The role of chemistry in air-sea fluxes

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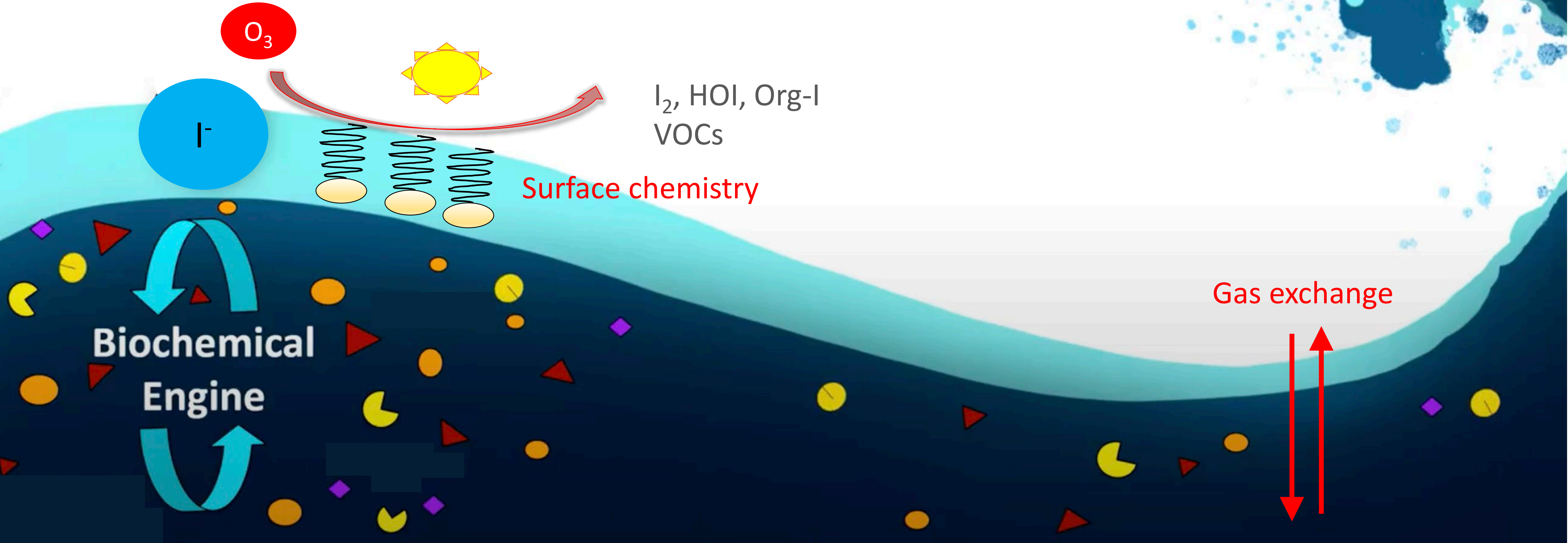
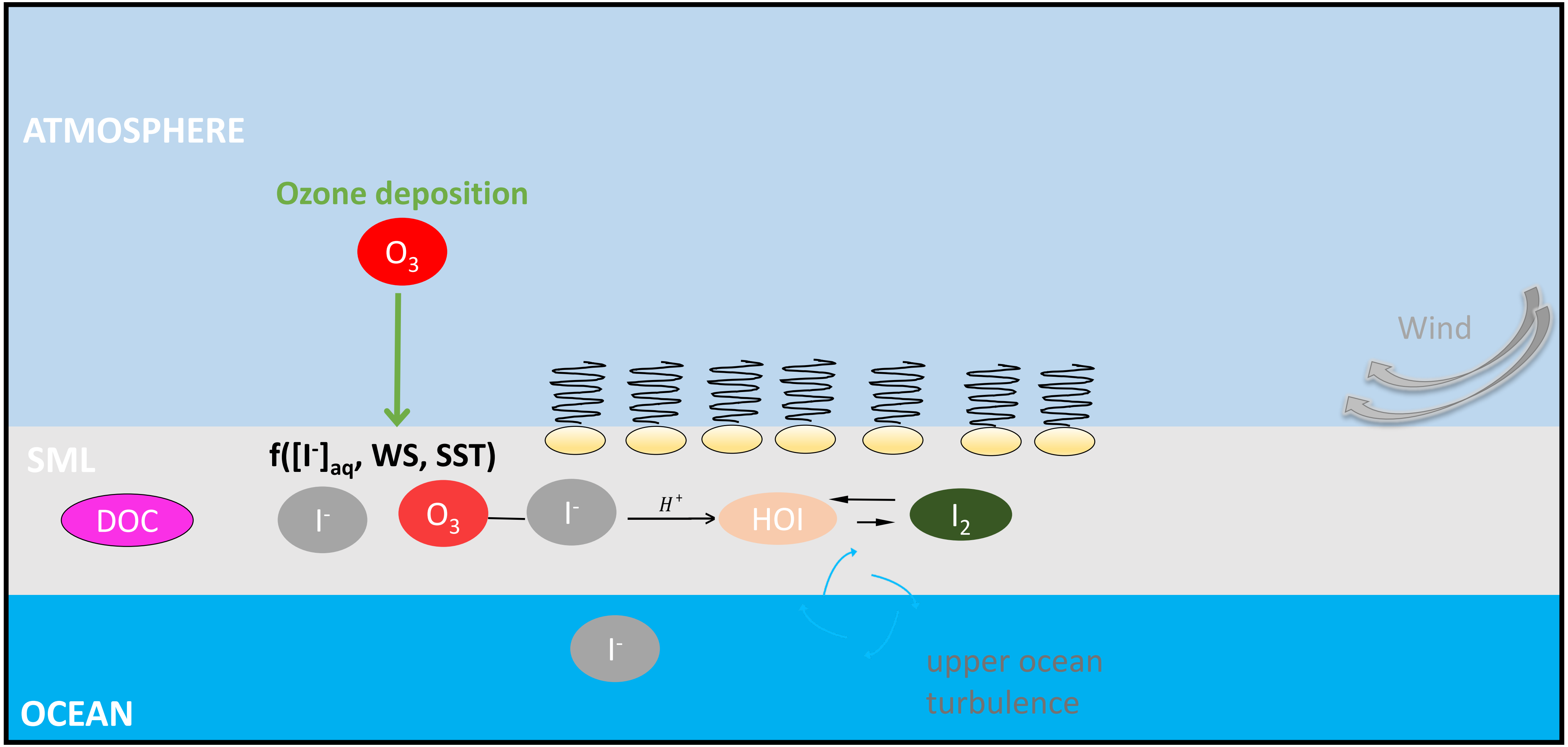
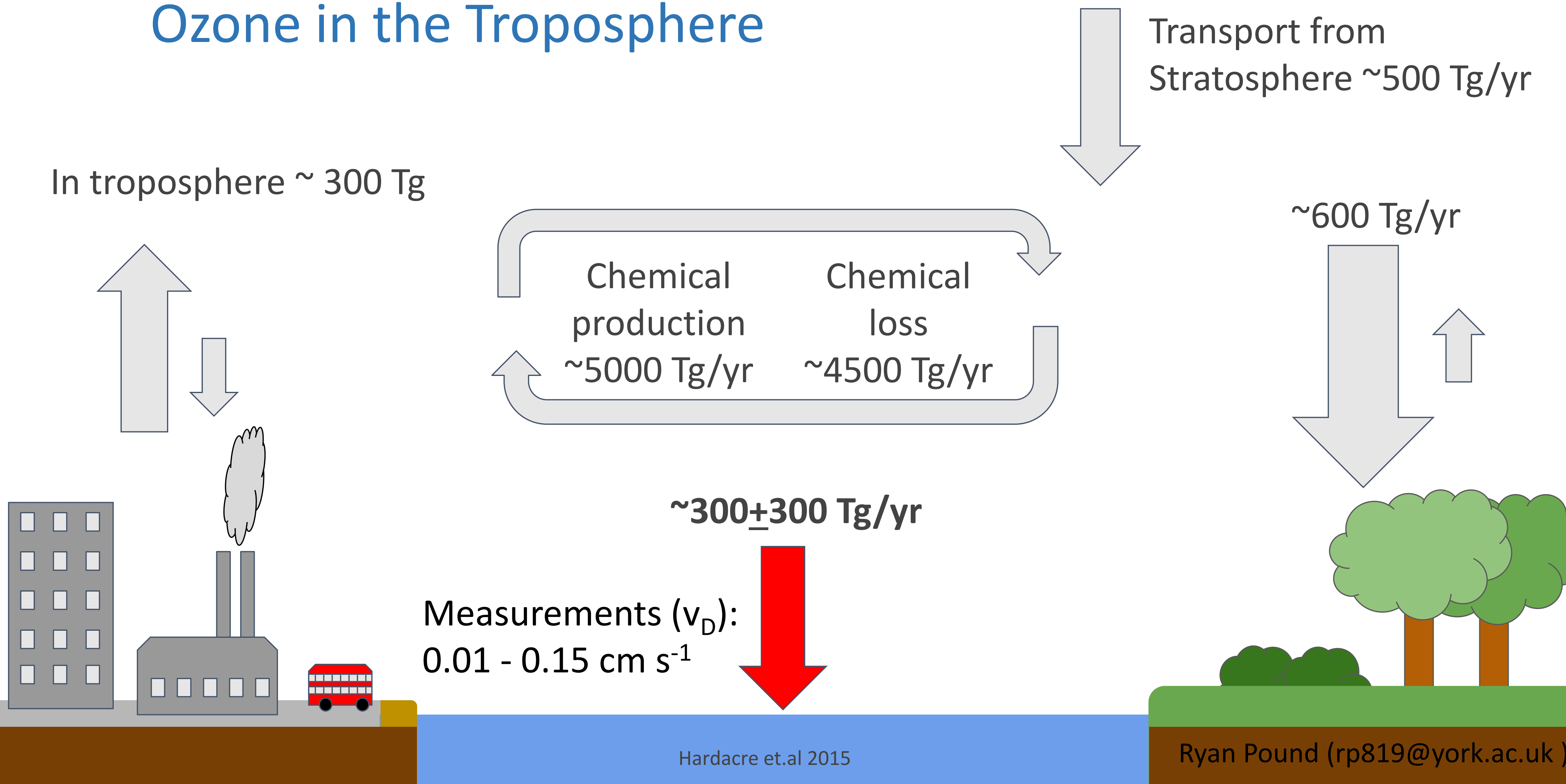


Ozone Deposition

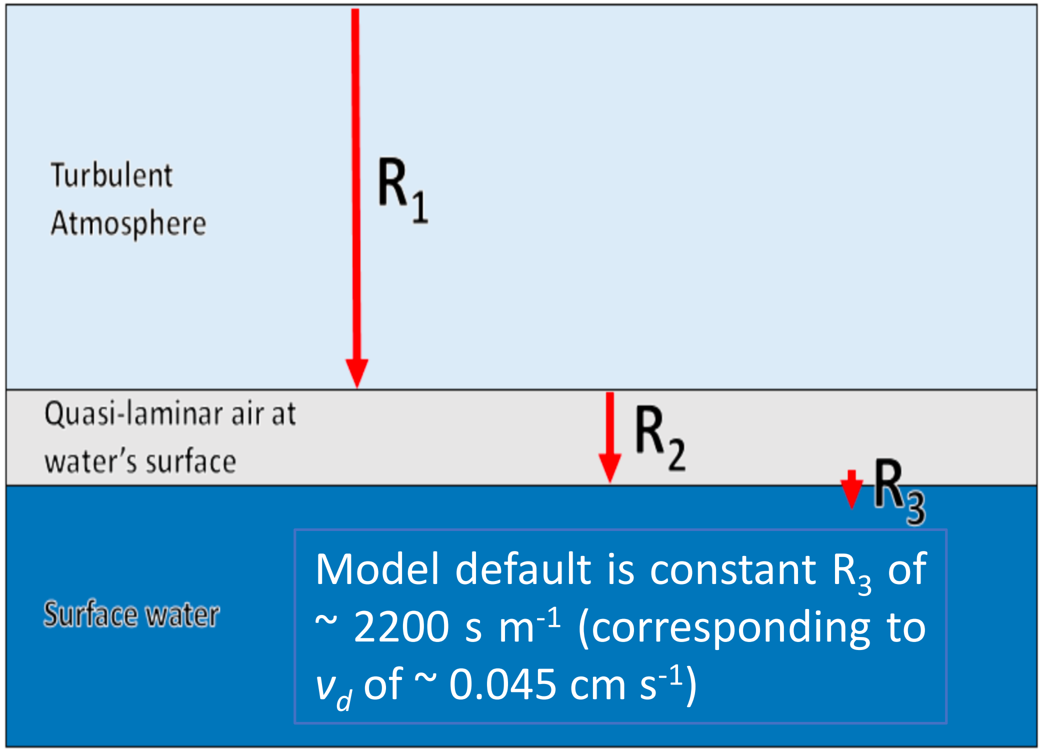


Ozone in the Troposphere

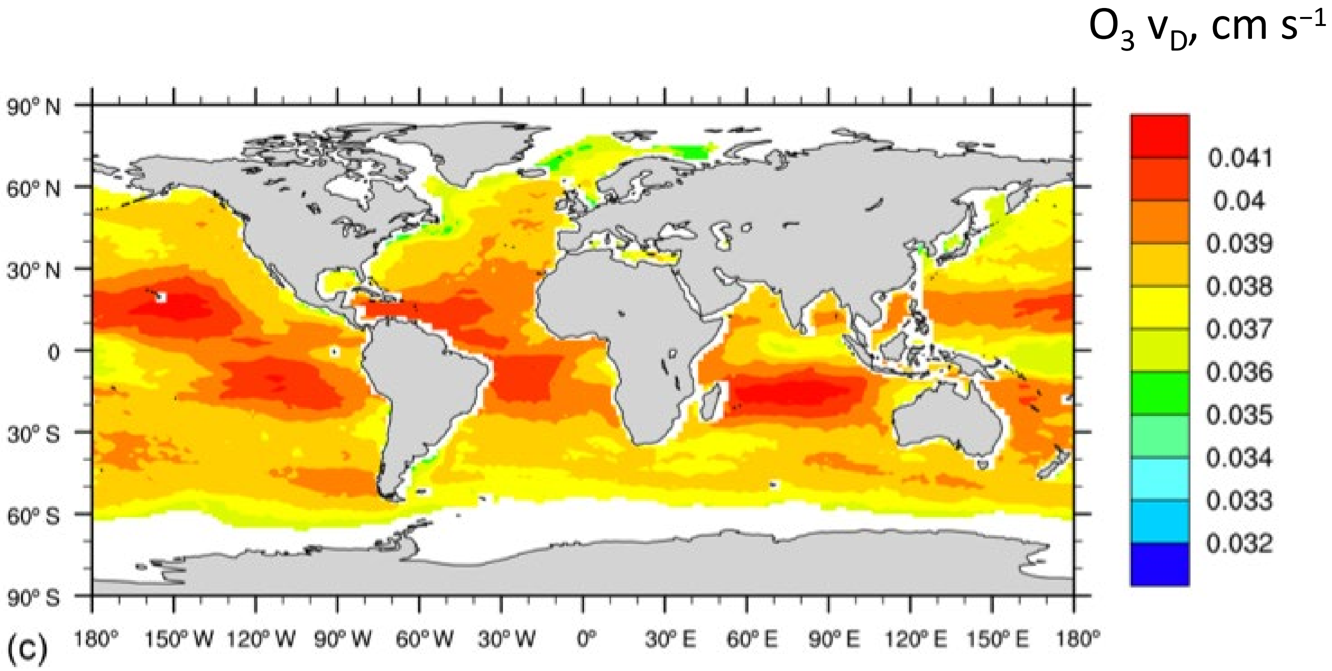


Calculating O_3 oceanic v_D – conventional approach

$$v_d = (R_1 + R_2 + R_3)^{-1}$$



Default model scheme with surface resistance = 2200 s m^{-1}



Luhar et al. 2017

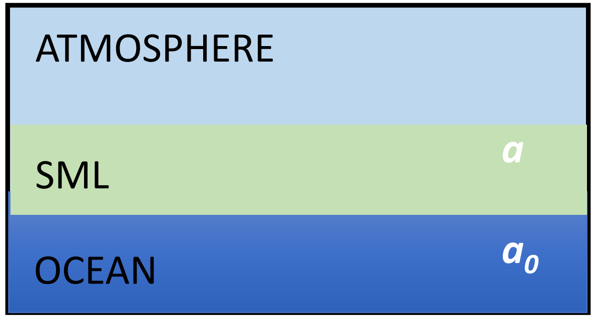
Calculating O_3 oceanic v_D – state of the art

Two layer model,
reaction and turbulence:

$$v_{dw} = \left((a + a_0)D\right)^{1/2}\left[\frac{-A_1 I_1(\xi_0) + B_1 K_1(\xi_0)}{A_1 I_0(\xi_0) + B_1 K_0(\xi_0)}\right]$$

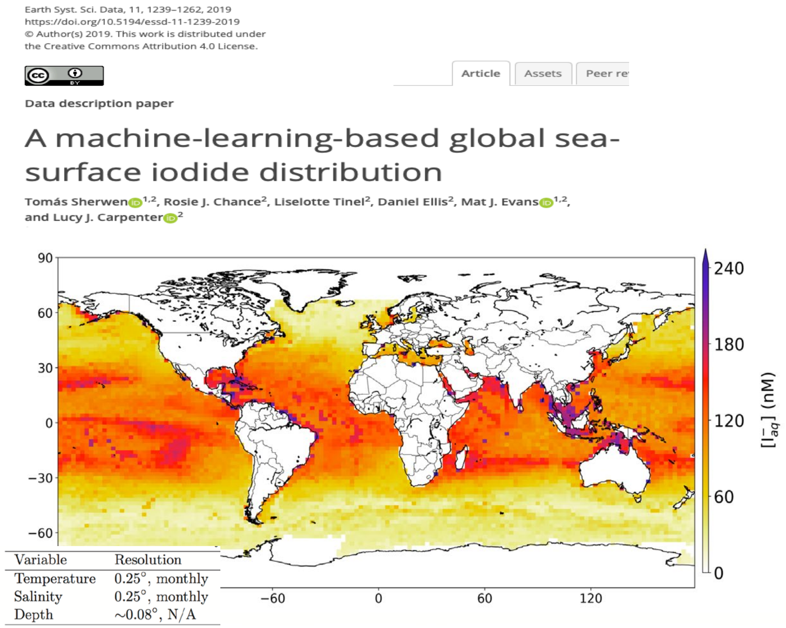
$$a = \Sigma\ (k_1[I^-] + k_2[X] + ...)$$

Fairall et al., 2007; Luhar et al., 2017, 2018; Pound et al. 2020



1-layer model

2-layer model


Earth Syst. Sci. Data, 11, 1239–1262, 2019
https://doi.org/10.5194/essd-11-1239-2019

Article Assets Peer re

Data description paper

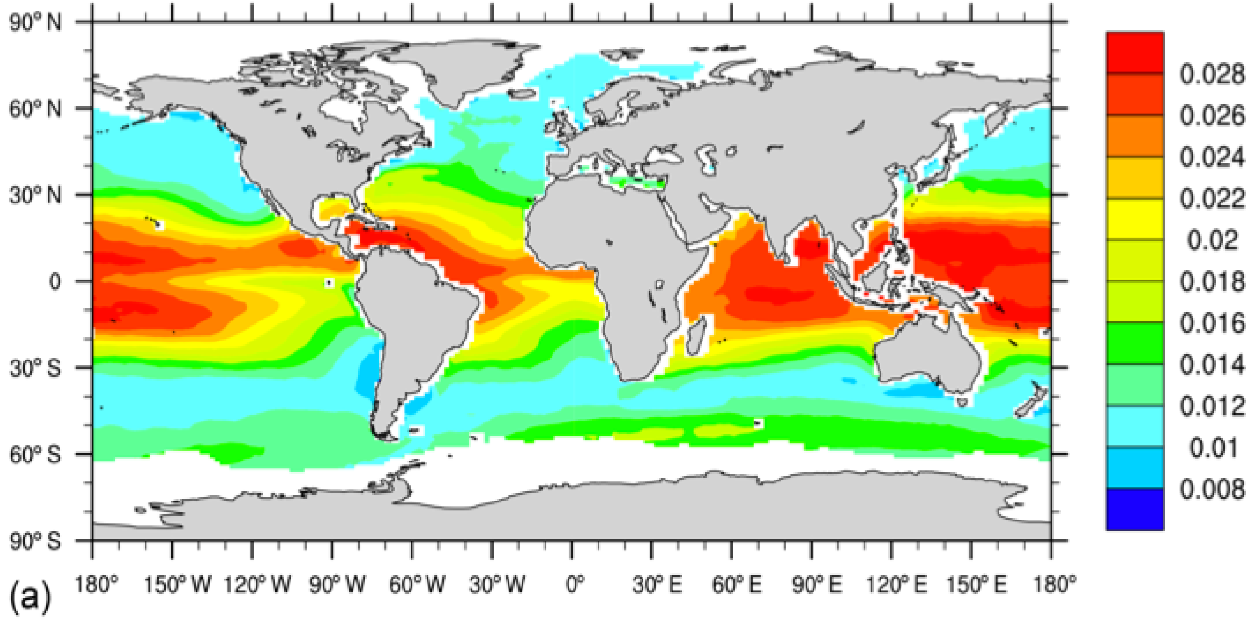
A machine-learning-based global sea-surface iodide distribution

Tomás Sherwen[1,2], Rosie J. Chance[2], Liselotte Tinel[2], Daniel Ellis[2], Mat J. Evans[1,2], and Lucy J. Carpenter[2]

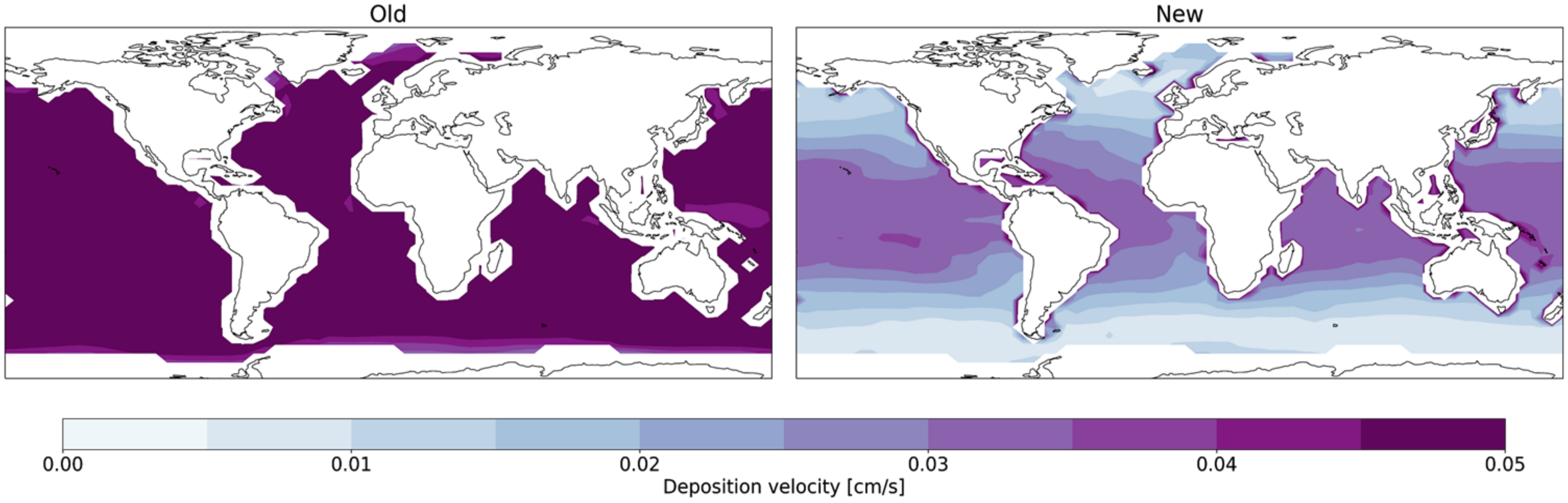
Variable	Resolution
Temperature	0.25°, monthly
Salinity	0.25°, monthly
Depth	~0.08°, N/A

***a* = k[I⁻]**

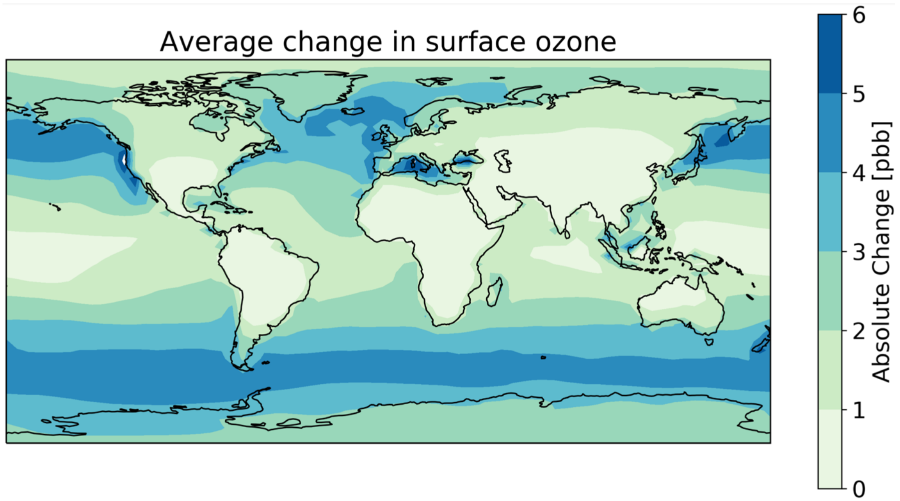
O_3 v_D, cm s^{-1}



Impact of new oceanic deposition velocity scheme

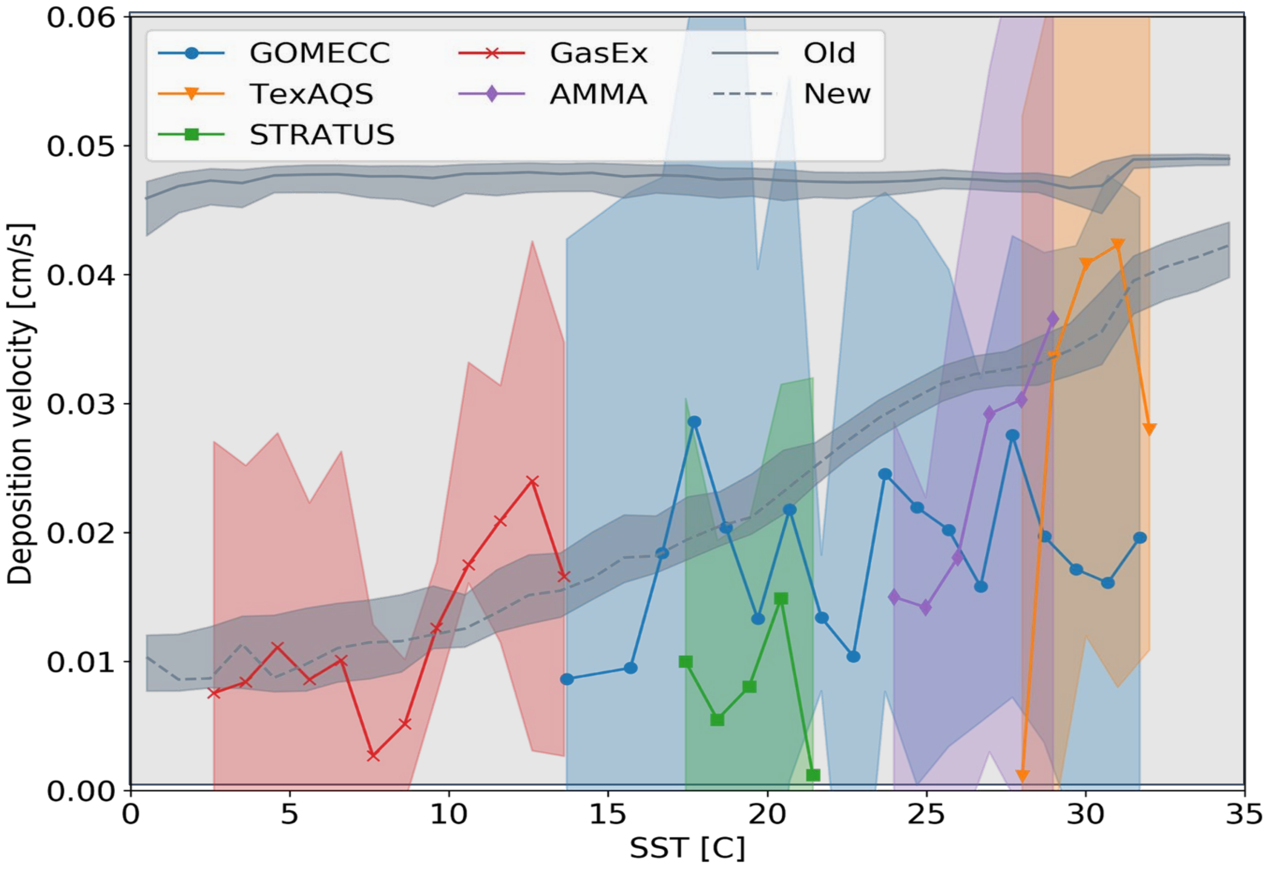


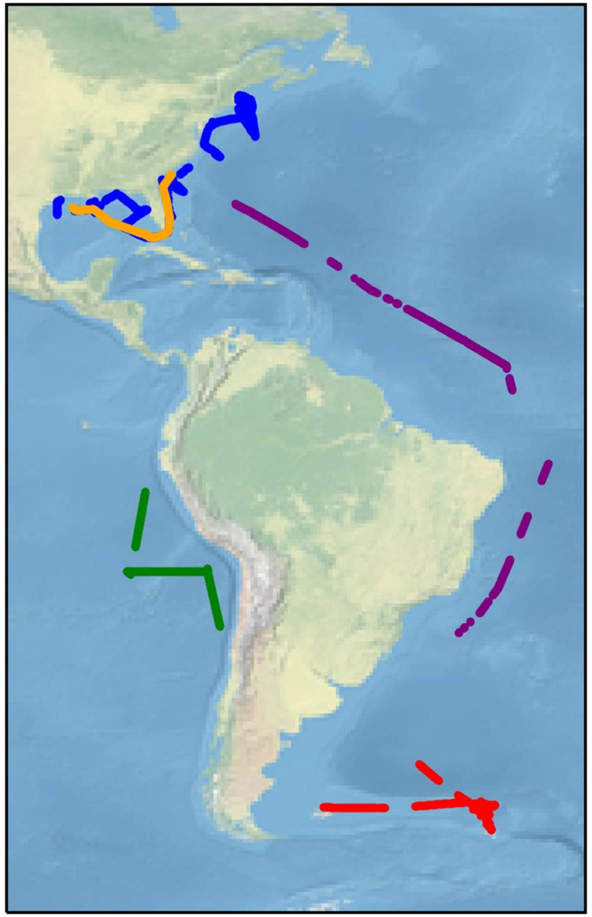
New-old:



R. Pound et al., *Atmos. Chem. Phys.*, 2020

Comparison with observations





Helmig et.al 2012

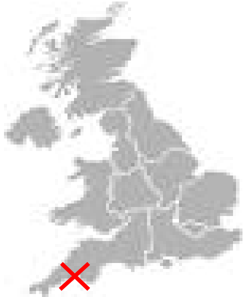
R. Pound et al., *Atmos. Chem. Phys.*, 2020

Ryan Pound (rp819@york.ac.uk)

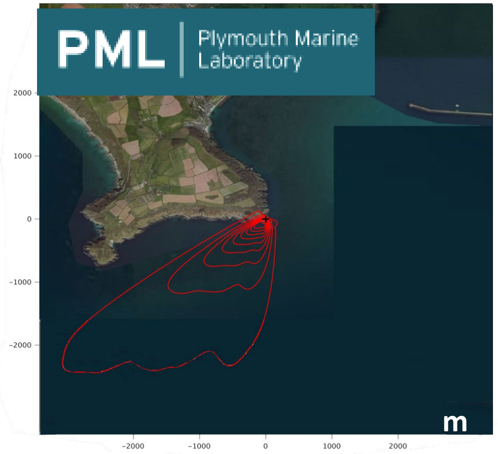
Open questions regarding “new” O_3 deposition models:

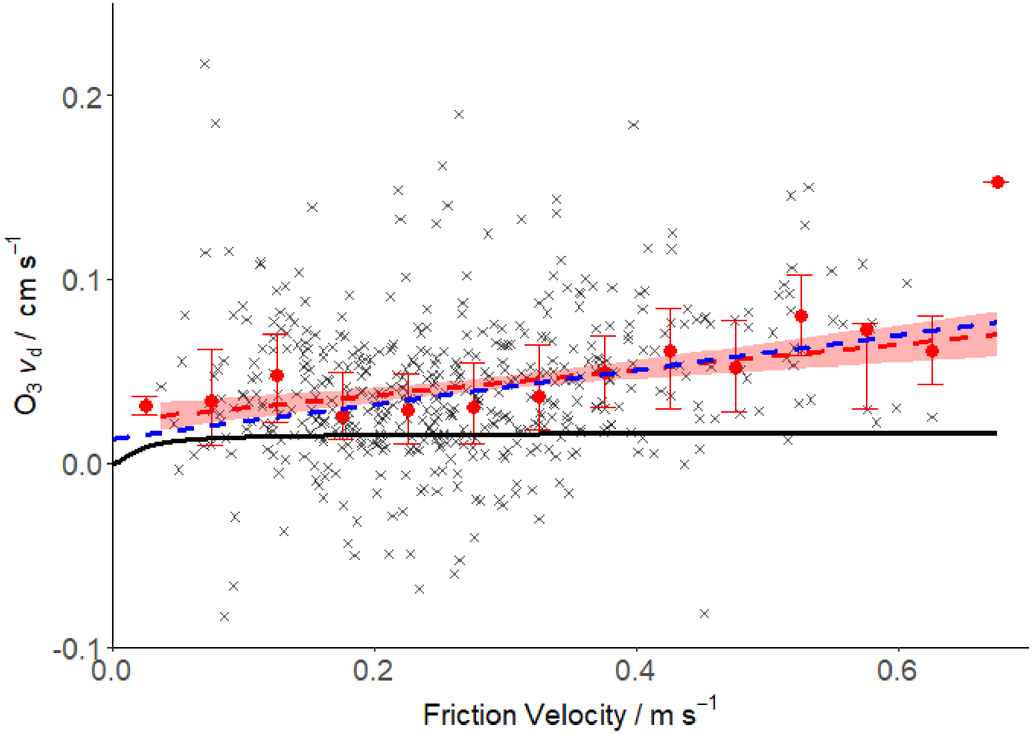
(1) Wind speed/friction velocity dependence of O_3 v_D

Ozone flux via chemiluminescence-eddy covariance



PPAO- Penlee Point





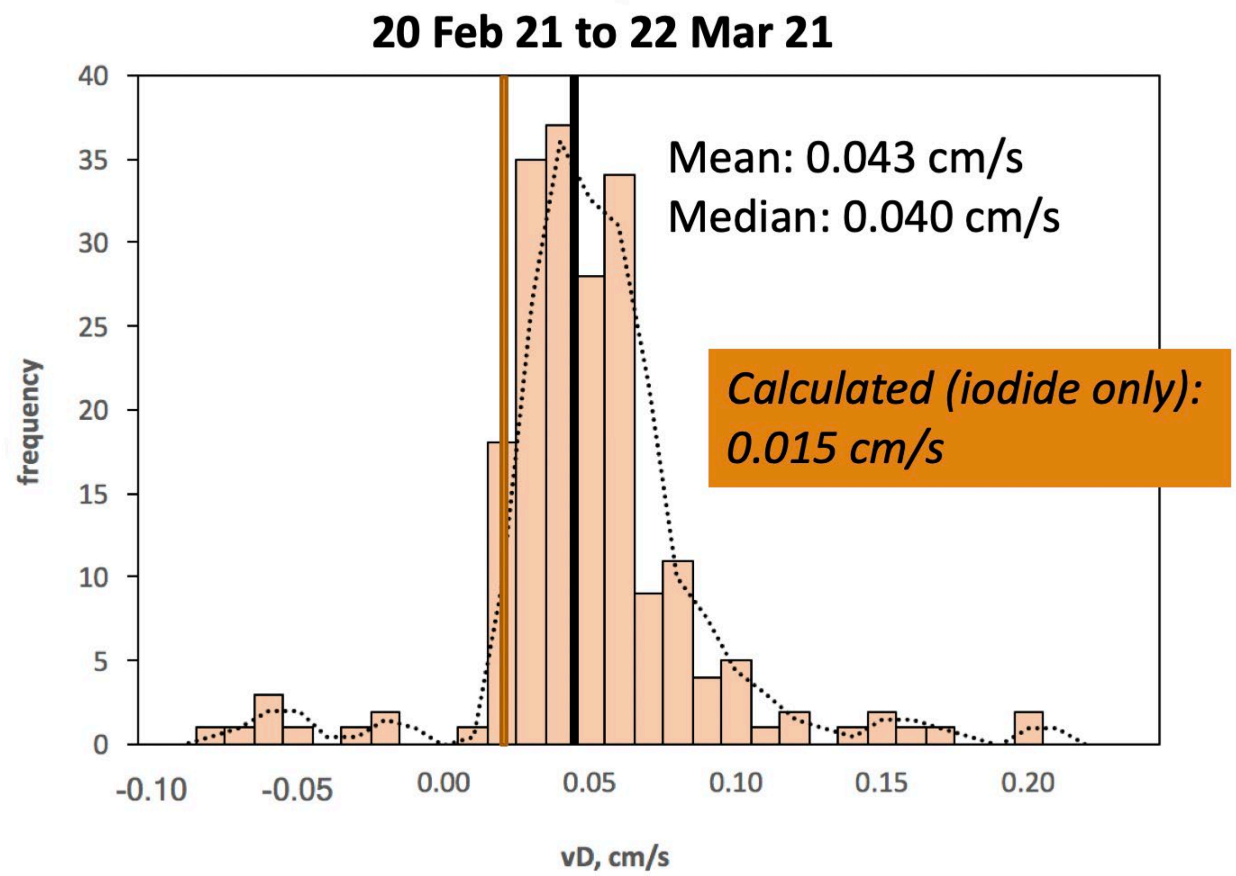
- Observed bin-averaged median v_D with interquartile ranges
- Fairall et al. (2007) one layer model
- Luhar et al. (2018) two layer model

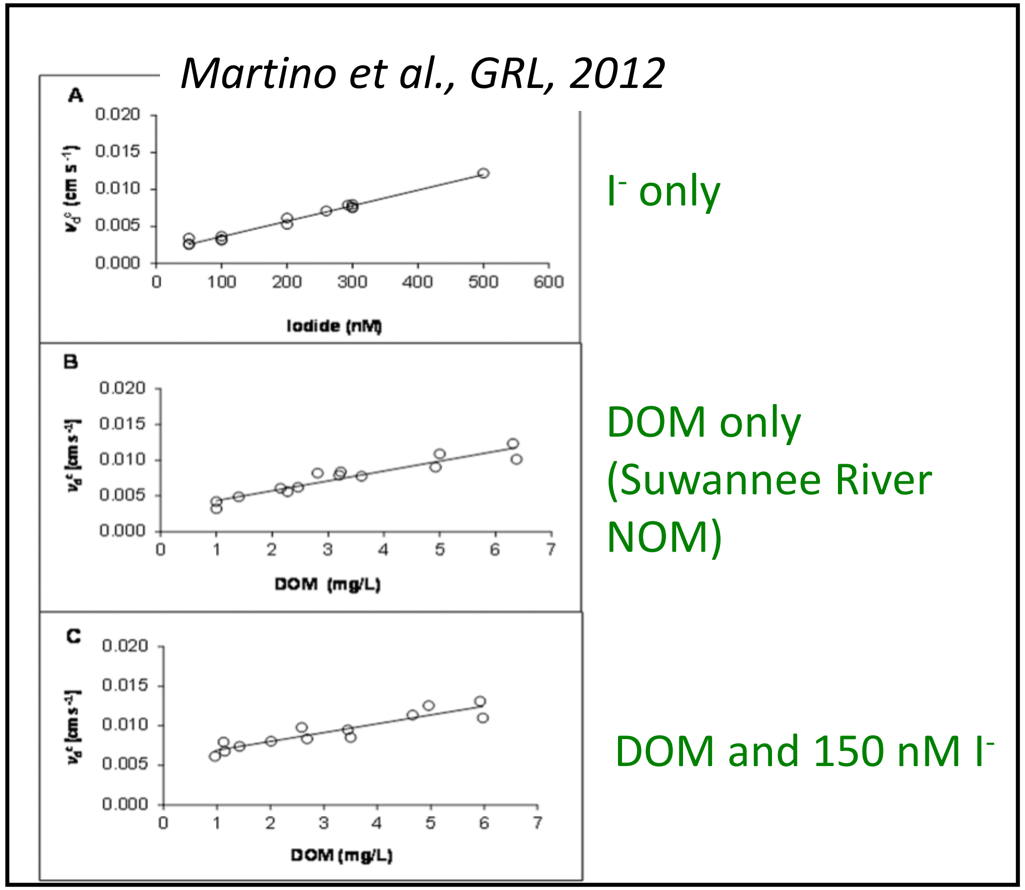
Loades et al. *AMT* 2020

Is it more appropriate to use 1- or 2- layer model?

(2) Organic reactivity in the SML?

Results from Penlee Point (PPAO)

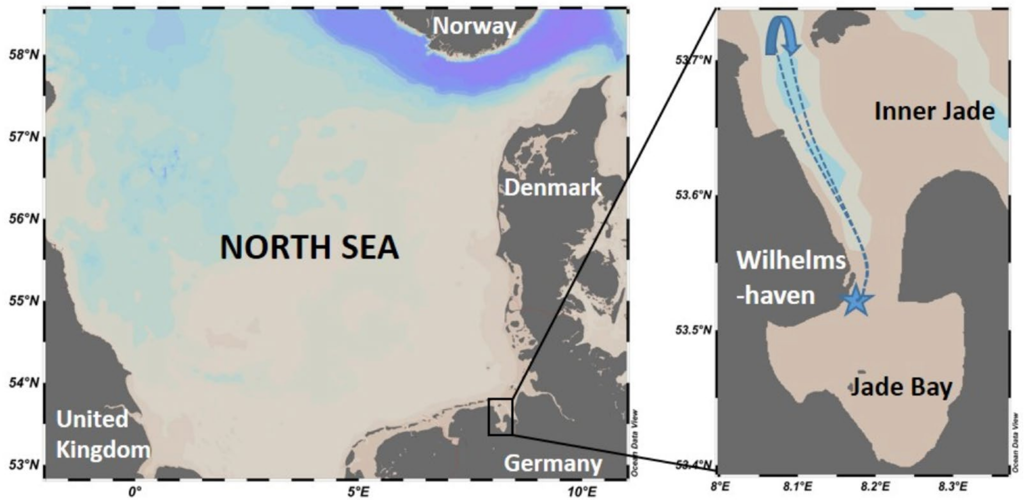


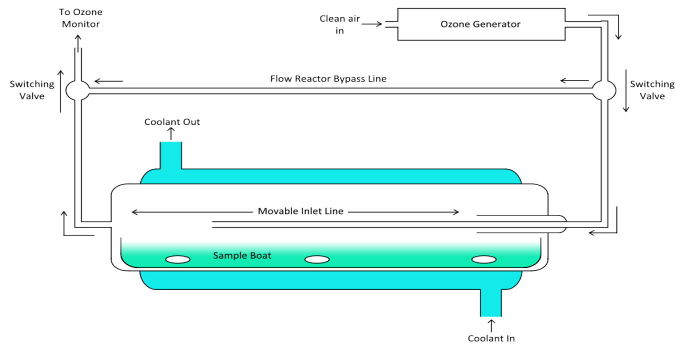


- Equates to similar reactivity for I^- and DOM

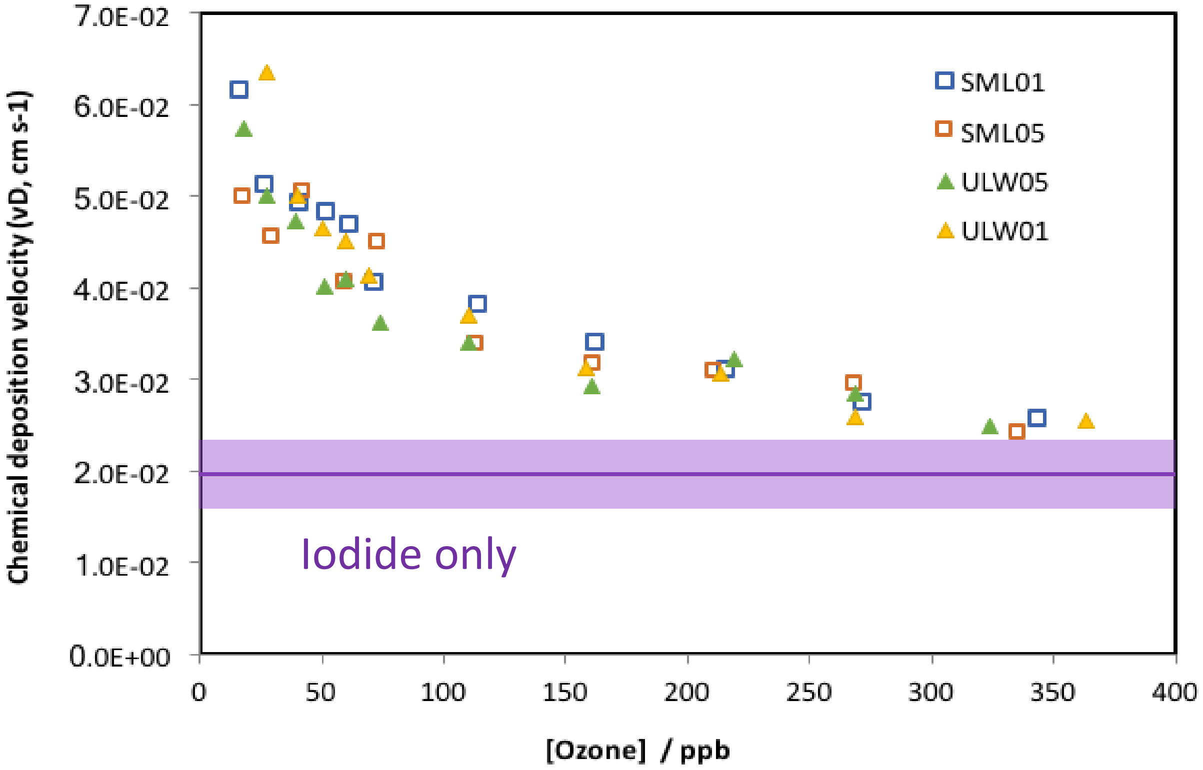
(2) Organic reactivity in the SML?

MILAN: Sea-surface MIcroLAyer functioning during the Night





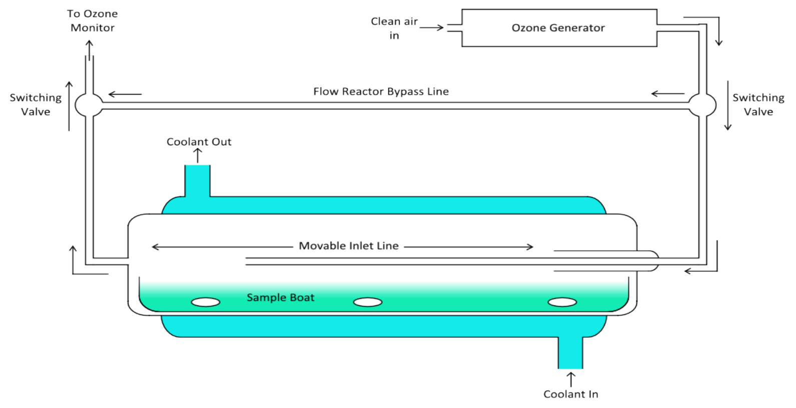
- M. Ribas-Ribas, N. I. Hamizah Mustaffa, J. Rahlff, C. Stolle and O. Wurl, *J. Atmos. Ocean. Technol.*, 2017, **34**, 1433–1448

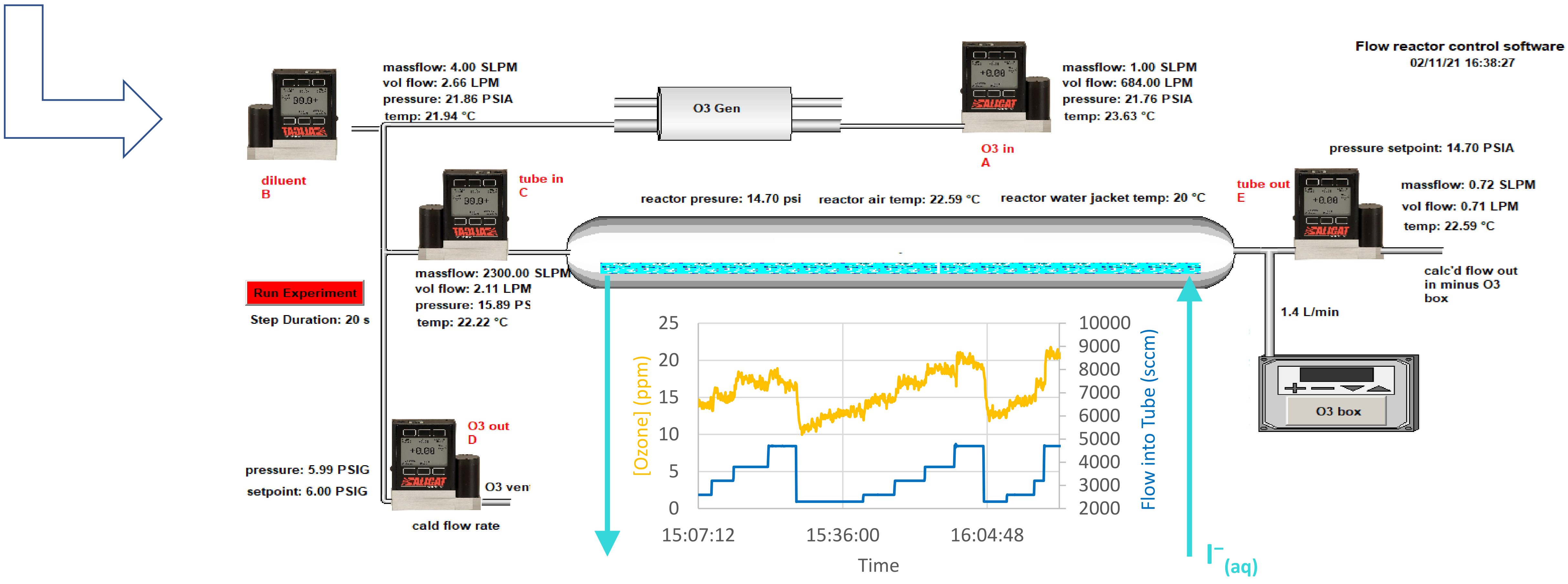


- [iodide] contributes 10-80% of chemical deposition velocity in the coastal sea

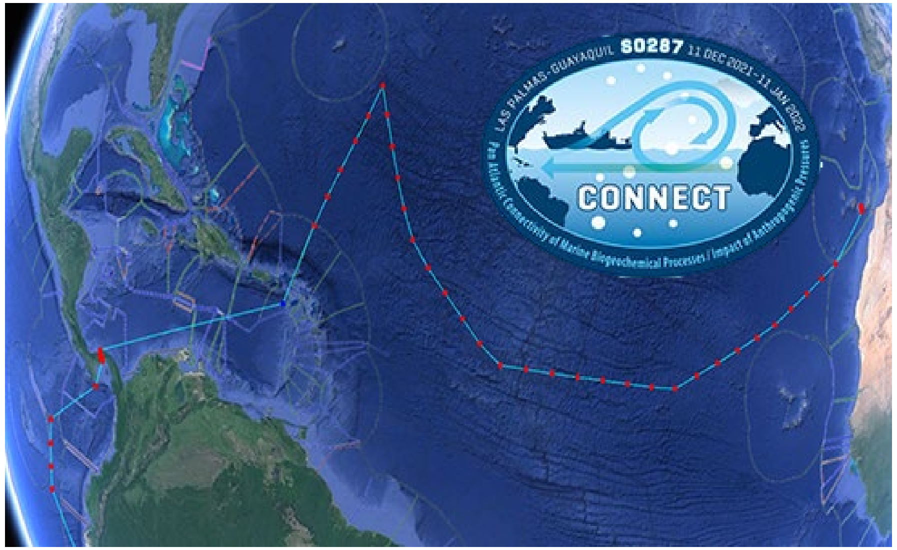
How should the contribution of organics be parameterized?

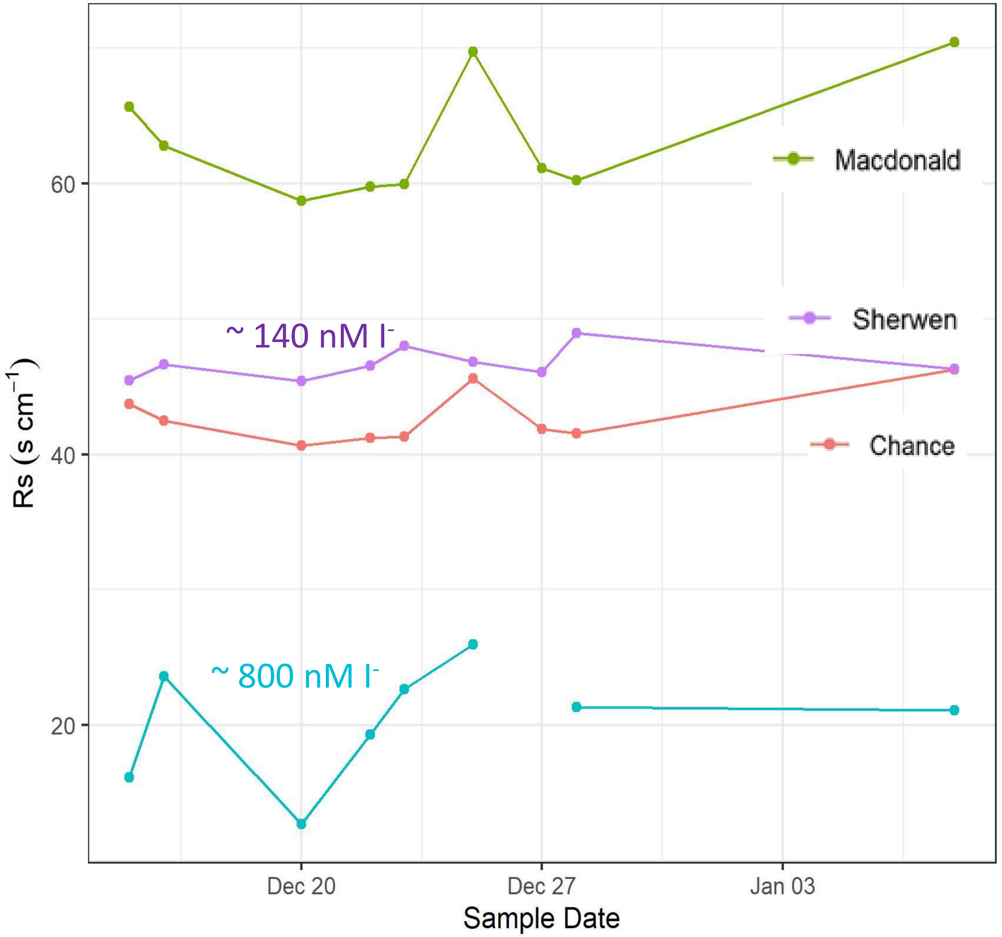
Variable flow reactor





(2) Evidence for organic reactivity (**open ocean, SML**)



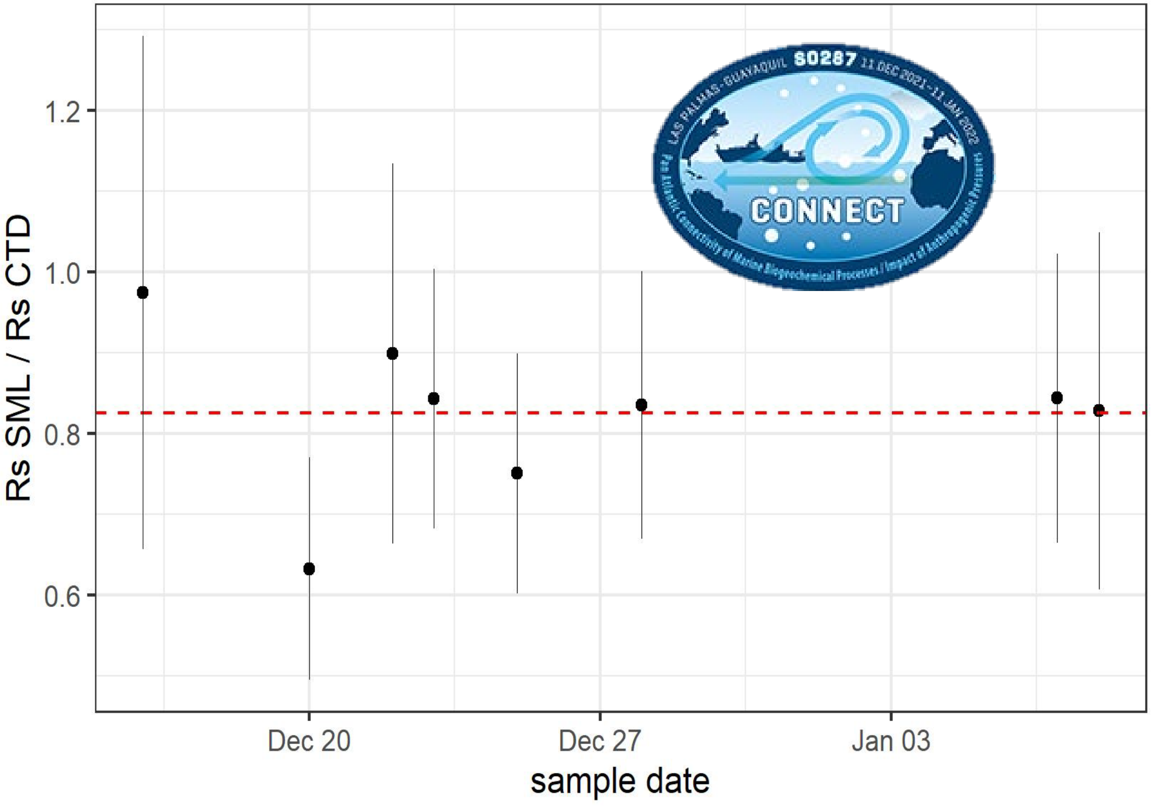


Calculated resistance using different climatologies for iodide

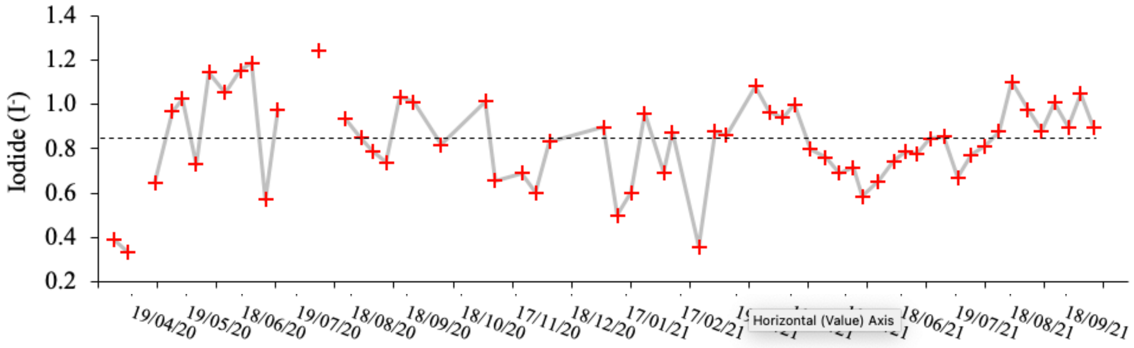
Measured resistance

$$\text{surface resistance } (R_s) = \frac{H}{\sqrt{k_i[I^-]D}}$$

(2) Enhanced reactivity in the SML (**open ocean**)



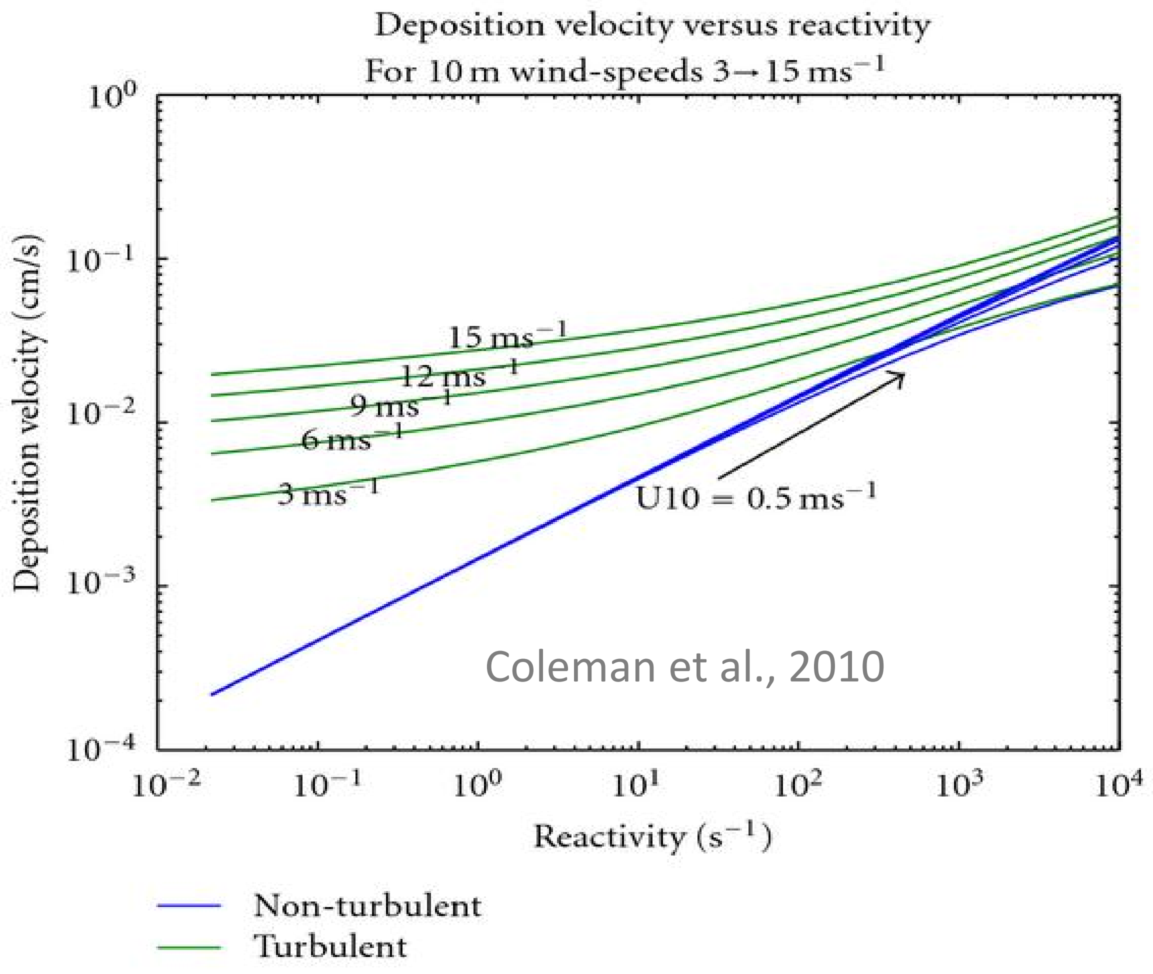
$[I^-]_{SML}$/ $[I^-]_{ULW}$ PPAO timeseries



- SML has ~20% lower surface resistance to ozone uptake compared to underlying water
- So reactivity to O_3 is at least 20% higher in the SML

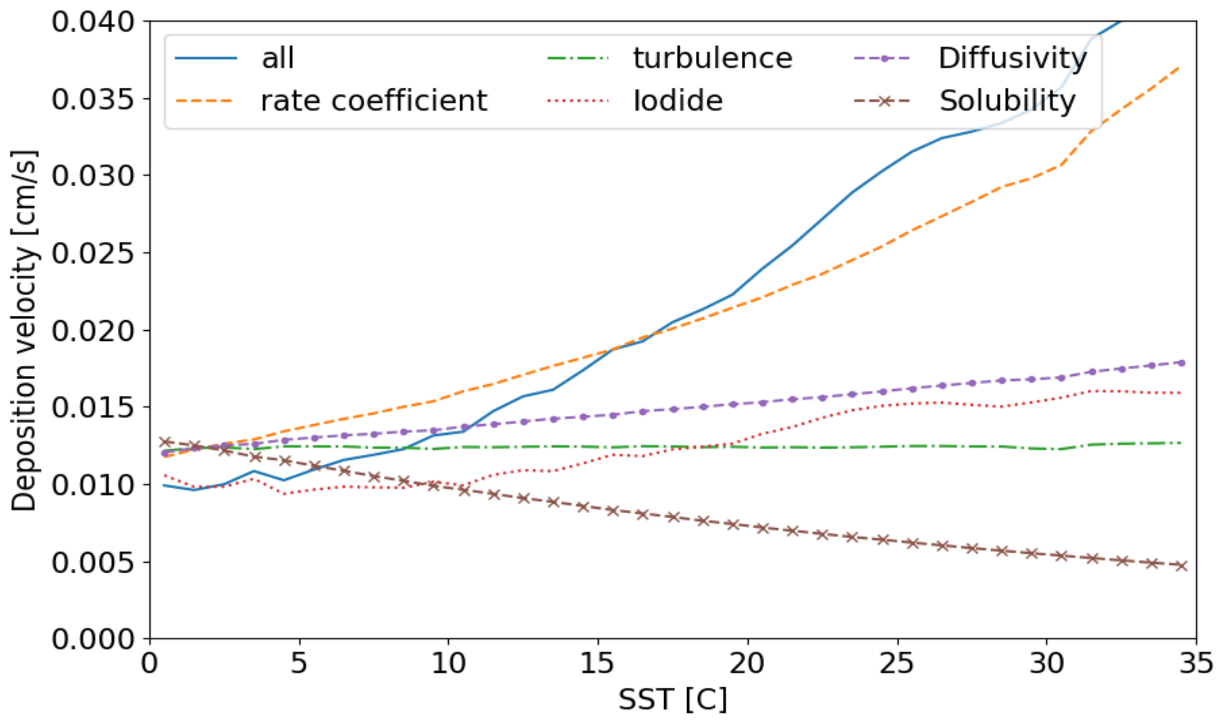
Interdependence of reactivity *a* and wind speed

$$v_{dw} = ((a + a_0)D)^{1/2} \left[\frac{-A_1 I_1(\xi_0) + B_1 K_1(\xi_0)}{A_1 I_0(\xi_0) + B_1 K_0(\xi_0)}\right]$$



We need to nail the reactivity, to understand the physical dependencies

(3) Temperature dependence of O_3 v_D



$I^-_{(aq)} + O_{3(g)} \rightarrow \rightarrow HOI_{(aq)} \rightleftharpoons I_{2(aq)}$

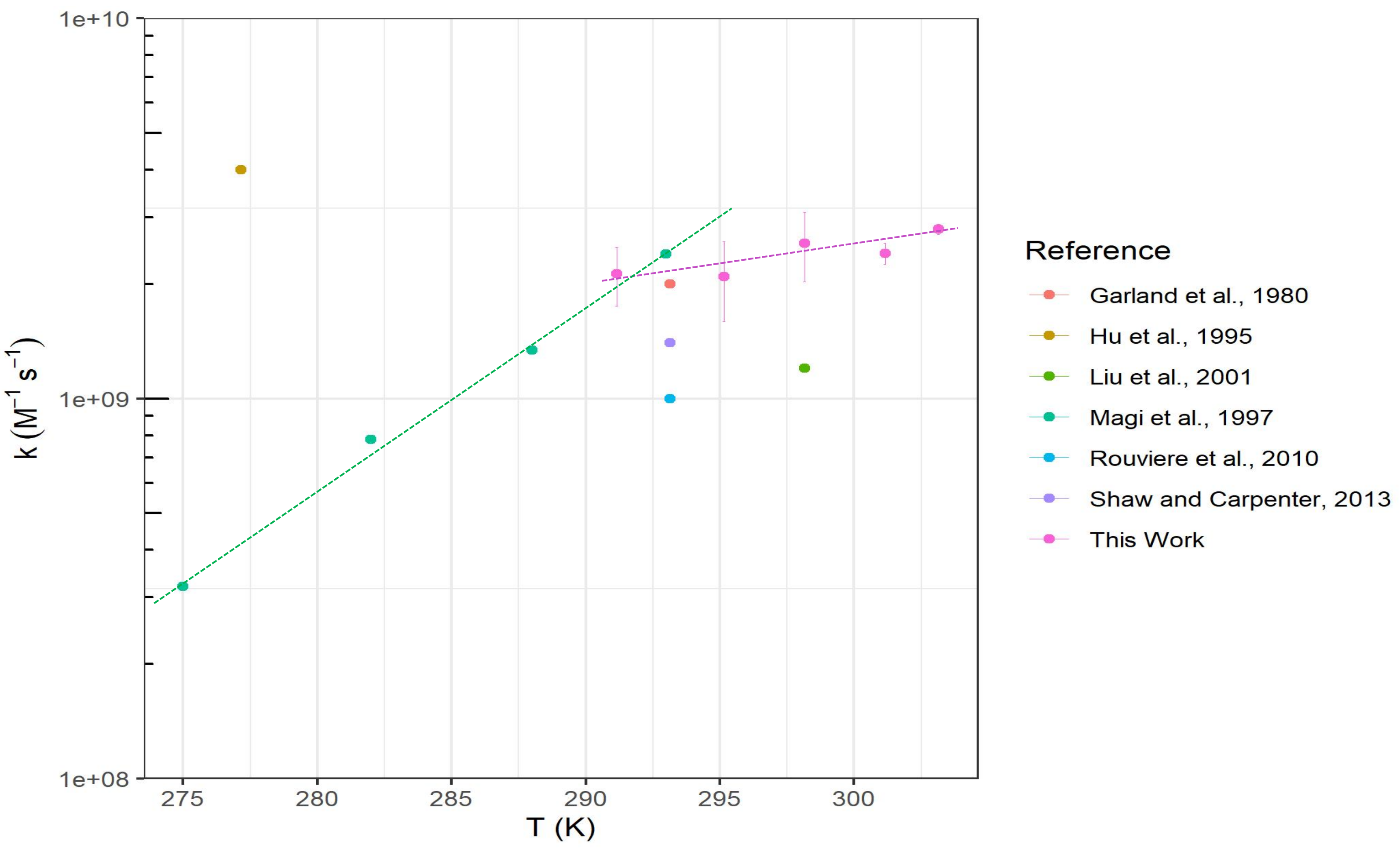
Magi et al., 1997:

$A = 1.4 \times 10^{22}\ M^{-1}\ s^{-1}$

$Ea = 73.08\ kJ\ mol^{-1}$ ($\pm$ 40%)

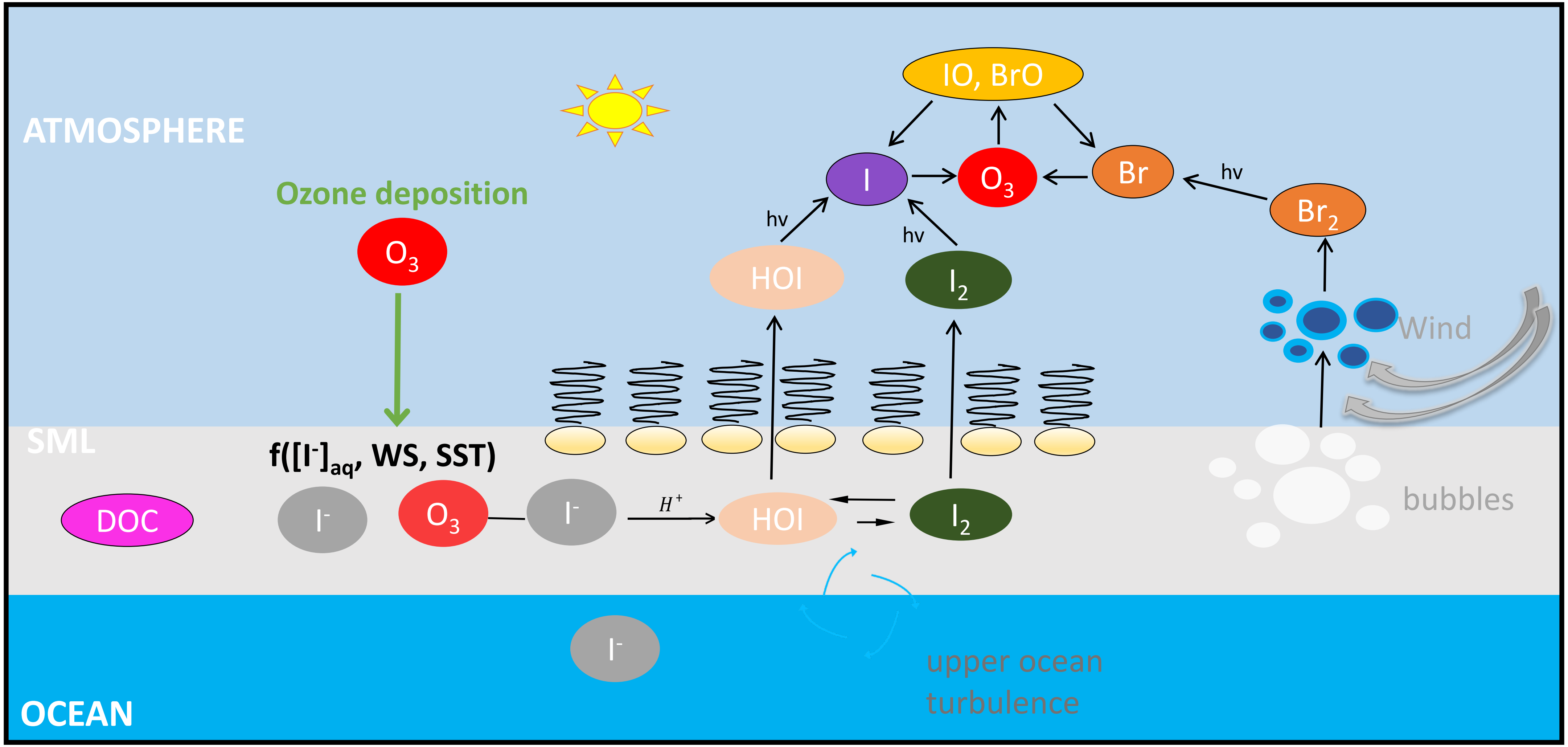
Is the temperature dependence of $k_{(I- + O3)}$ correct?

First results

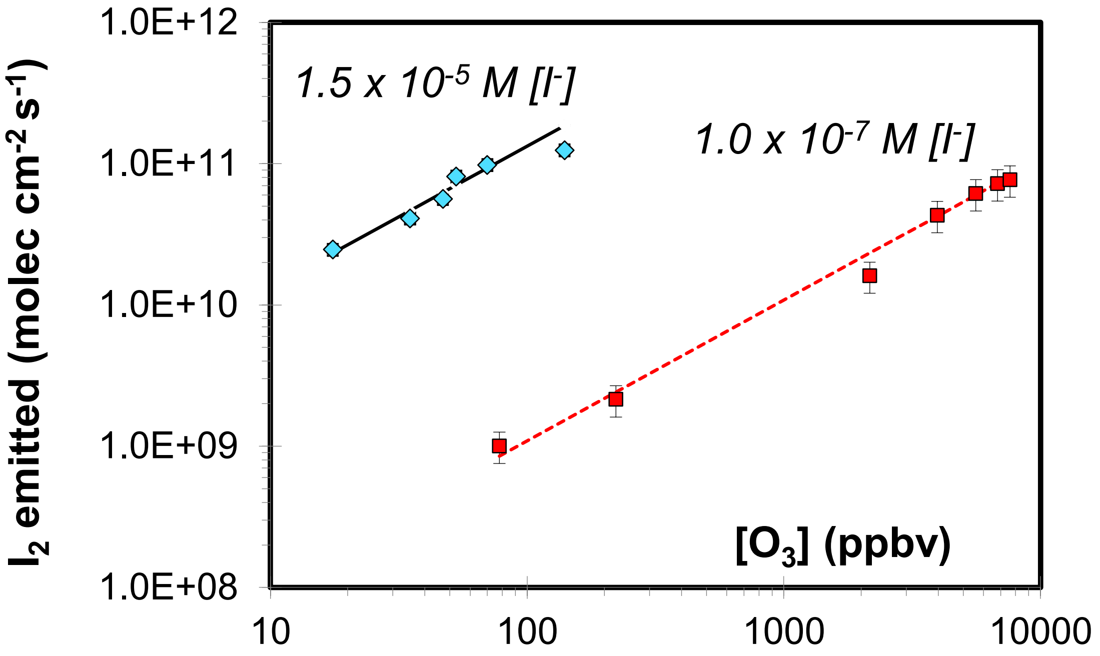


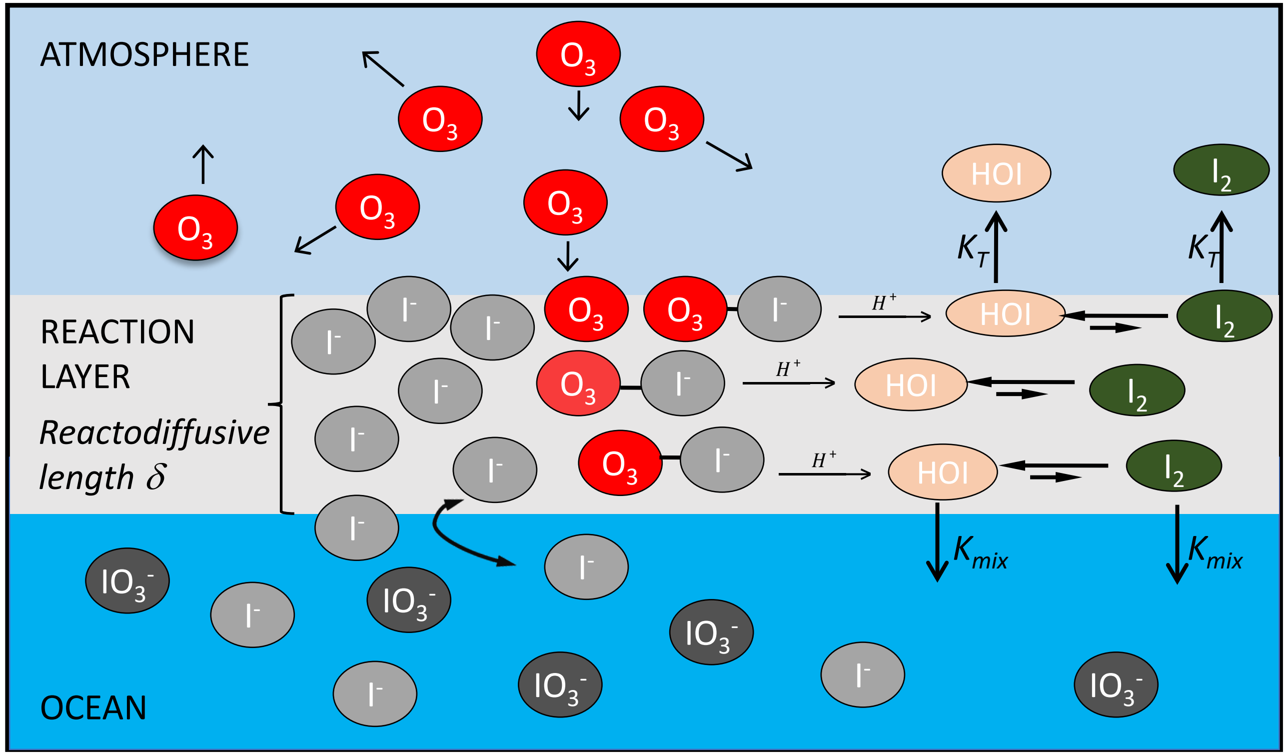
- Ozone deposition studies require re-evaluation

Ozone Deposition ⟶ Iodine emissions



Iodine sea-air emissions

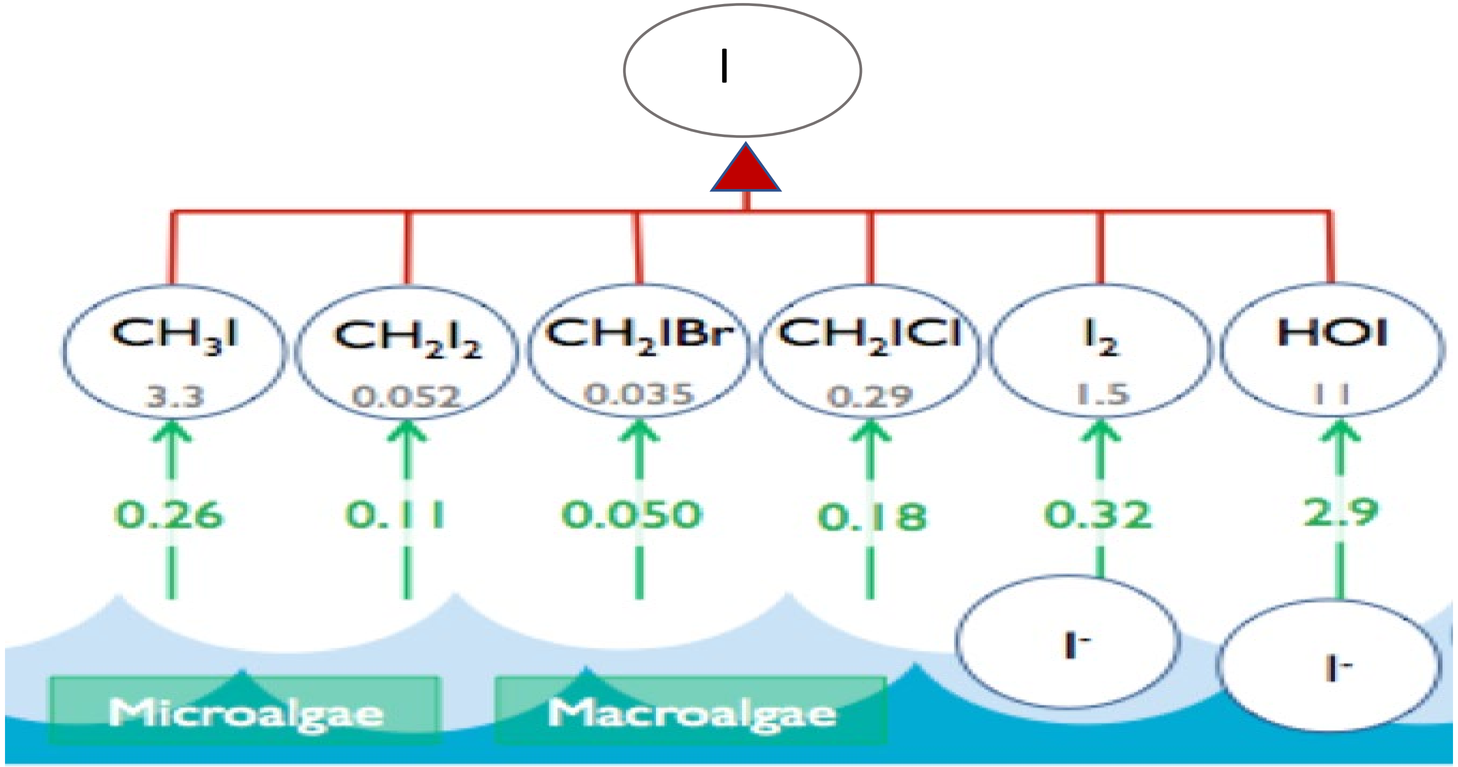




Red -IOP method
Turquoise - spectrophotometric method

Carpenter et al., Nature Geosciences, 2013

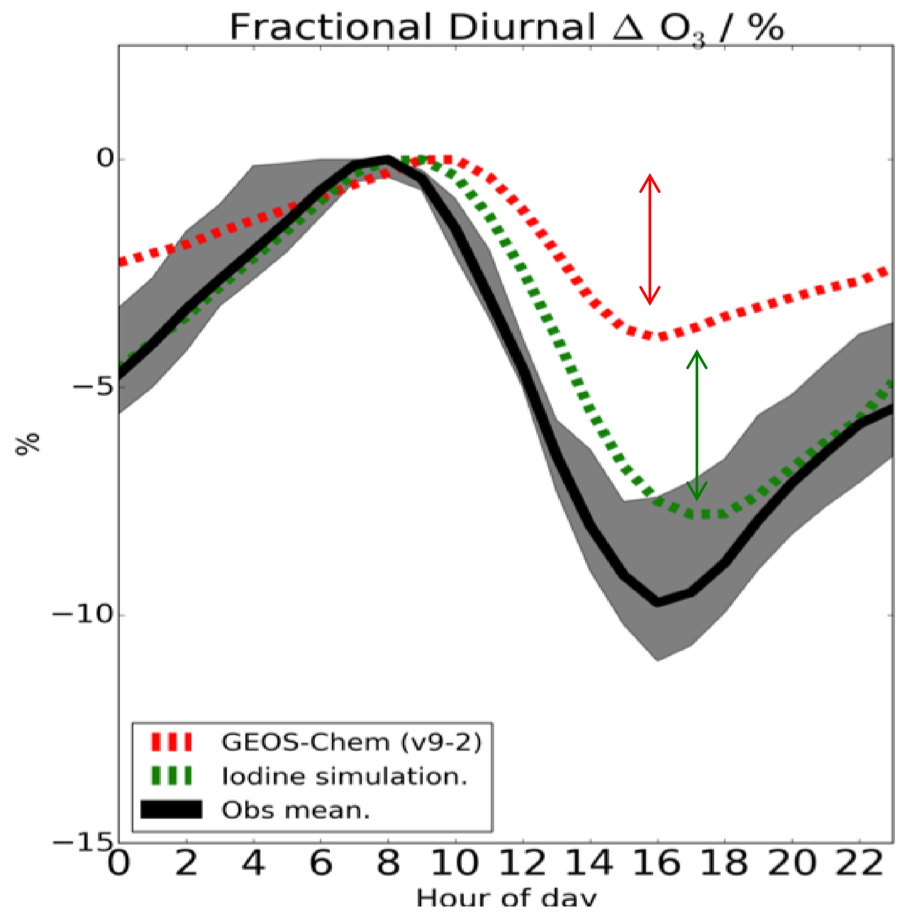
Iodine sea-air emissions



Emissions Tg/yr

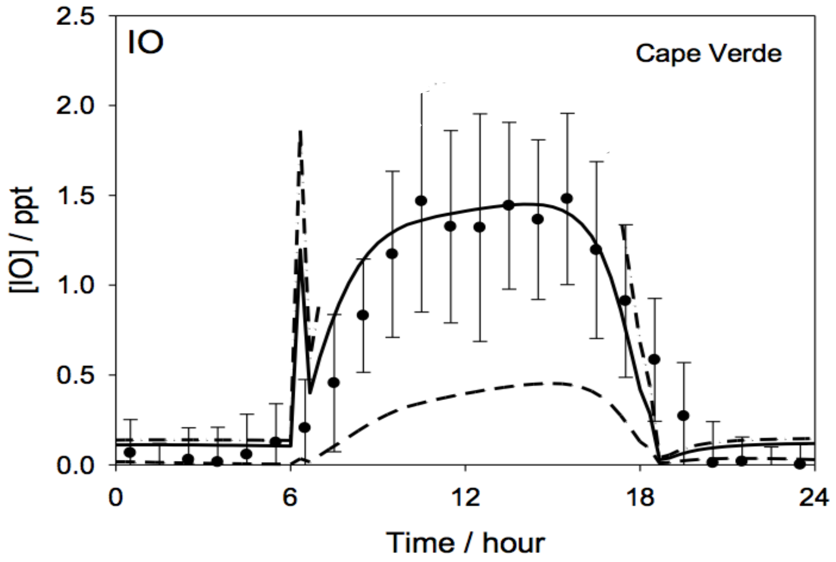
Sherwen et al., 2016, Carpenter et al. 2021

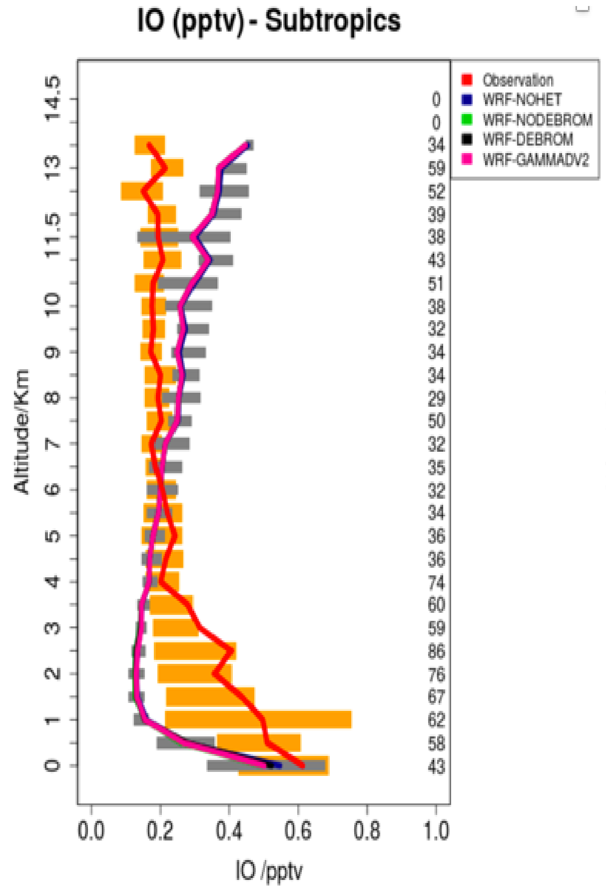
Evidence for halogen-catalysed ozone loss



Read et al., Nature, 2008
Sherwen et al. ACP, 2016, 2018

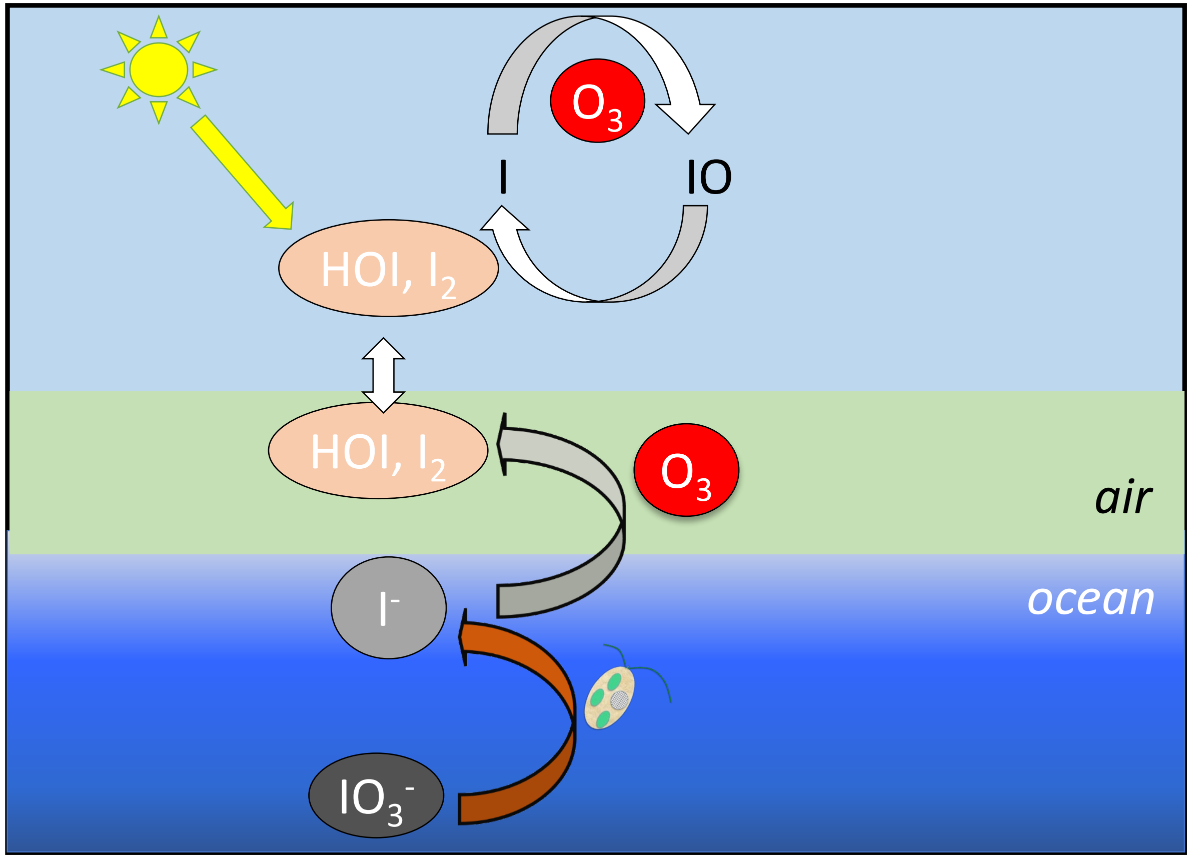
- Expected ozone change (O_3+hυ+H_2O)
- Plus IO and BrO chemistry

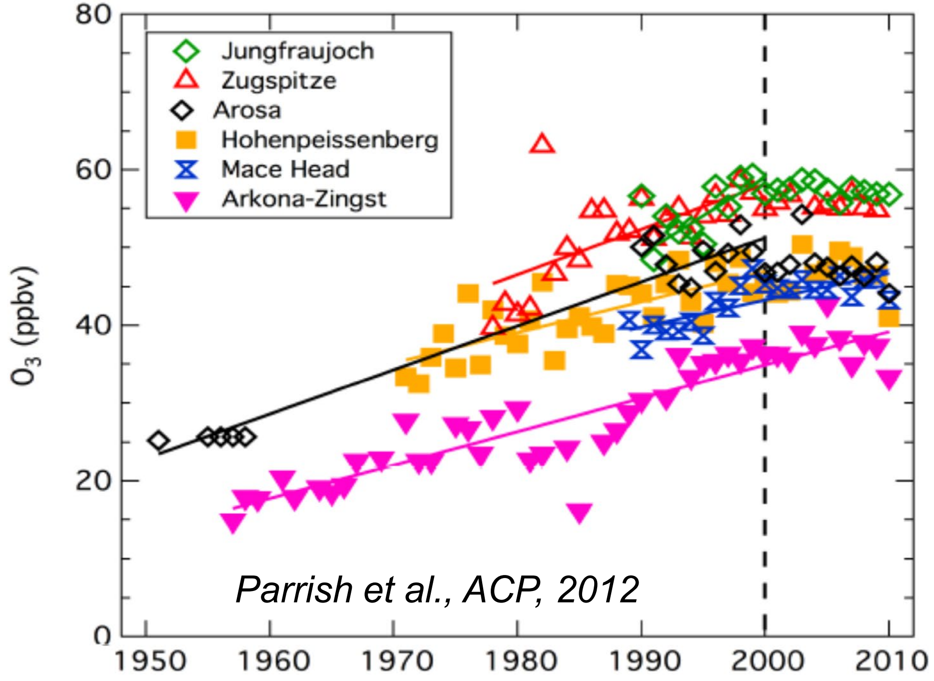


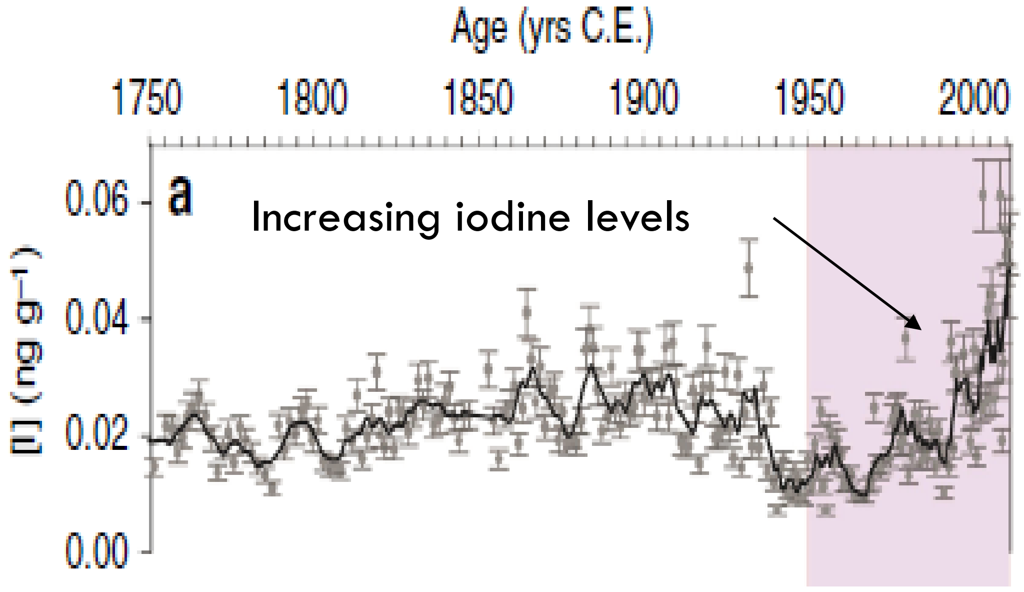


East Pacific. Badia et al., 2018

Negative feedback on O_3



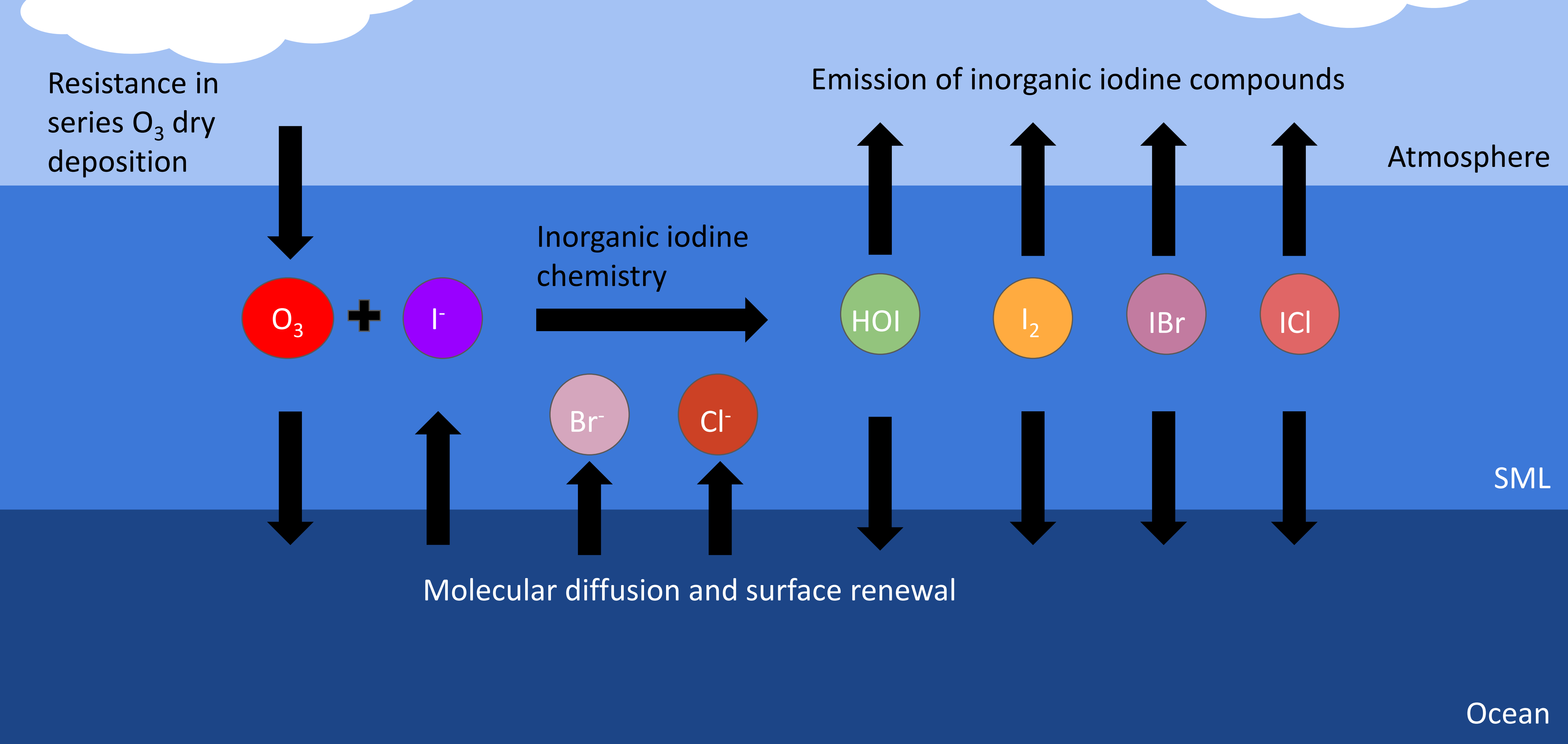




Ice core data

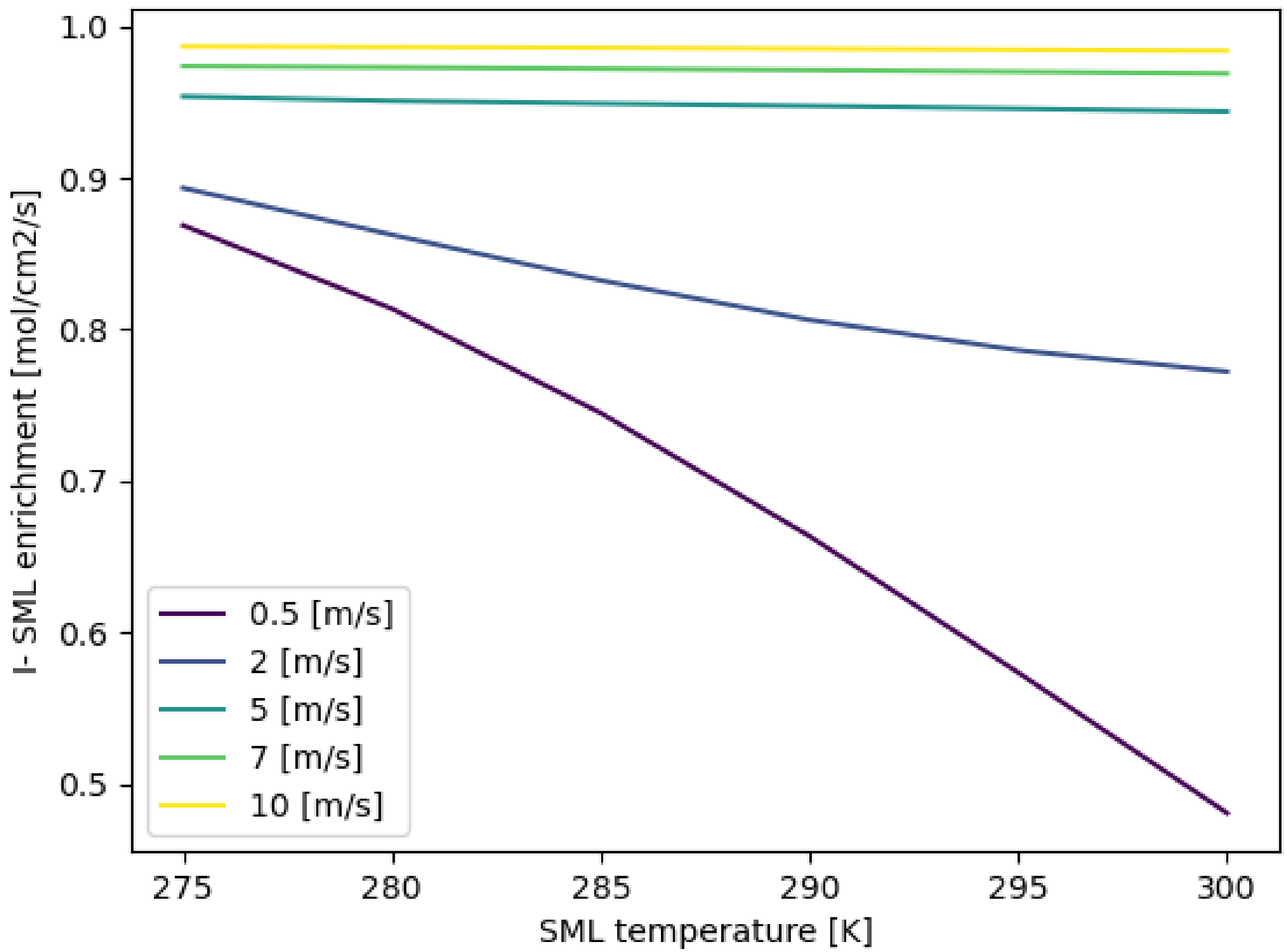
Cuevas et al., 2018; Legrand et al., 2018

Interactive O_3 deposition-iodine emission model

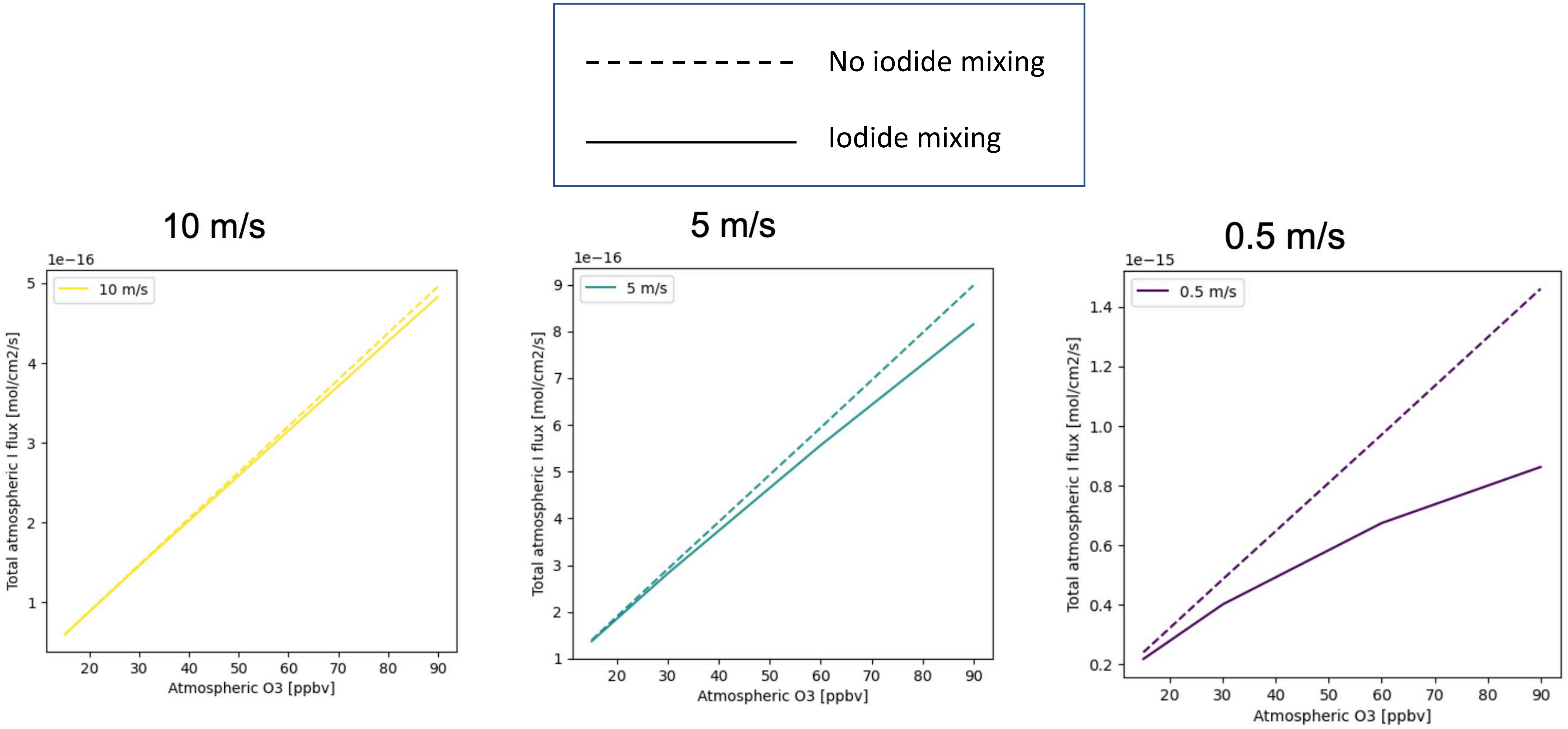


Depletion of iodide in the SML at low wind speeds

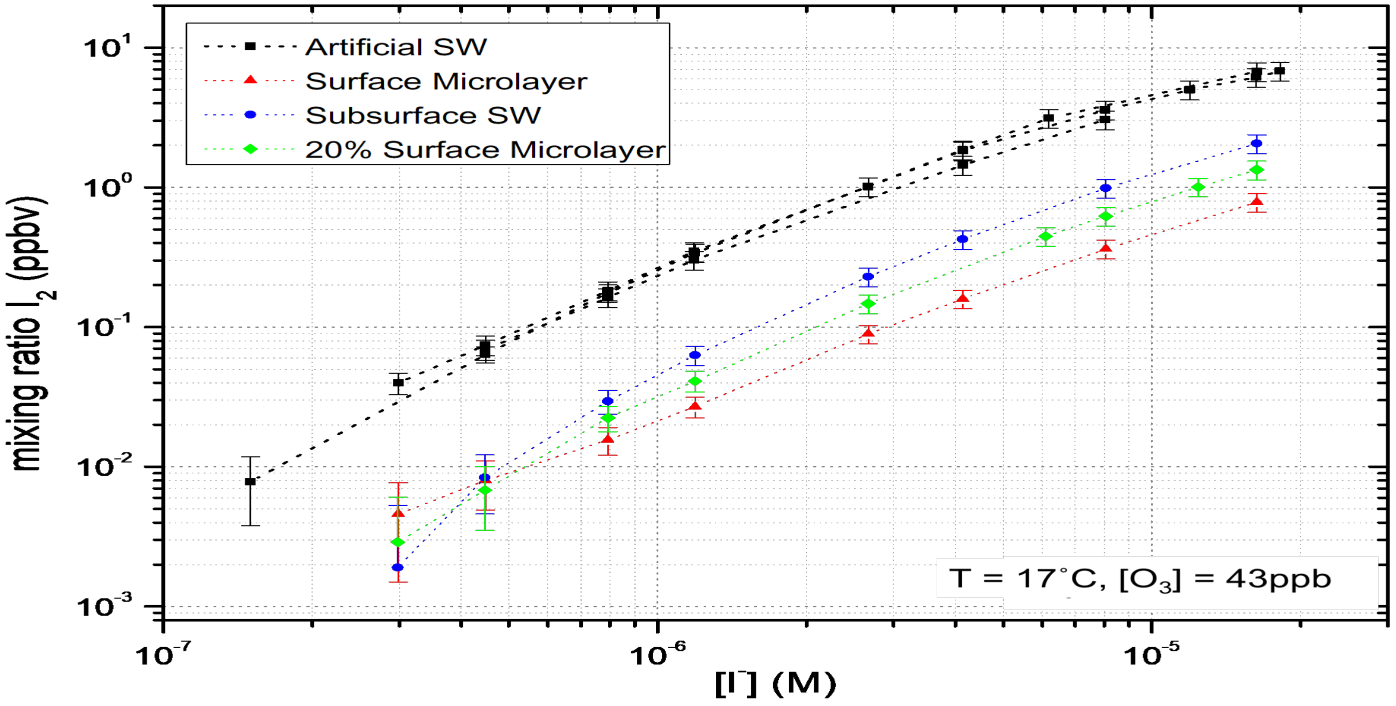
- Slower mixing of I^- at low wind speeds results in depletion of I^-
- Becomes more significant at higher temperatures due to faster O_3 + I^- rate



Impact of SML I^- depletion



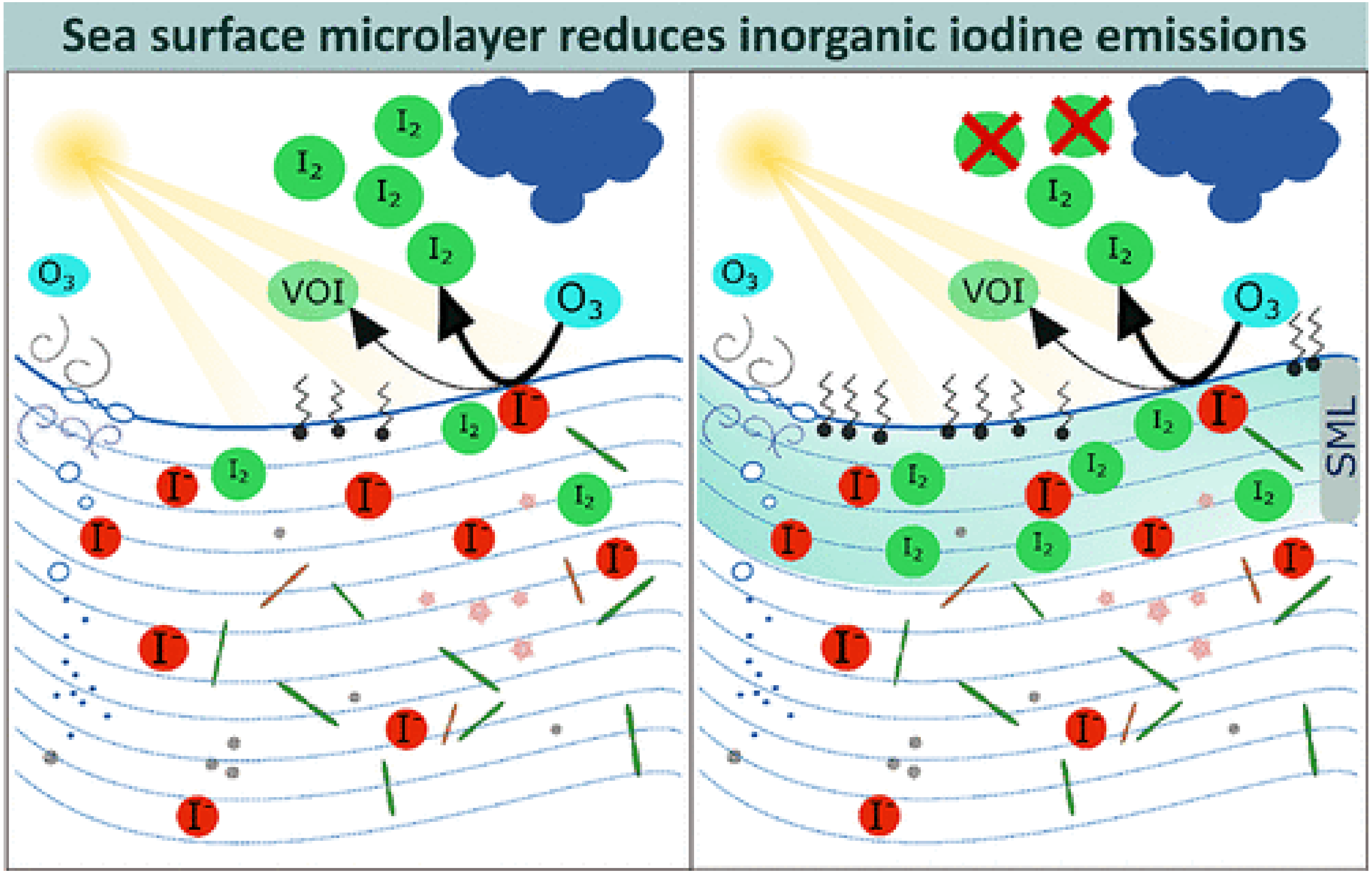
Role of organics in I_2 emission from $O_3 + I^-$



I_2 emissions from SML ≈ factor of 10 lower than from artificial seawater

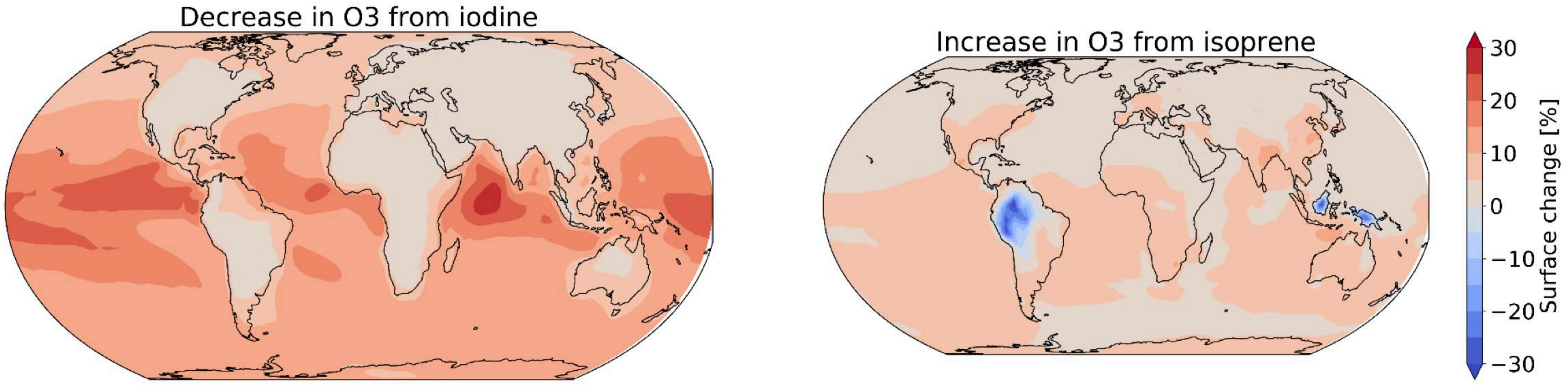
UNIVERSITY OF LEICESTER

Tinel et al. ES&T, 2020



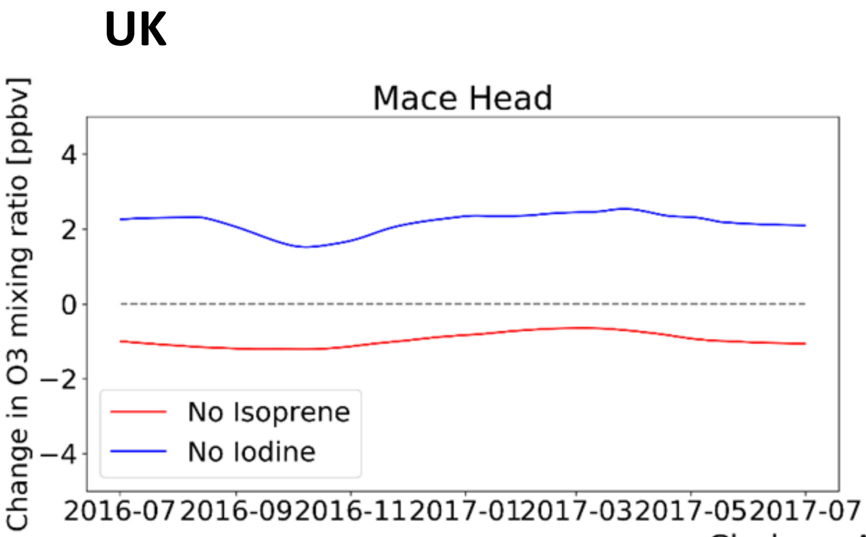
Tinel et al. ES&T, 2020

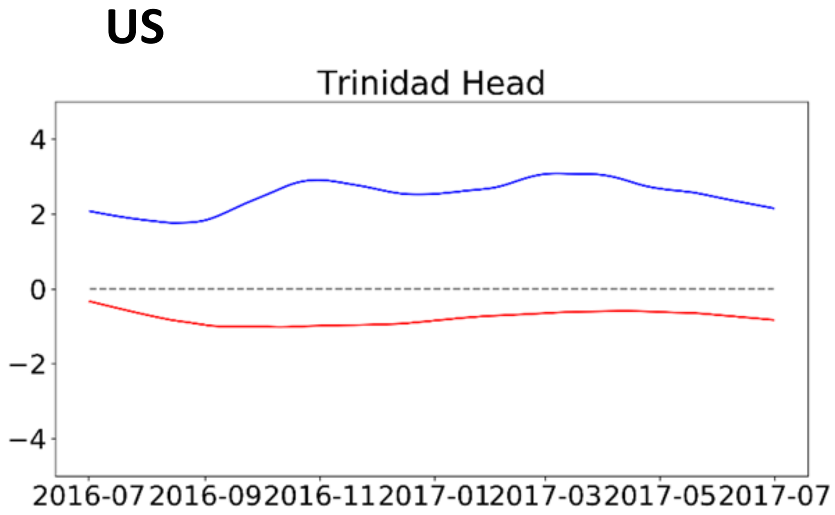
Why should we care about atmosphere iodine?



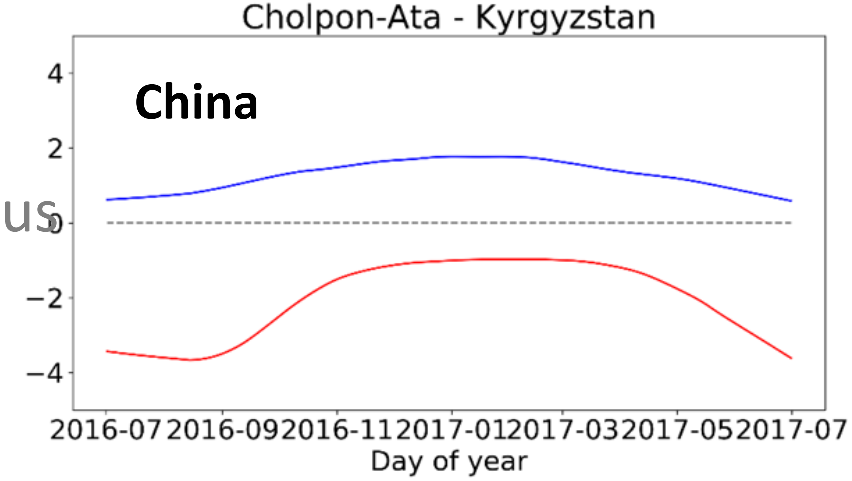
Includes total impact from O_3 deposition and gas phase iodine

How much should we care?





Impact on air inflow to various countries



Conclusions

- Ocean chemistry matters for tropospheric ozone deposition, but in ways we don't yet fully understand

- The SML has a higher reactivity to O_3 than underlying water, despite having a lower [iodide], implying a significant role for organics

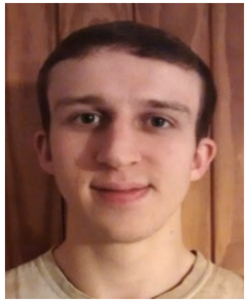
- In addition to chemistry, the roles of temperature and wind speed on O_3 $v_{D.}$ are also highly uncertain

- The organic enrichment of the SML and the depletion of iodide are important for volatile iodine release.

With thanks to..!

THE UNIVERSITY of York

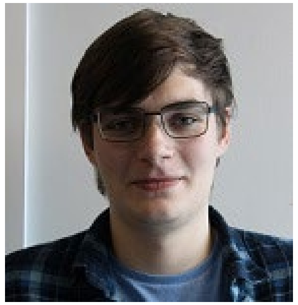
Many collaborators and colleagues



David Loades

Lucy Brown

Rosie Chance



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The CONNECT team:
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The MILAN team:
Leibniz-Institute for Baltic Sea Research, Germany; Carl-von-Ossietzky Universität Oldenburg, Germany

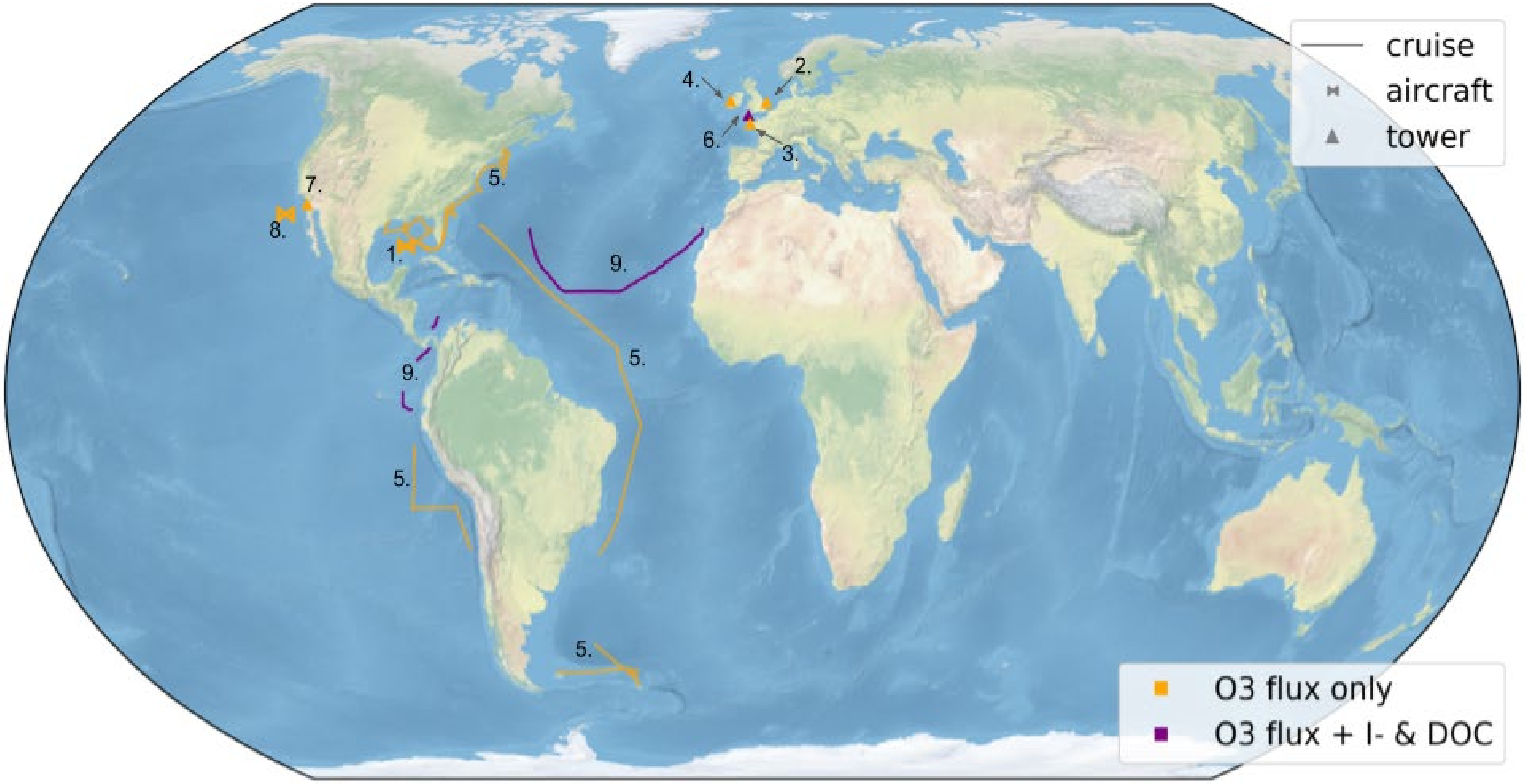
The PPAO (PML) sampling team:

National Centre for Atmospheric Science
NATURAL ENVIRONMENT RESEARCH COUNCIL

WACL
Wolfson Atmospheric Chemistry Laboratories

erc
European Research Council
Established by the European Commission

Oceanic O_3 fluxes (by EC): available observations



1. Lenschow et.al. 1982 2. Gallagher et.al. 2001 3. Whitehead et.al. 2009 4. McVeigh et.al. 2010

5. Helmig et.al. 2012 6. Loades et.al. 2020 + Unpublished 7. Novak et.al. 2020

8. Hannun et.al 2020 9. UoY Unpublished