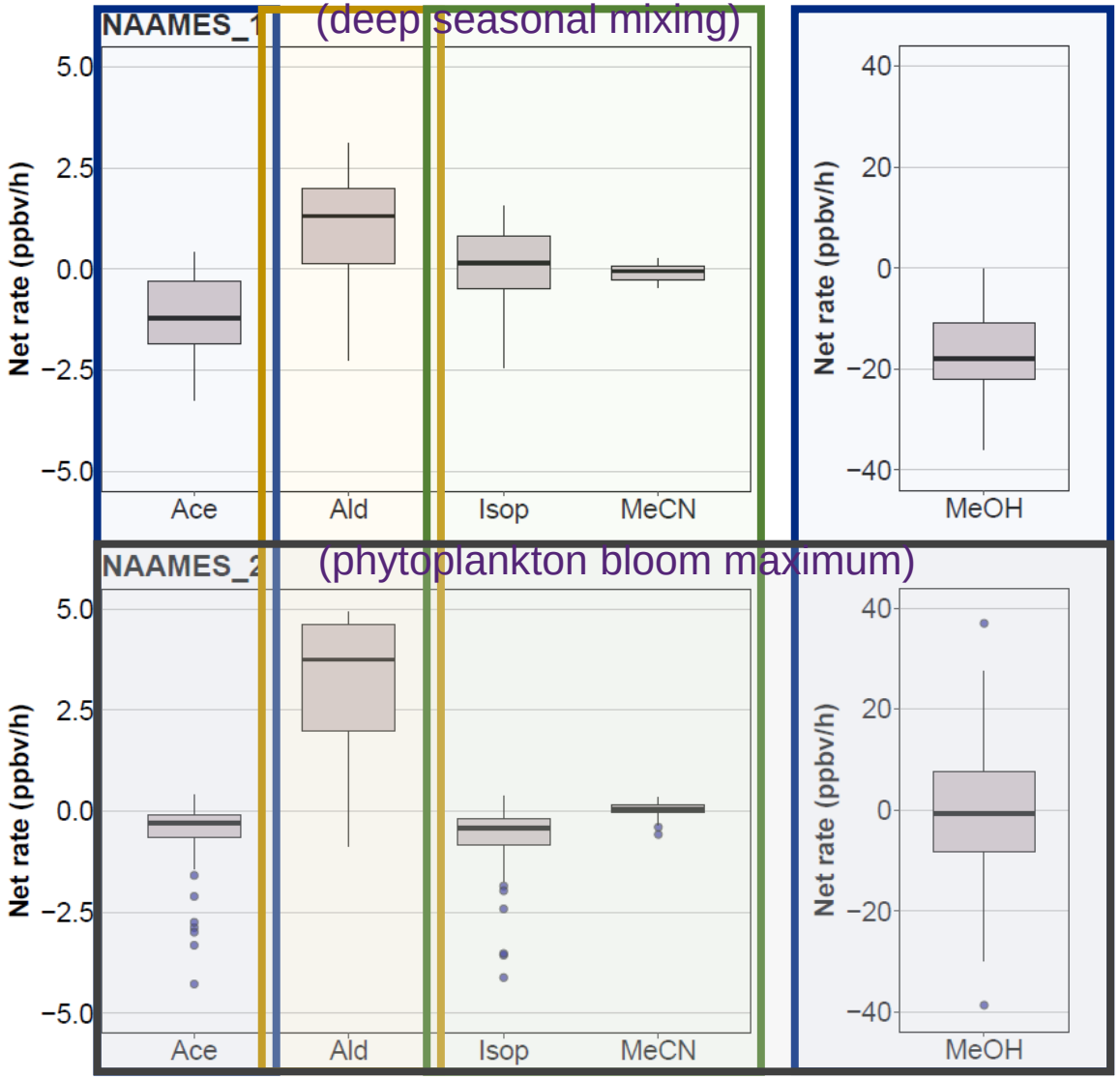
[seawater] ↑ or ↓

Biological drivers of VOC flux

UNCOUPLED



Results: Range of net rates

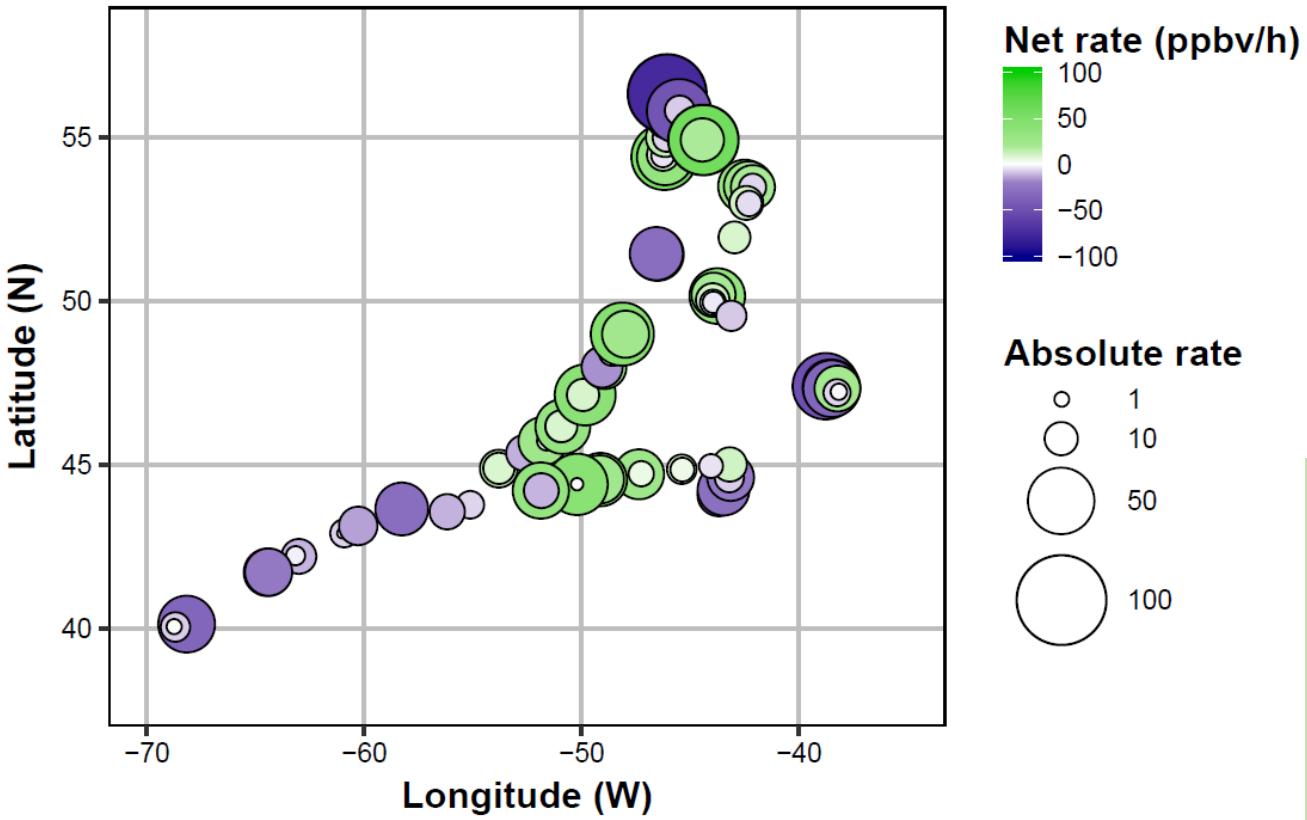


- **Methanol** and **acetone** usually showed **net consumption** (negative net rates)
- **Acetaldehyde** usually showed **net production** (positive net rates)
- **Isoprene** and **acetonitrile** showed **lower** net rates and/or were more **tightly coupled**
- **NAAMES_2** rates generally more **positive**

Experiments for **5 m** seawater collected during **daylight hours** (dawn-dusk) and incubated in the **light**

Comparisons between NAAMES_1 and NAAMES_2

How to interpret bubble plots



- Sampling location is plotted as a circle (by **latitude** *vs.* **longitude**)

- **Color shading** indicates the magnitude and direction of the rate
  - → **purple** = net consumption
  - → **green** = net production
- **Size of bubble** indicates the absolute magnitude of the rate

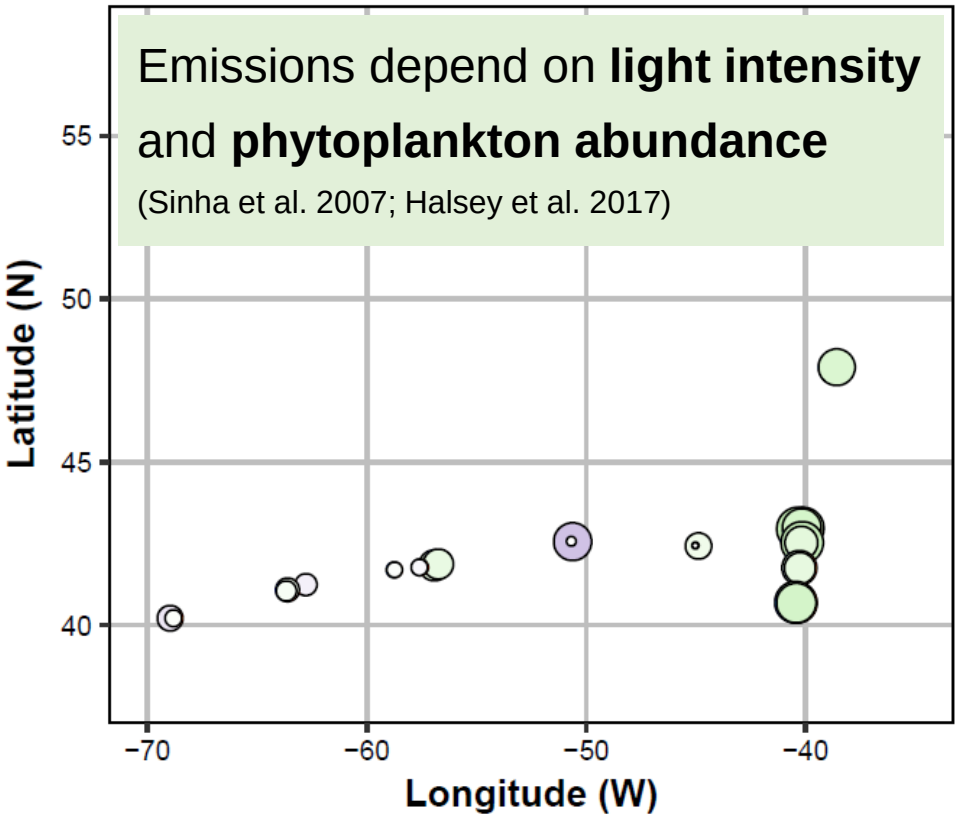
- **Large, brightly colored bubbles:** system is uncoupled
- **Small, pale bubbles:** tighter coupling
- **Large purple and green bubbles:** high variability in the rates

Results: Acetaldehyde

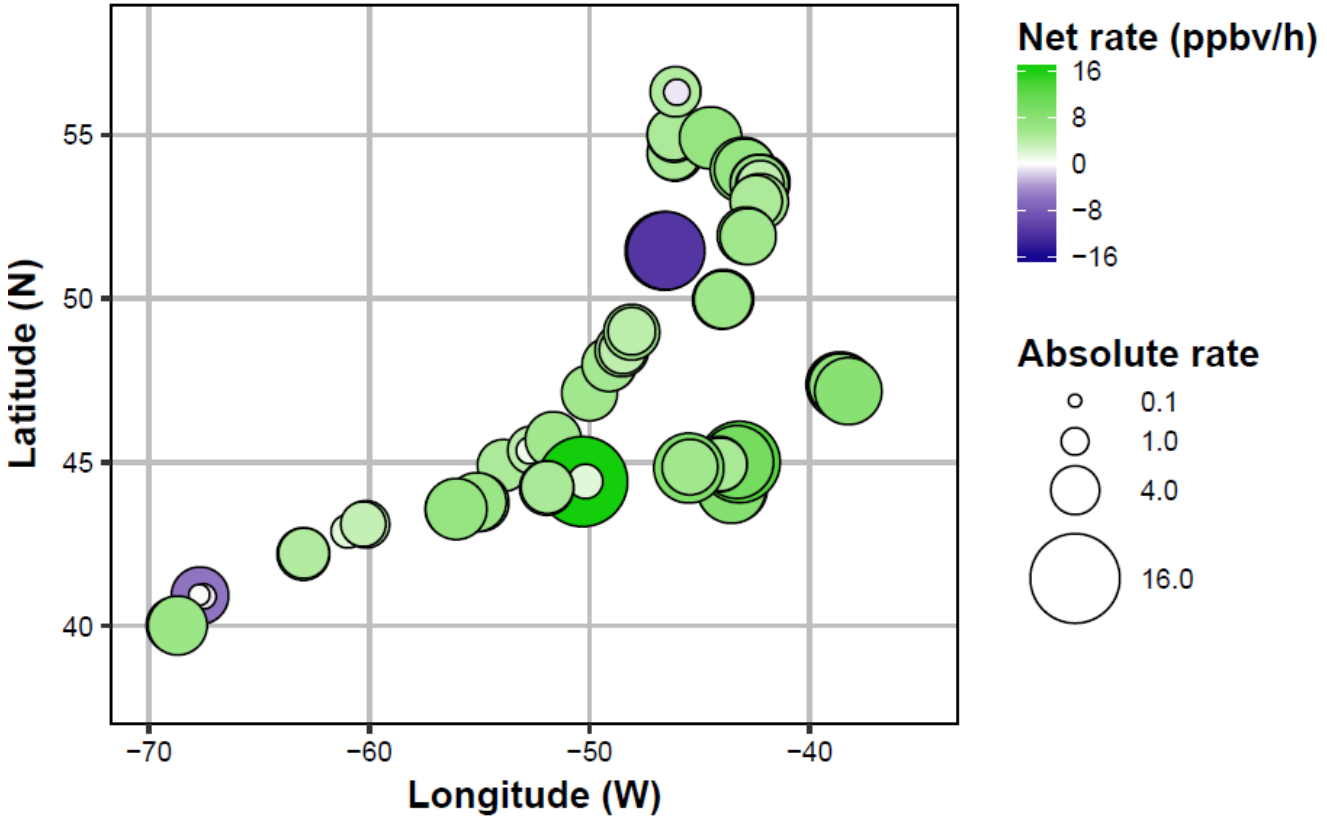
NAAMES_1 (deep seasonal mixing)

Emissions depend on **light intensity** and **phytoplankton abundance**

(Sinha et al. 2007; Halsey et al. 2017)



NAAMES_2 (phytoplankton bloom maximum)

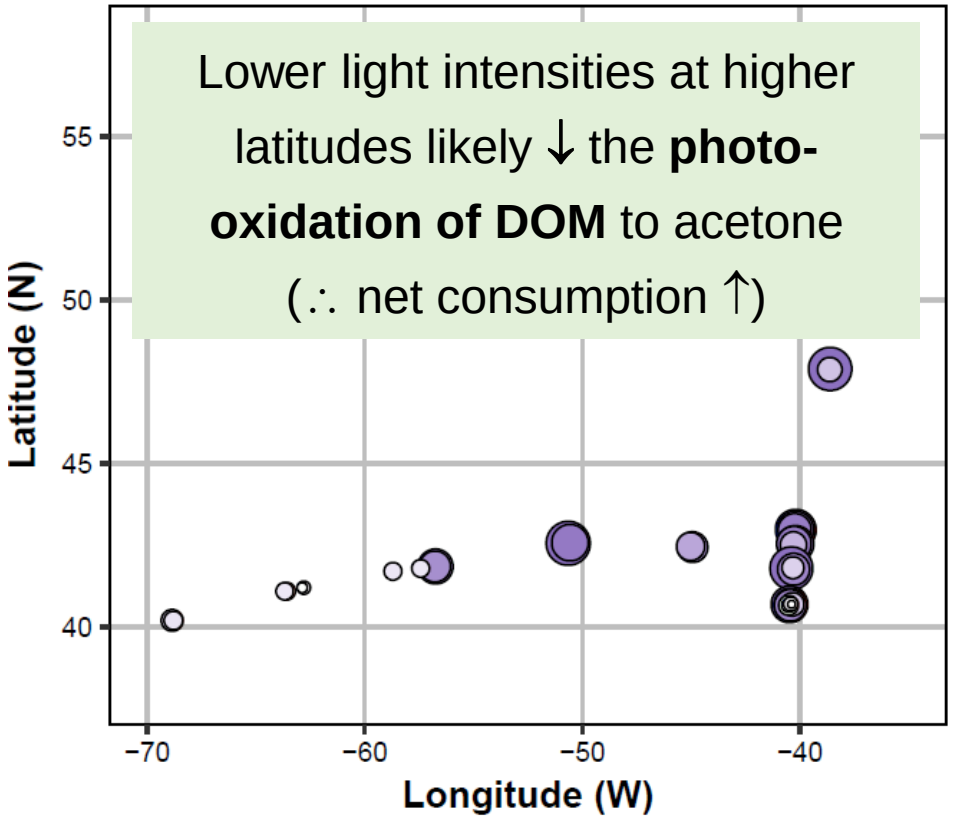


- Tightly coupled but with a tendency towards production in the open ocean
- Greater uncoupling and increased production relative to NAAMES_1

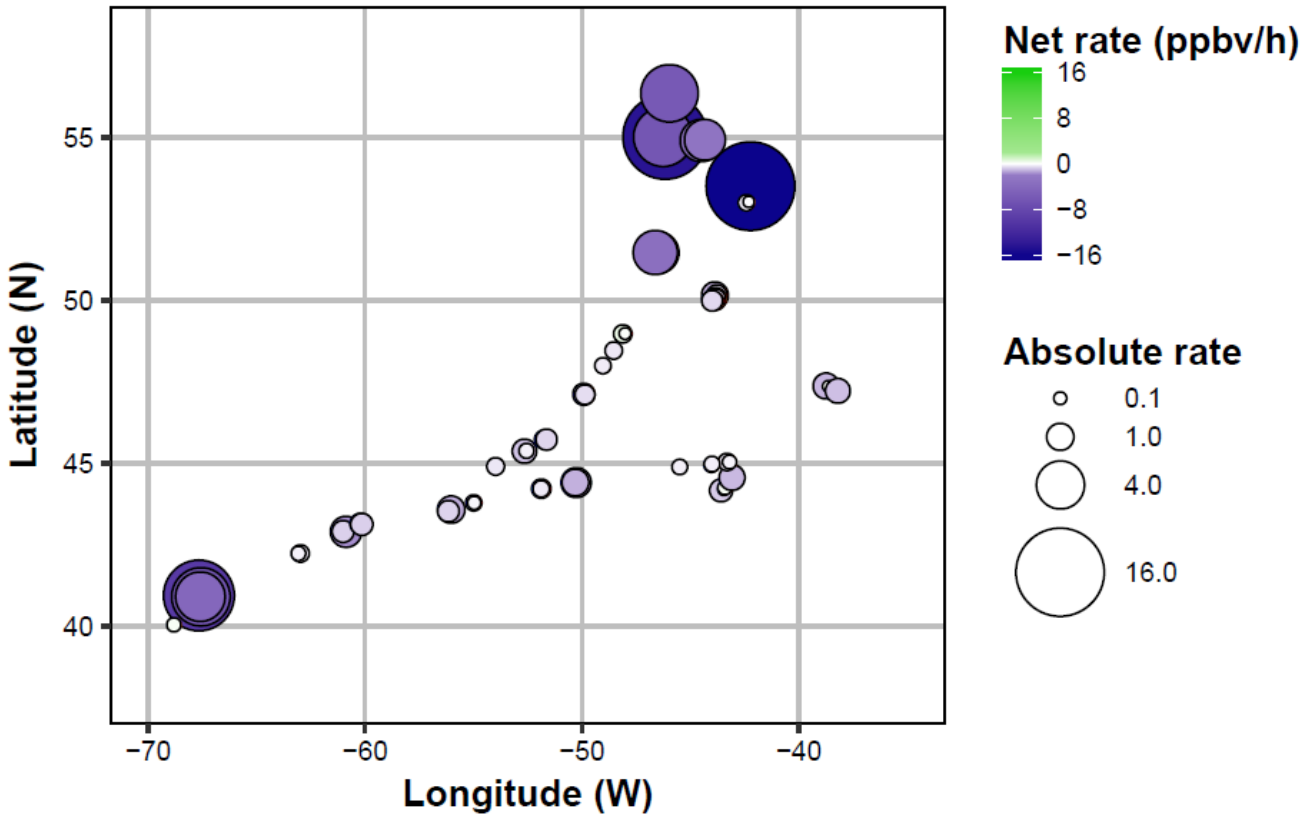
Results: Acetone

NAAMES_1 (deep seasonal mixing)

Lower light intensities at higher latitudes likely ↓ the **photo-oxidation of DOM** to acetone (∴ net consumption ↑)

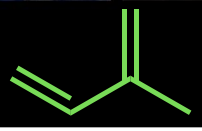


NAAMES_2 (phytoplankton bloom maximum)

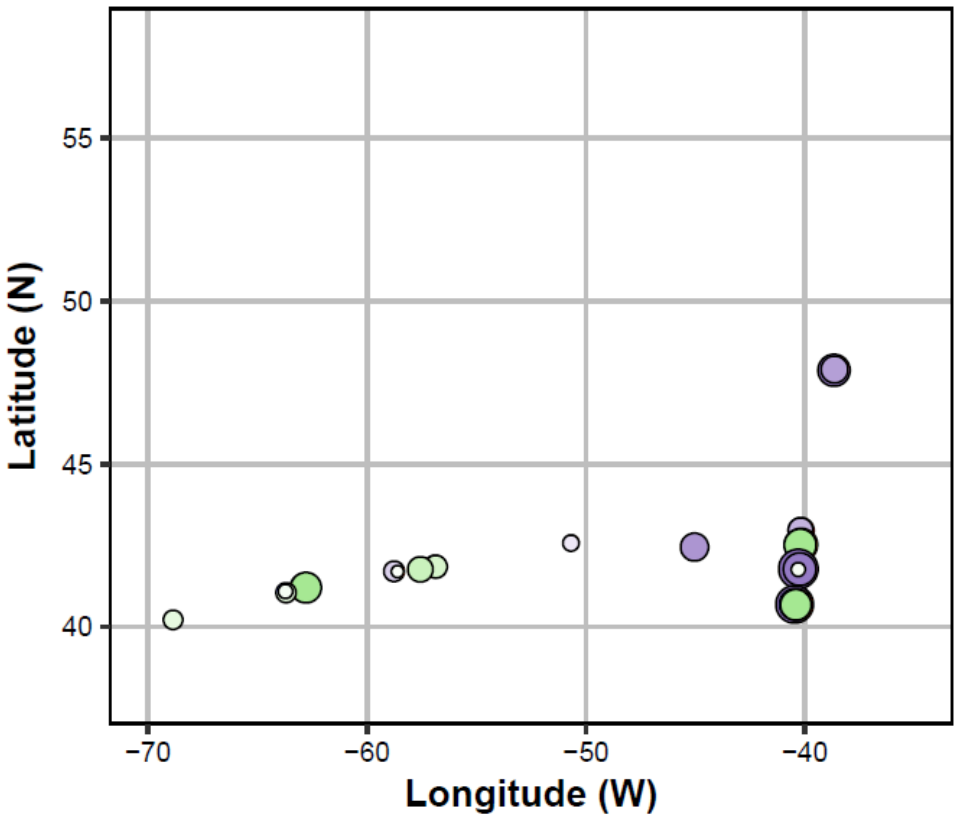


- Tightly coupled near the coast tending towards net consumption in the open ocean
- Large uncoupling at the coastal and northern-most sites (net consumption)

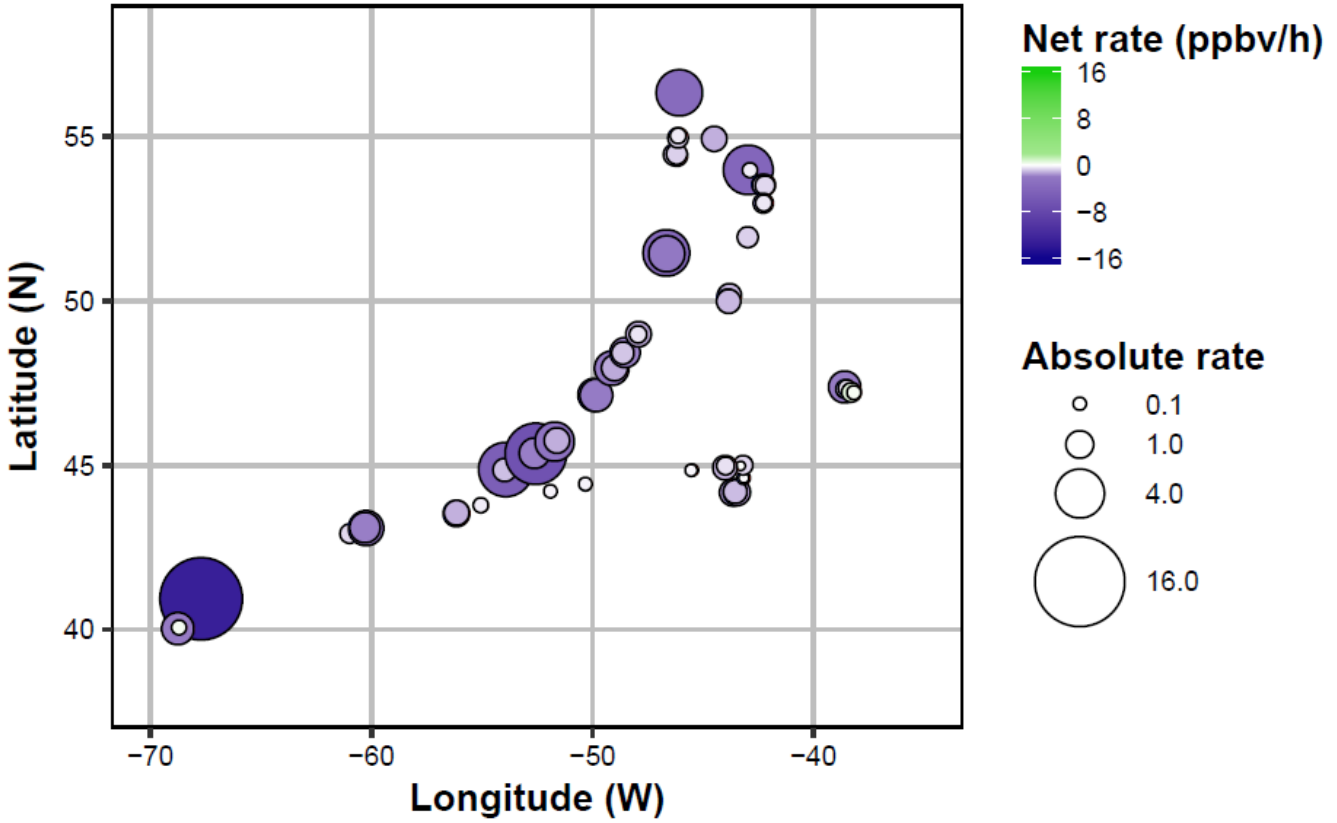
Results: Isoprene



NAAMES_1 (deep seasonal mixing)



NAAMES_2 (phytoplankton bloom maximum)

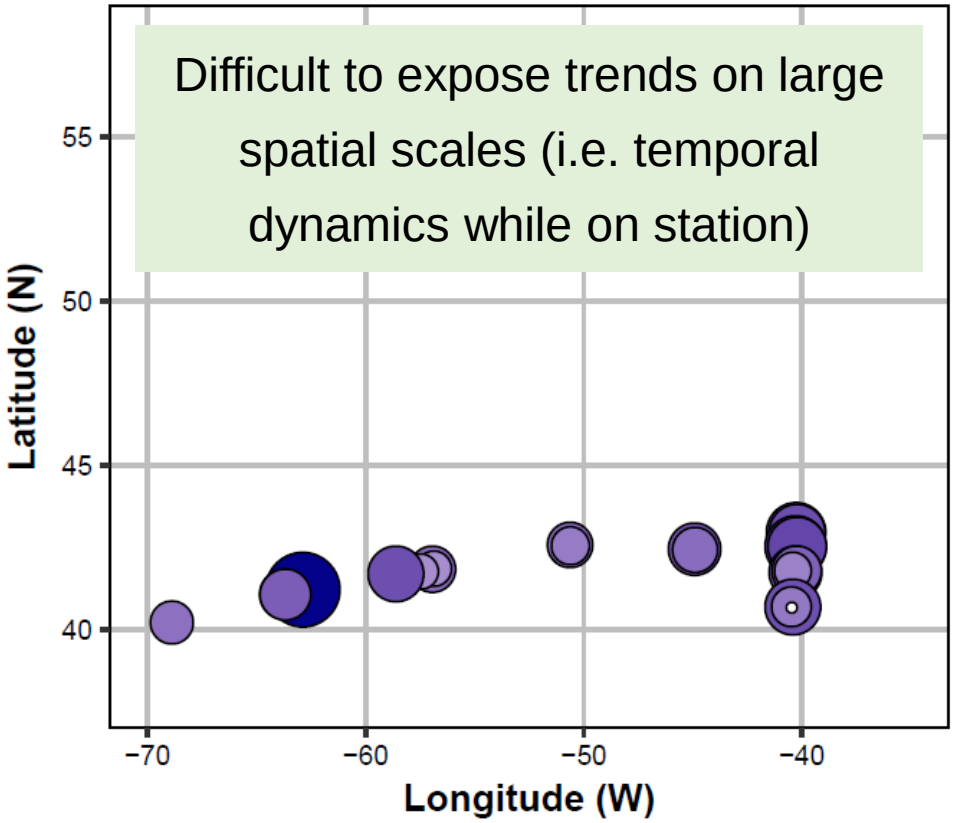


- Tightly coupled
- Becoming more uncoupled at the coastal and more northerly sites (similar to acetone)

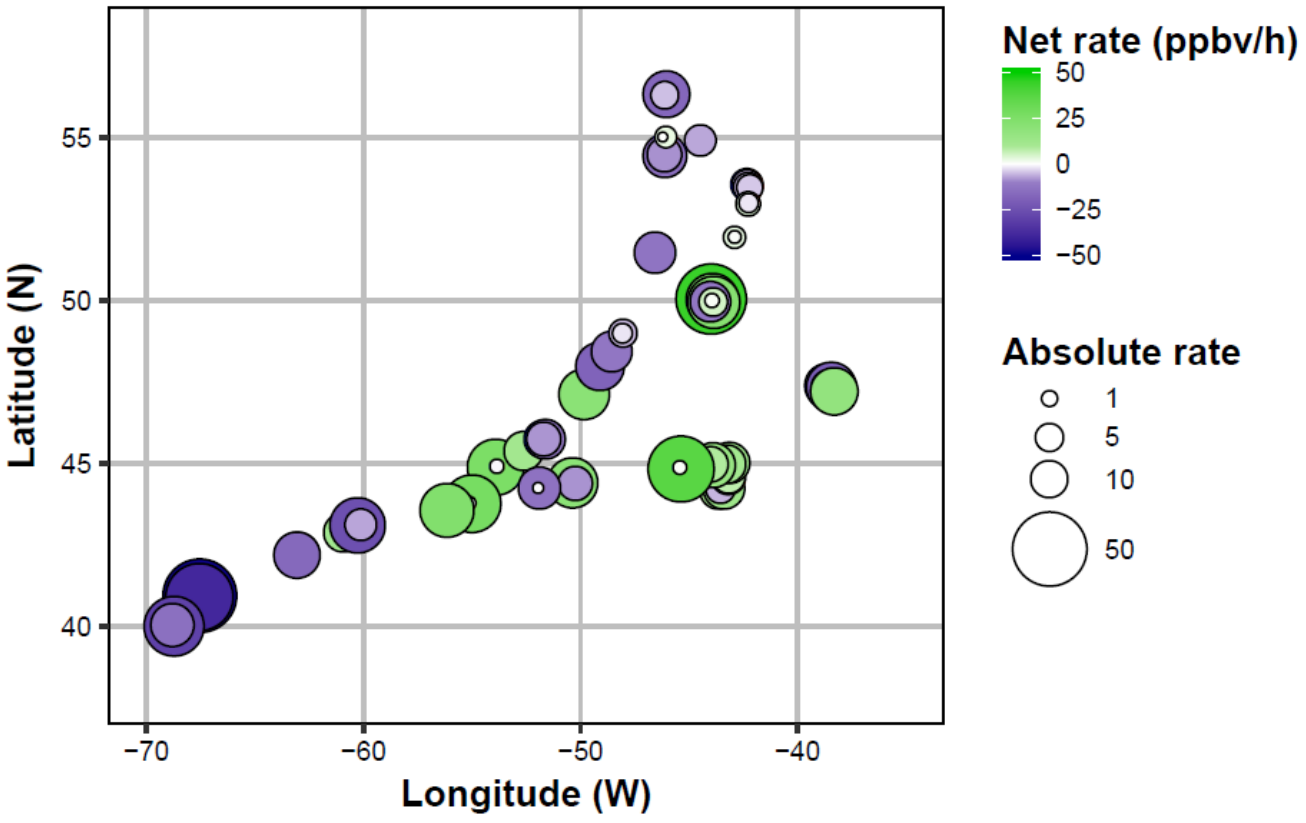
Results: Methanol —OH

NAAMES_1 (deep seasonal mixing)

Difficult to expose trends on large spatial scales (i.e. temporal dynamics while on station)



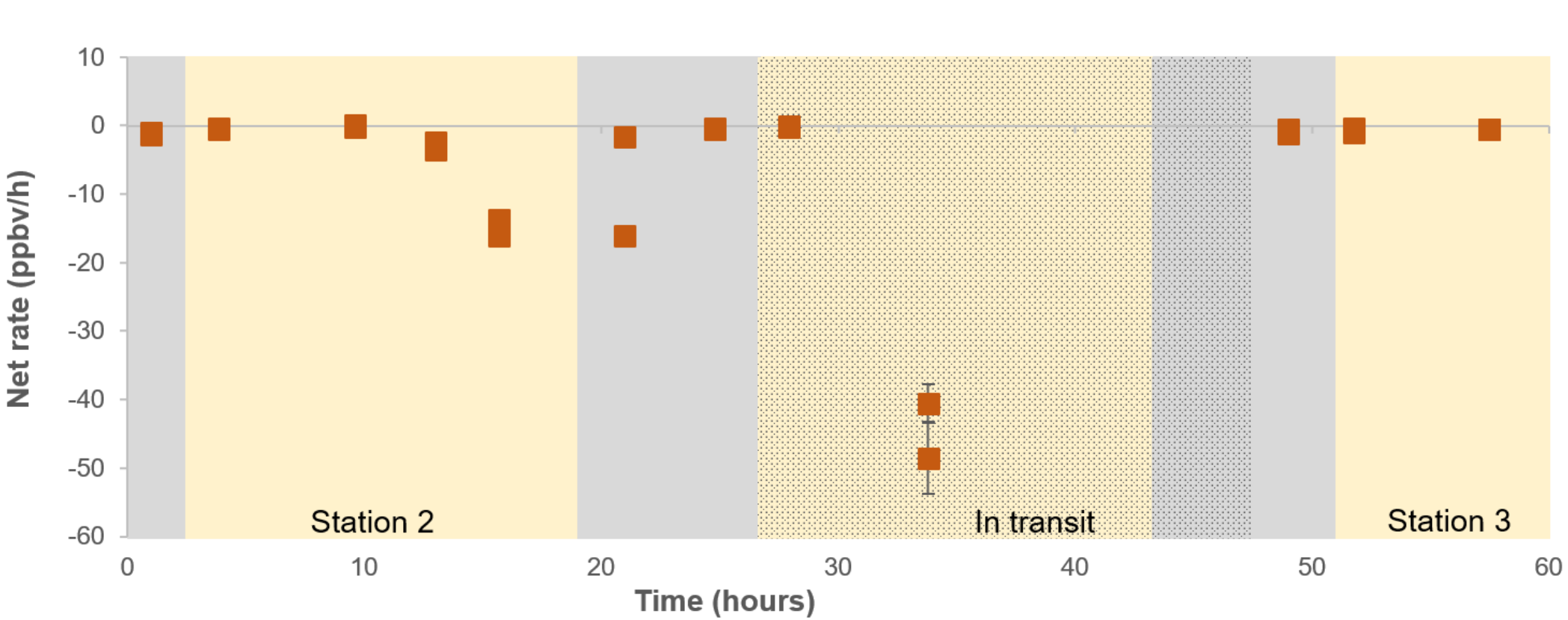
NAAMES_2 (phytoplankton bloom maximum)

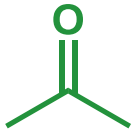


- Consistent net consumption, larger net rates
- Consumption at coastal and northern-most sites with greater production seen in the open ocean

NAAMES_2: Station 2-3 time course

Acetone

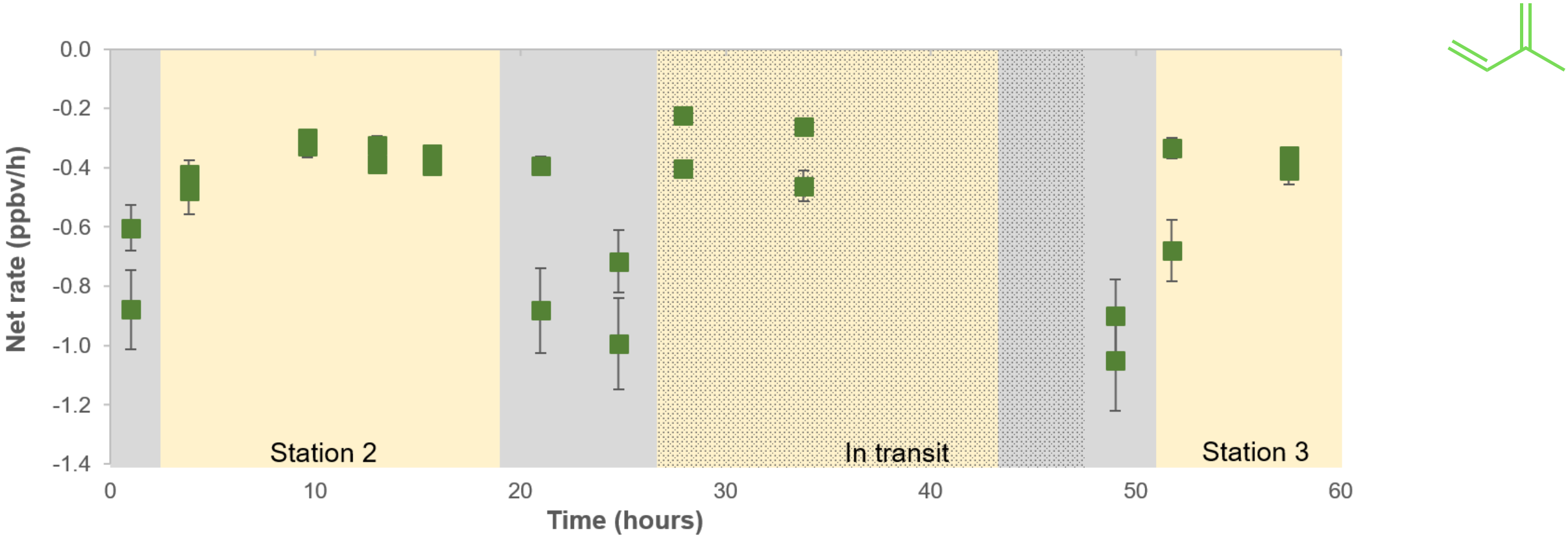




- Consumption increased in the late afternoon but we see tighter coupling at night and in the early morning
- Previous measurements in marine boundary air suggest **acetone is taken up by the ocean**, unless there is high light intensity and biological activity (Sinha et al. 2007)

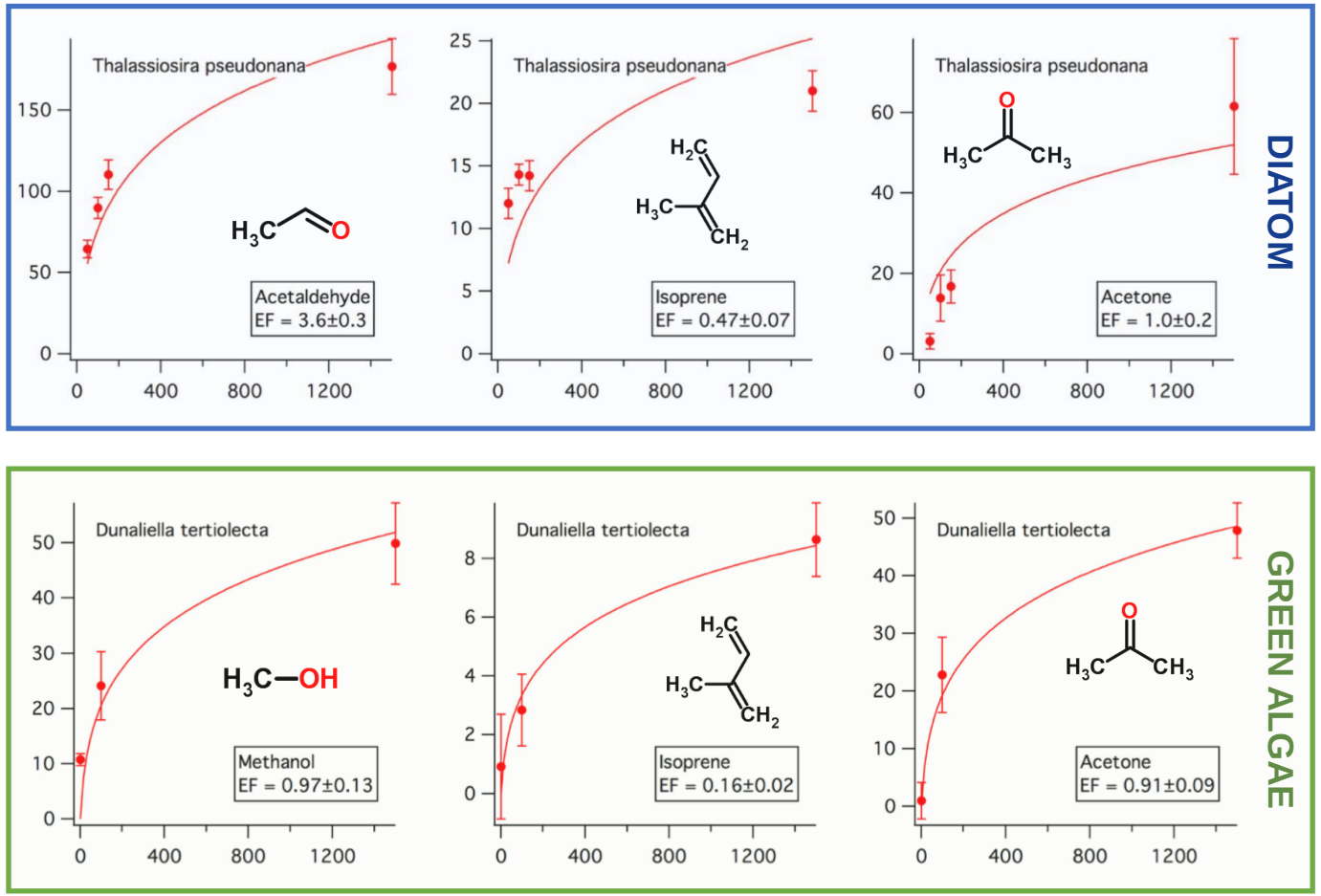
NAAMES_2: Station 2-3 time course

Isoprene



- Appears to be a **diel cycle**: rates more positive during daylight hours and more negative at night
- Provides additional evidence that marine isoprene emissions are **light-dependent**

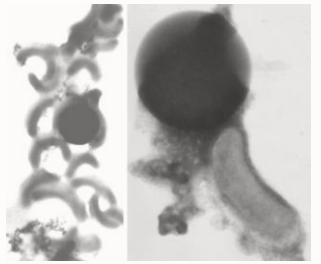
Further evidence for biogenic VOCs from cultures

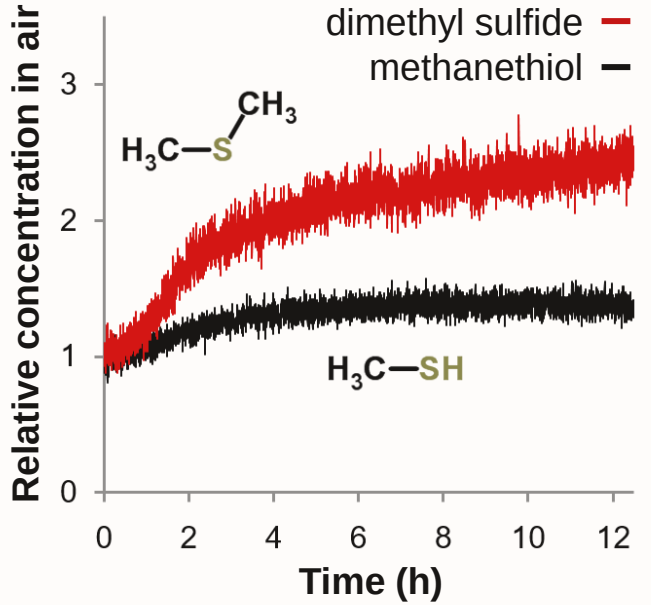


The light-dependent VOC metabolome of **diatoms** (*T. pseudonana)* is distinct from **green algae** (*D. tertiolecta*)

BACTERIA

Also oxidizes **acetaldehyde**





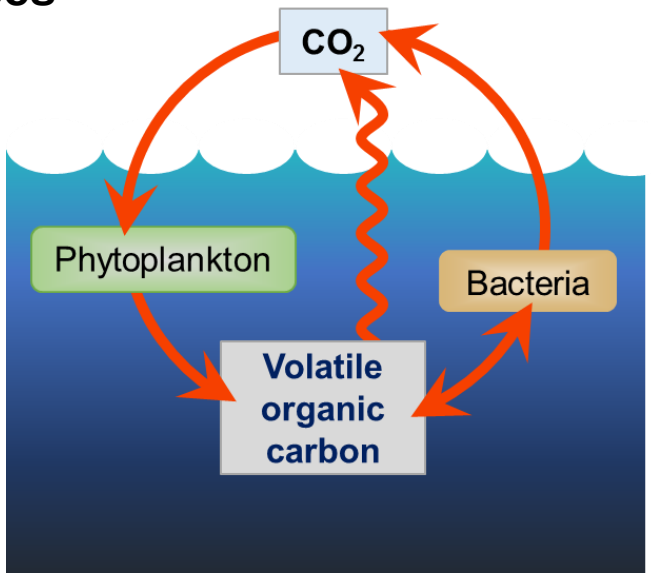
The globally abundant heterotrophic bacterium, *Pelagibacter,* simultaneously produces both **dimethyl sulfide** and **methanethiol**

Halsey et al. **2017**, *Limnology and Oceanography*, DOI: 10.1002/lno.10596
Sun et al. **2016**, *Nature Microbiology*, 1, 1-5, DOI: 10.1038/nmicrobil.2016.65

Next steps and conclusions

- Correlations with other measurements in NAAMES to link biology to atmosphere:
  - Ocean properties
  - Community composition
  - VOC flux and air concentrations (biological vs. physical drivers)
  - Aerosol properties
  - Modelled or satellite parameters
- Non-targeted analysis using ToF/MS data to identify *new* biogenic marine VOCs
- Culture-based experiments to tease out organism-specific VOC profiles and relationships

- VOCs are a conduit for **carbon transfer** between phytoplankton and bacteria → the remainder is available for escape to and reaction in the atmosphere
- This work will help to quantify biologically mediated **sources** and **sinks** of marine VOCs



Acknowledgements

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- NAAMES Researchers
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- Staci Massey Simonich
- Martin Graus
- Todd Rogers
- Jing Sun
- Joost de Gouw

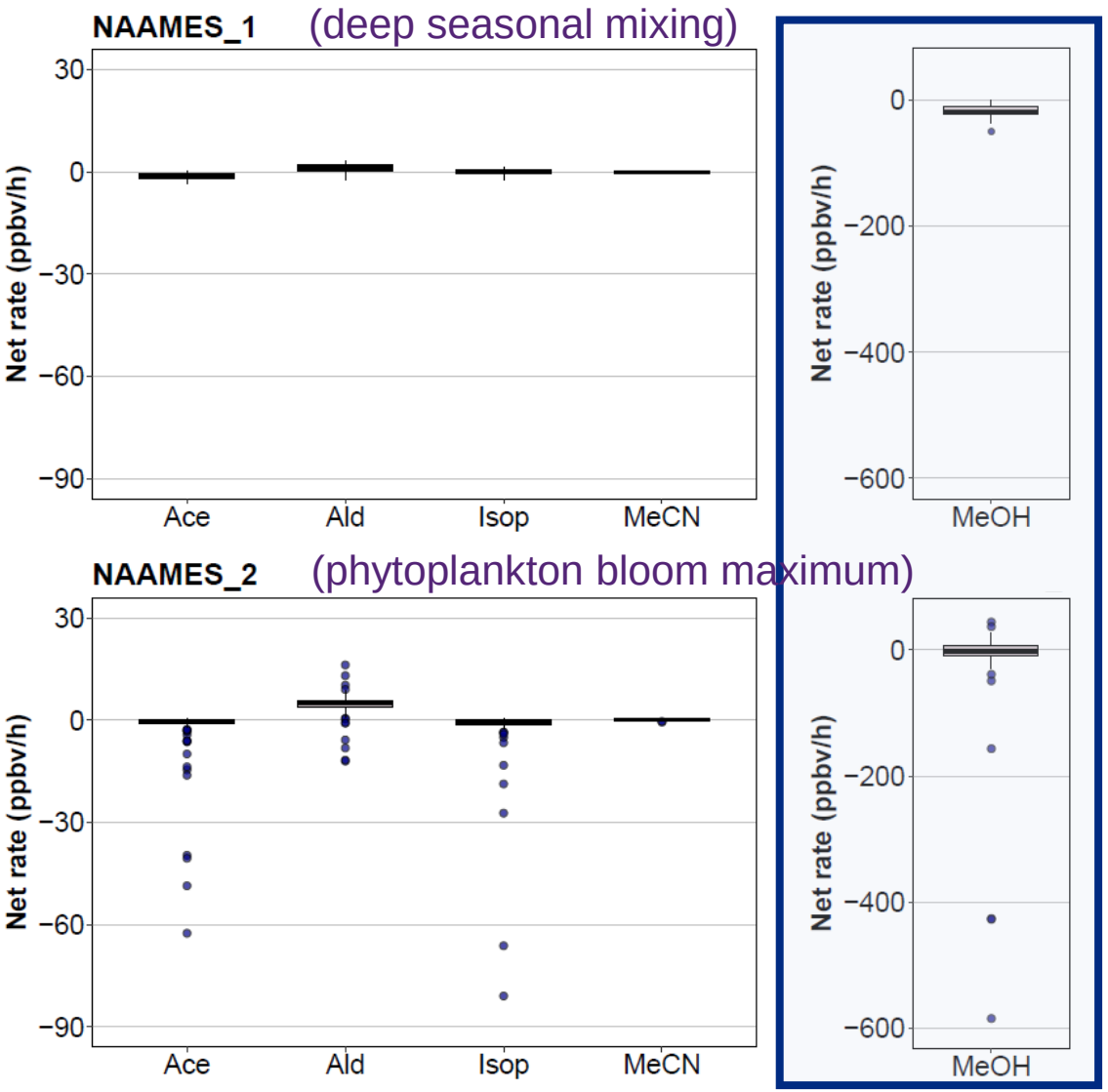
Oregon State University

Team TOX

VOCs associated with the marine environment

VOCs	Source(s)	Biogeochemical roles in marine ecosystems	Examples of metabolic roles	Seawater concentrations	Net production rate
Dimethylsulfide	Direct or stress-induced release by plankton	Climate-active gas	Oxidative stress protection, signal molecule	2-200 nM	
Isoprene	Plankton, terrestrial plants	Aerosol/cloud condensation nuclei formation	Chlorophyll synthesis	10-200 pM	3-25 μM (g Chl*a* h)$^{-1}$
Acetaldehyde	Photooxidation of DOM		Metabolic intermediate	2-37 nM	13-35 nM d^{-1}, 60-160 μM (g Chl*a* h)$^{-1}$
Methanol	Plankton	Rainwater acidification, O_3 formation	Cell wall, growth substrate	15-304 nM	22-428 nM d^{-1}, 10-50 μM (g Chl*a* h)$^{-1}$
Acetone	Photooxidation of DOM	Tropospheric photochemistry (source of •OH)		2-20 nM	2-26 nM d^{-1}, 15-60 μM (g Chl*a* h)$^{-1}$
Acetonitrile	Biomass burning, terrestrial plants	Reactions with •OH			

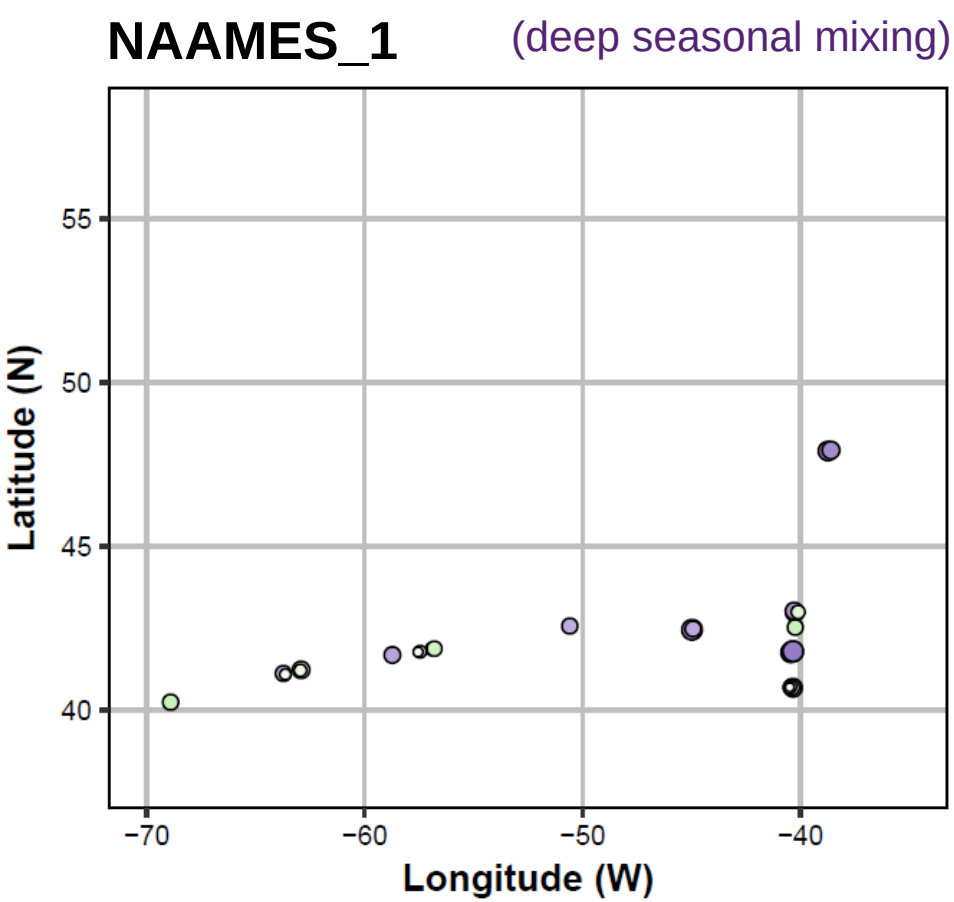
Results: Range of net rates

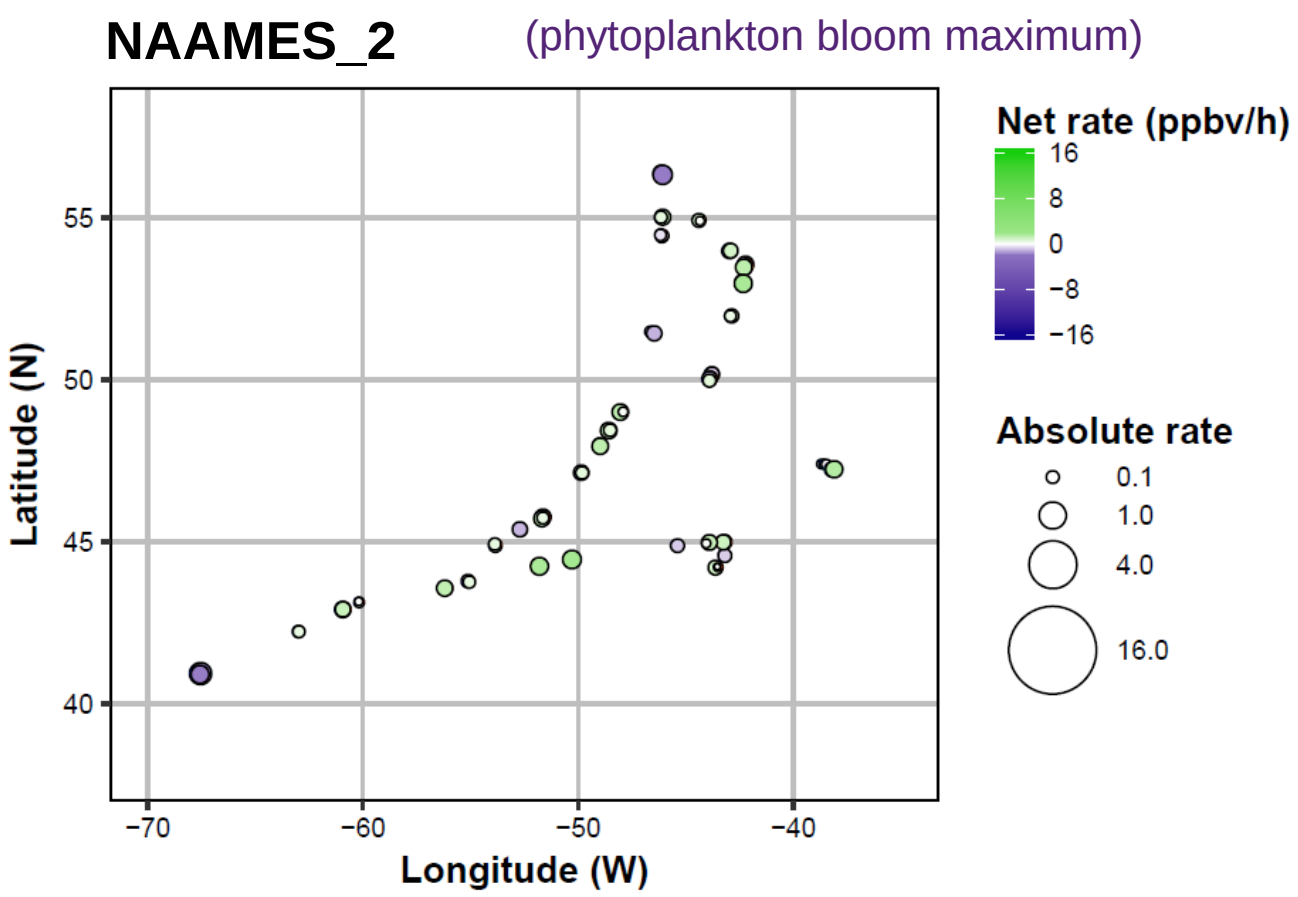


- **Methanol** rates were much **larger (uncoupled)** with **greater errors** than the other VOCs
  - → Higher concentrations in seawater
  - → Analytical difficulties due to ‘stickiness’

Experiments for **5 m** seawater collected during **daylight hours** (dawn-dusk) and incubated in the **light**

Results: Acetonitrile





- Variable but very small net rates (i.e., tightly coupled)
- Difficult to expose trends large spatial scales (temporal dynamics on station…)