Oceanic physicochemical processes affecting tropospheric O_3

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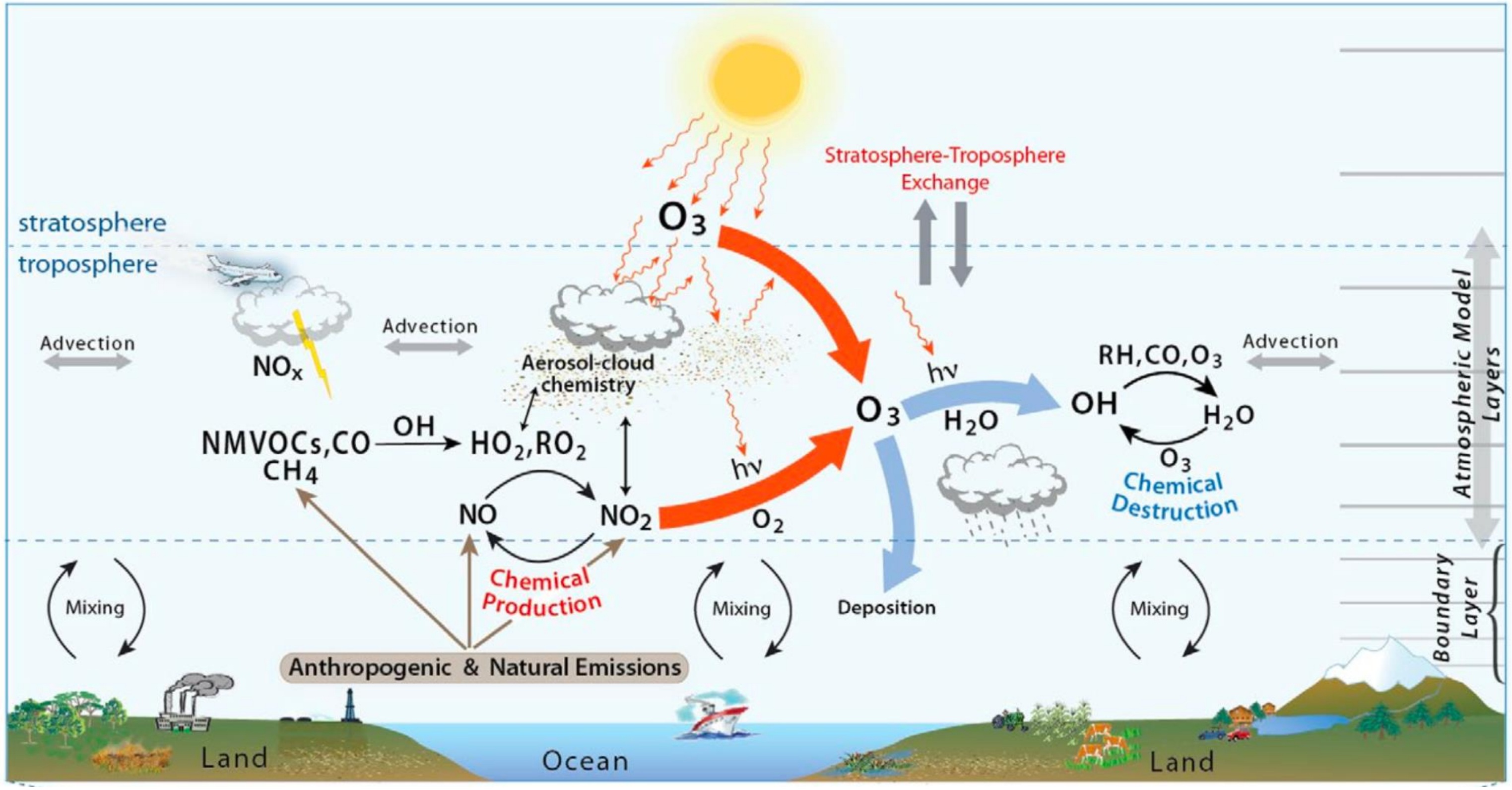
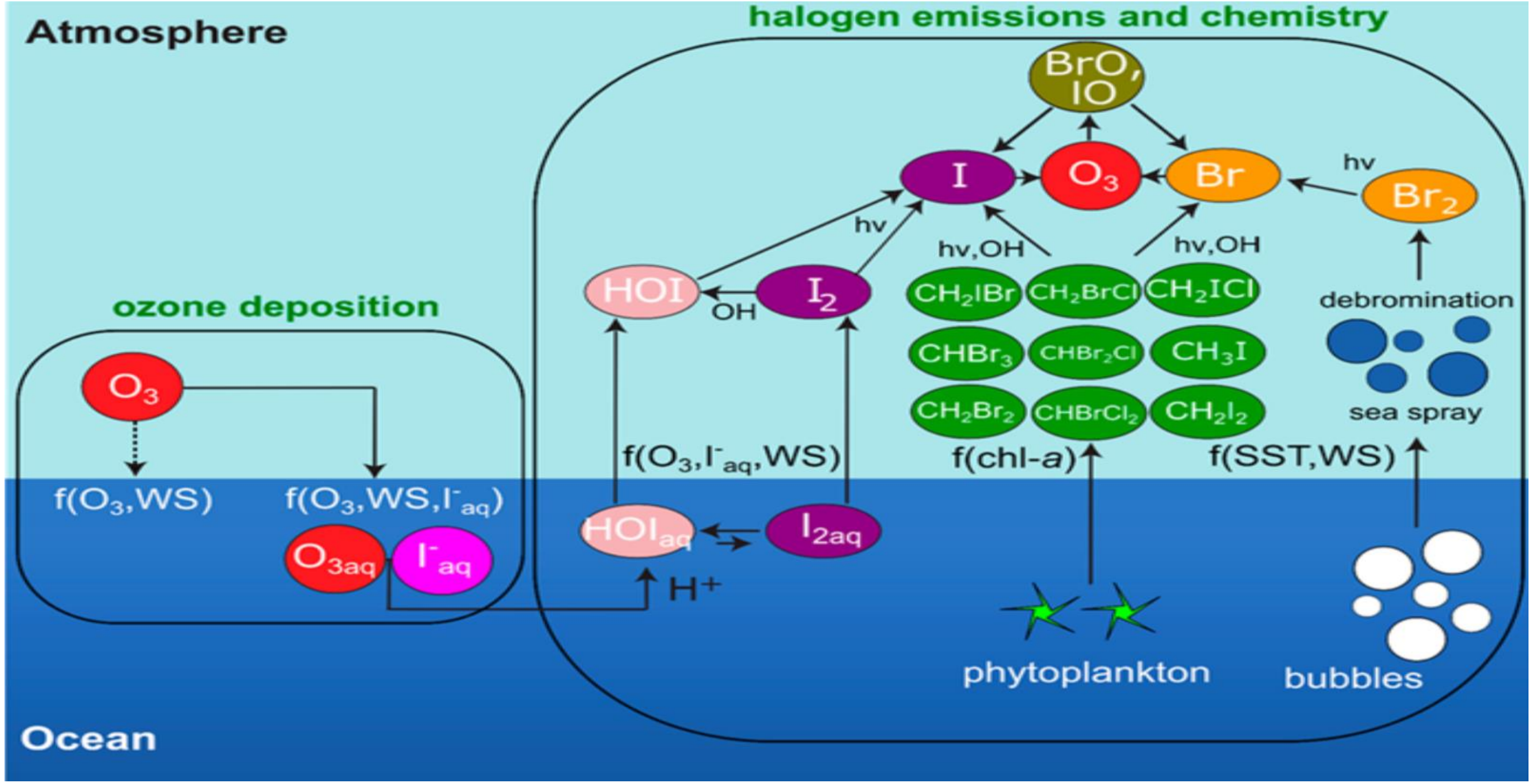
ACM 2018

Tropospheric O_3 processes



Young et al: Tropospheric Ozone Assessment Report, 2018

O_3-destroying processes over the ocean

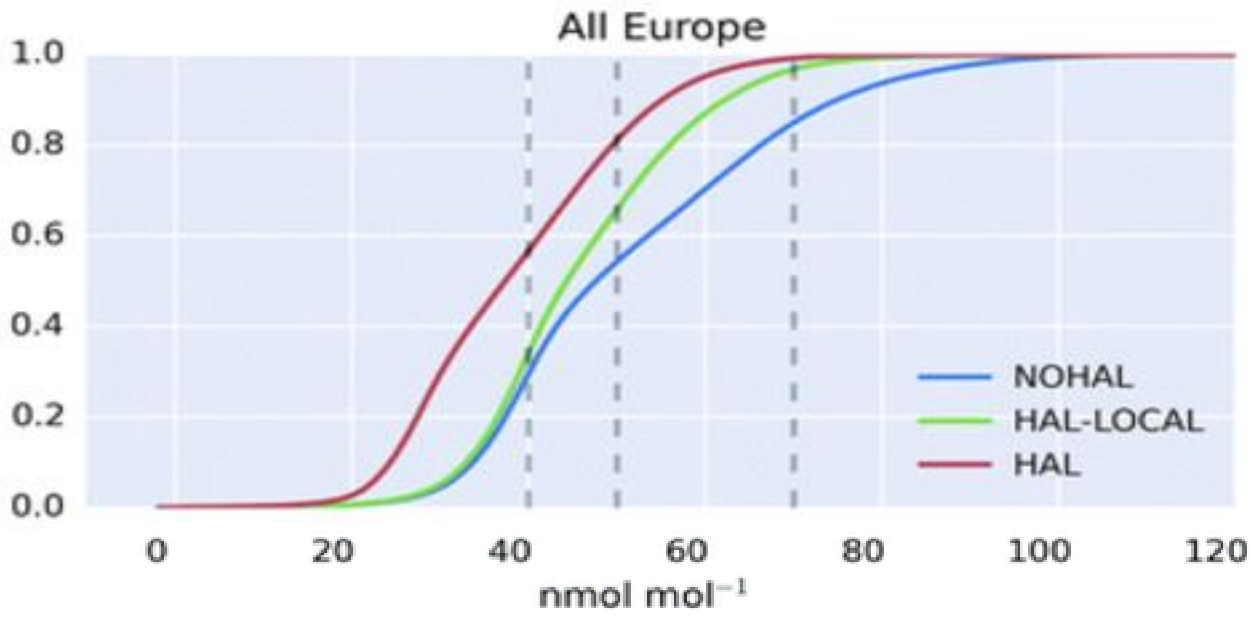


Global impact of tropospheric halogen cycling

Scenario	O_3 Burden (Tg)	[OH] mean (1×10^5 molec. cm^{-3})
No halogens	416	14.0
+ I, Br, Cl	339	12.8
% diff	-18.6	-8.2

- O_3, OH concentrations ↓ with halogens
- Relative to bromine, iodine chemistry is >4 times more effective in reducing ozone in NH

Regional impact - Europe

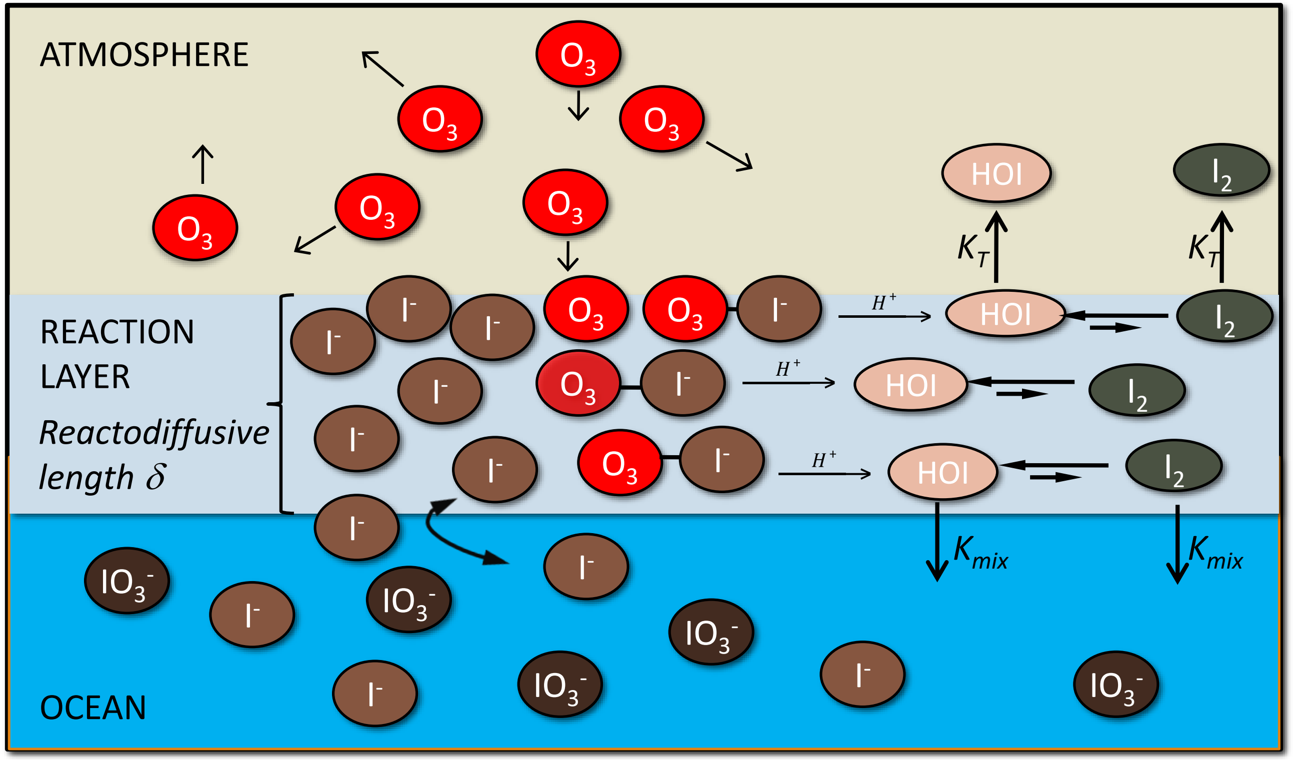


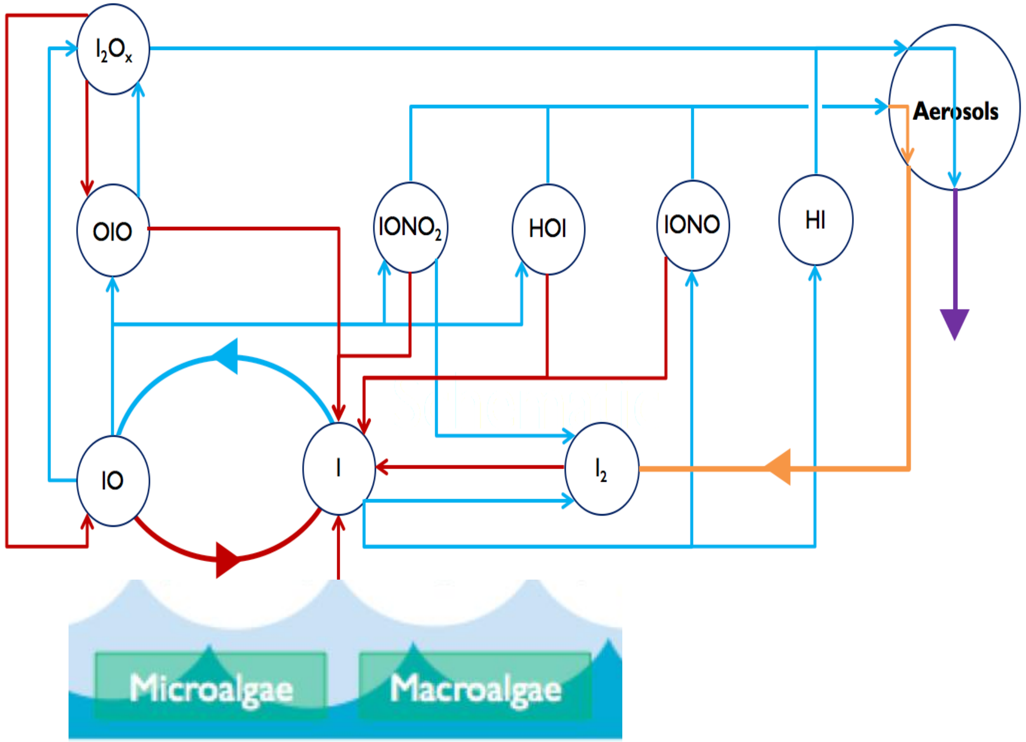
O_x sinks	
$O_3 + H_2O + h\nu$	20.4
$O_3 + HO_2$	10.2
$O_3 + OH + O_2$	6.2
Bromine O_x sinks	1.1
Iodine O_x sinks	8.0
Chlorine O_x sinks	0.3
Total chemical O_x sinks	50.6
O_3 dry deposition	69

95th percentile mixing ratios:

NOHAL: 77 ppbv **HAL-LOCAL: 65 ppbv** **HAL: 58 ppbv**

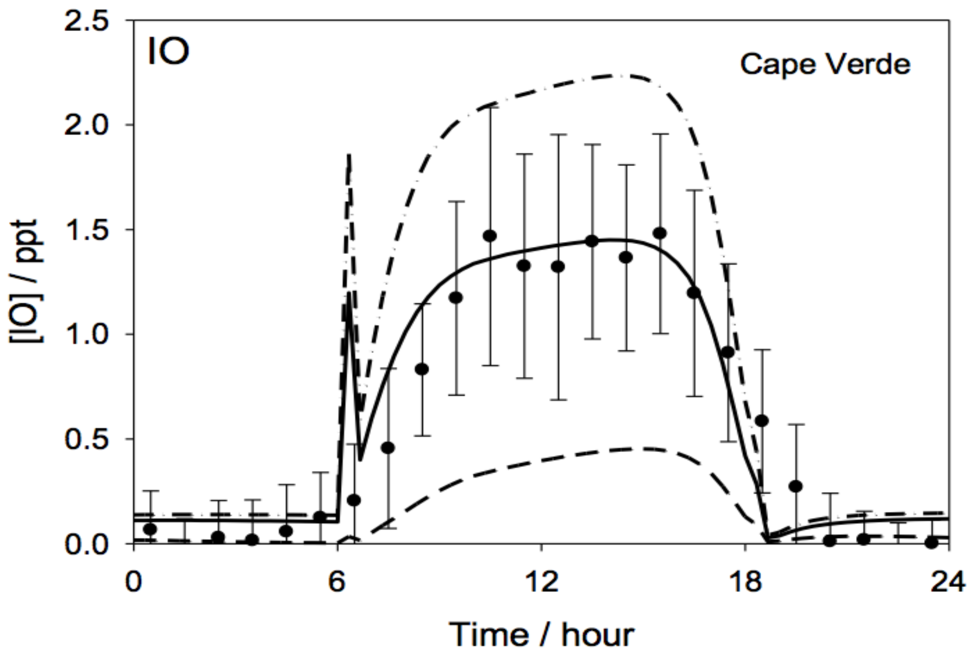
Iodine processes



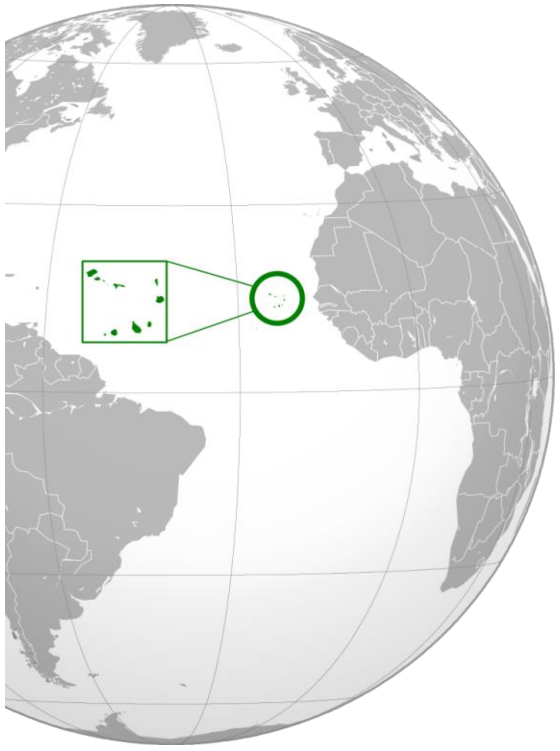


Carpenter et al., Nature Geoscience, 2013

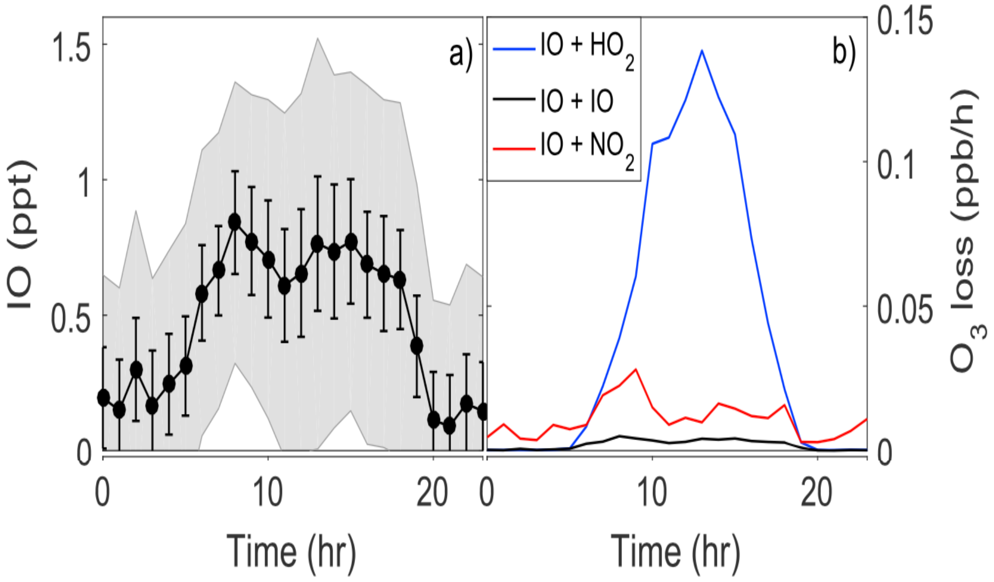
Evidence for halogen chemistry



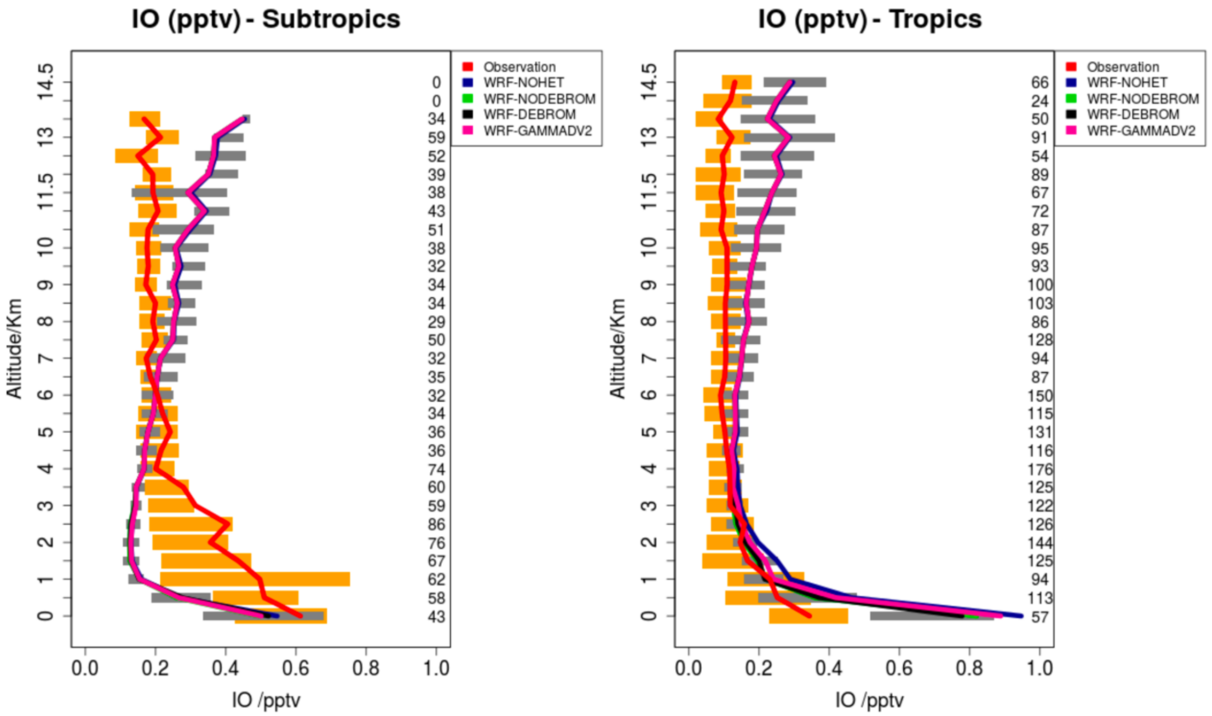
Reed et al., Nature, 2008



Evidence for iodine chemistry



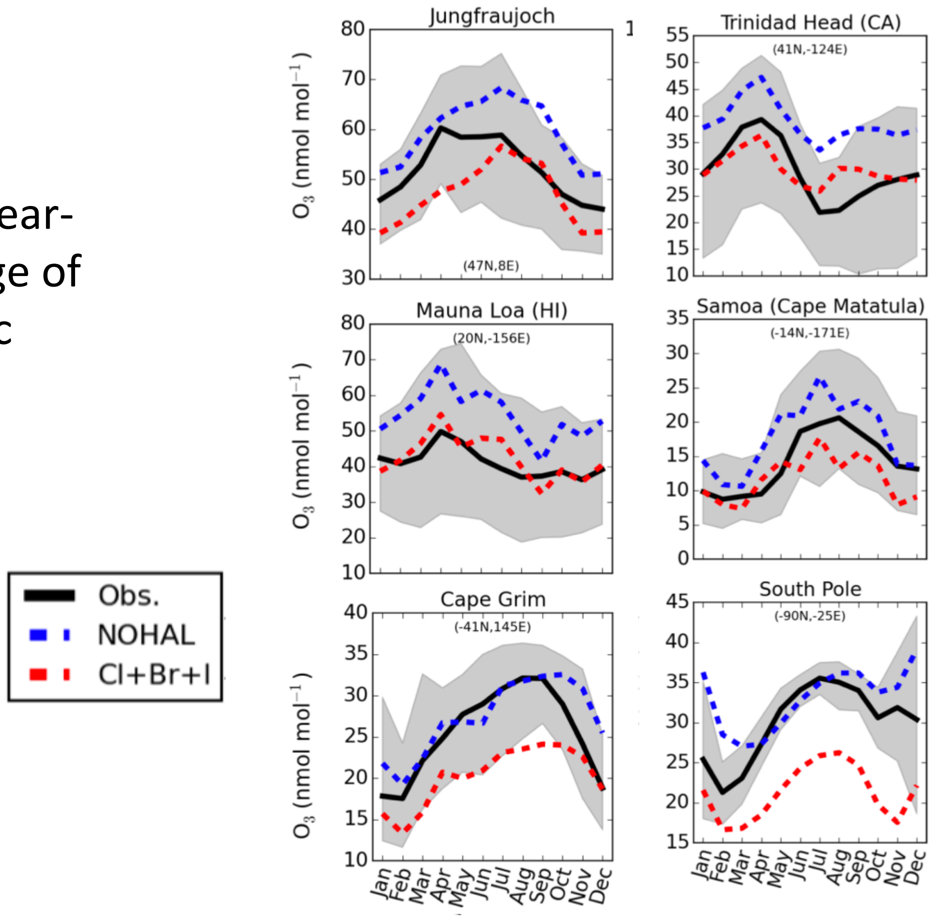
Golf of Mexico. Tuite et al. GRL, 2018



East Pacific. Badia et al., ACPD, 2018

Surface ozone predictions

Seasonal cycle of near-surface O_3 at a range of Global Atmospheric Watch (GAW) sites

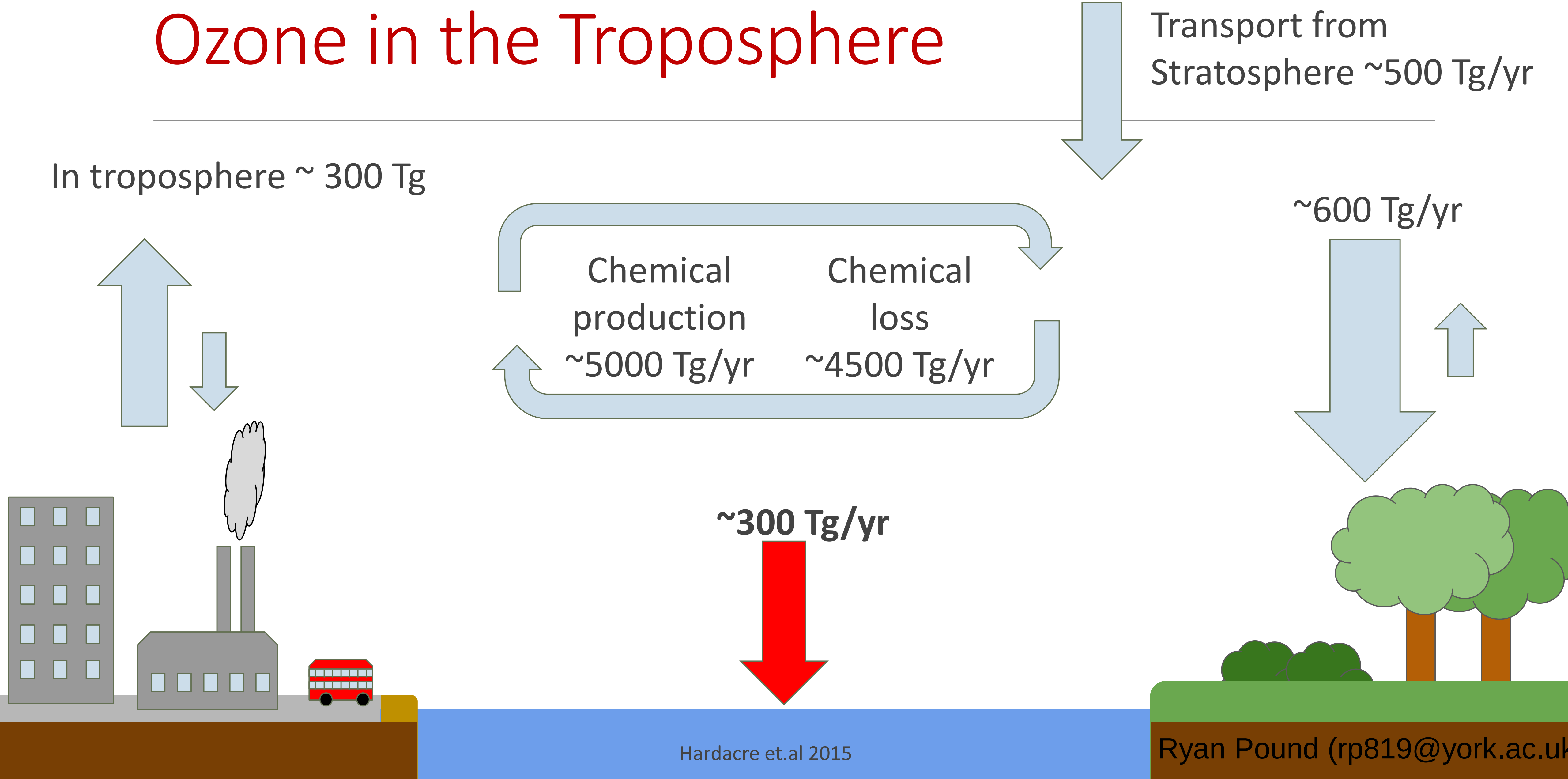


Northern mid latitudes

Tropics/ sub tropics

Southern Ocean

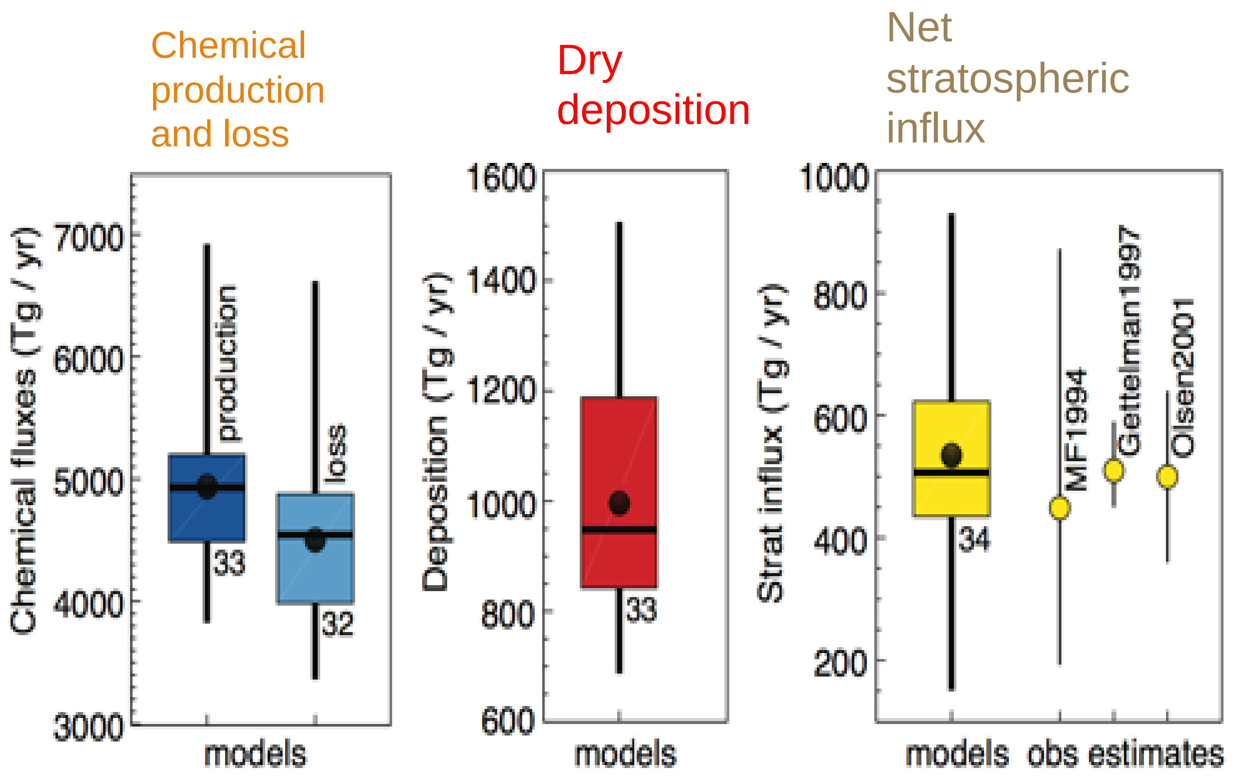
Ozone in the Troposphere



Ozone oceanic dry deposition

- Oceanic deposition flux ~ 360 $\pm$ 335 Tg yr^{-1} *
- Measurements (v_D): 0.01 - 0.15 cm s^{-1}

**Hardacre et al. ACP 2015*



Numbers of models are indicated next to the boxes.

Young et al., 2018.

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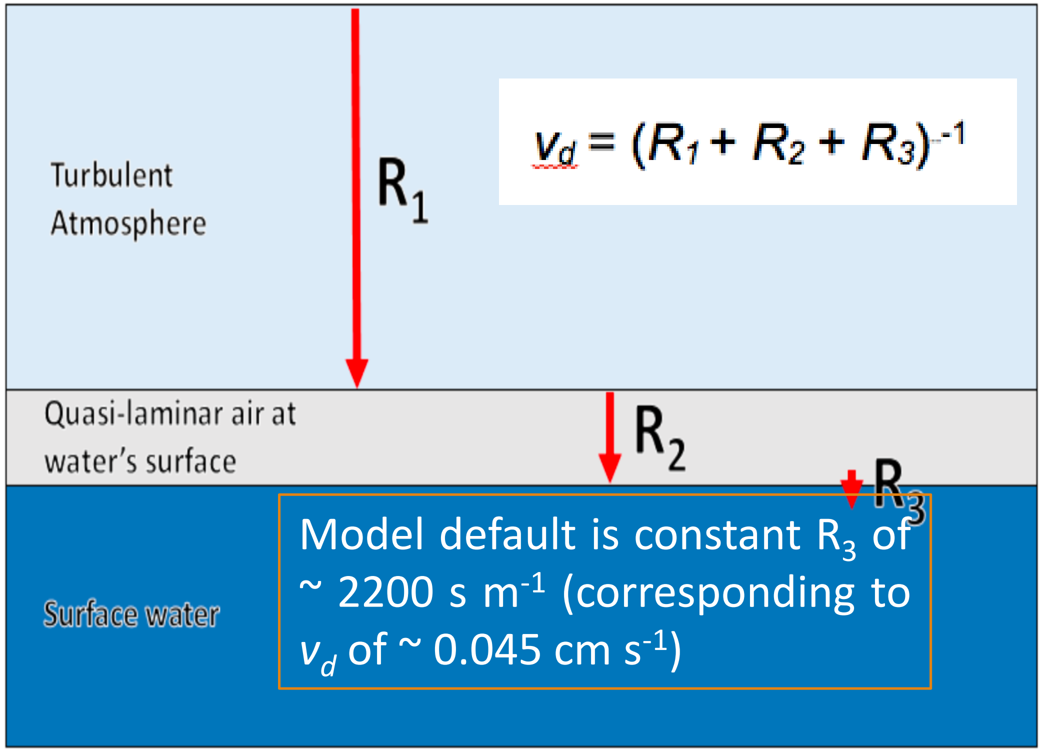
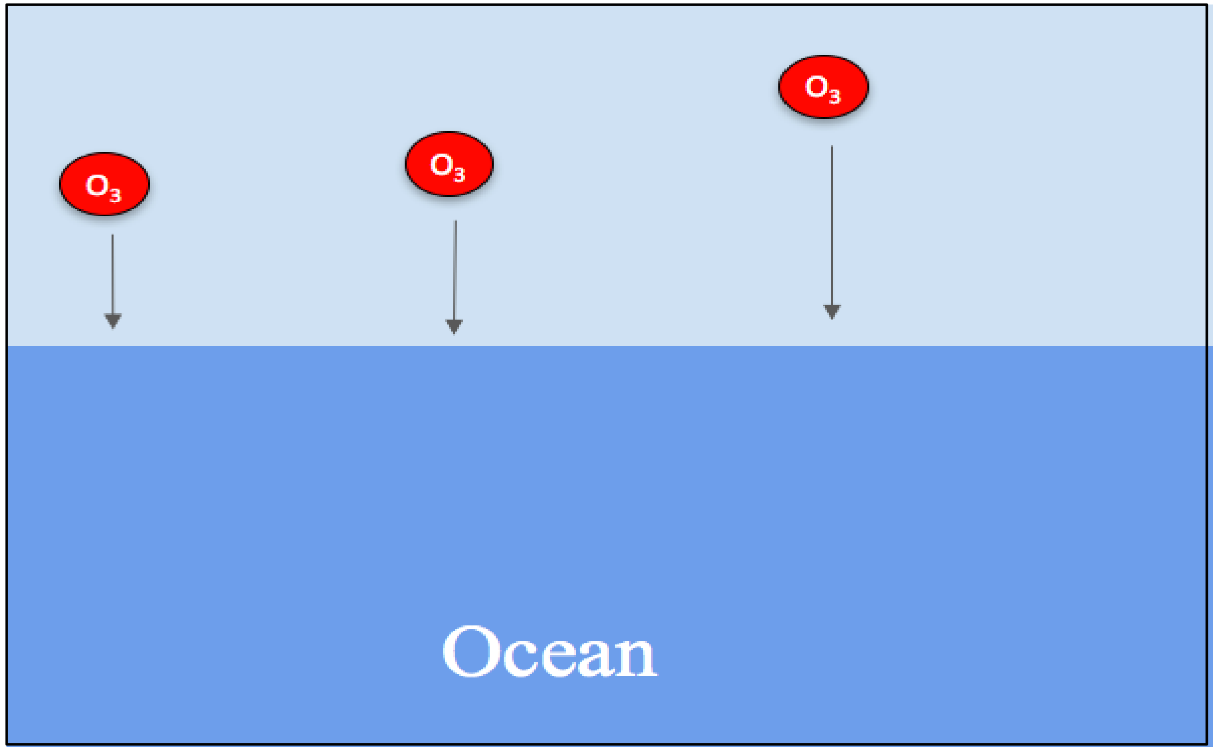
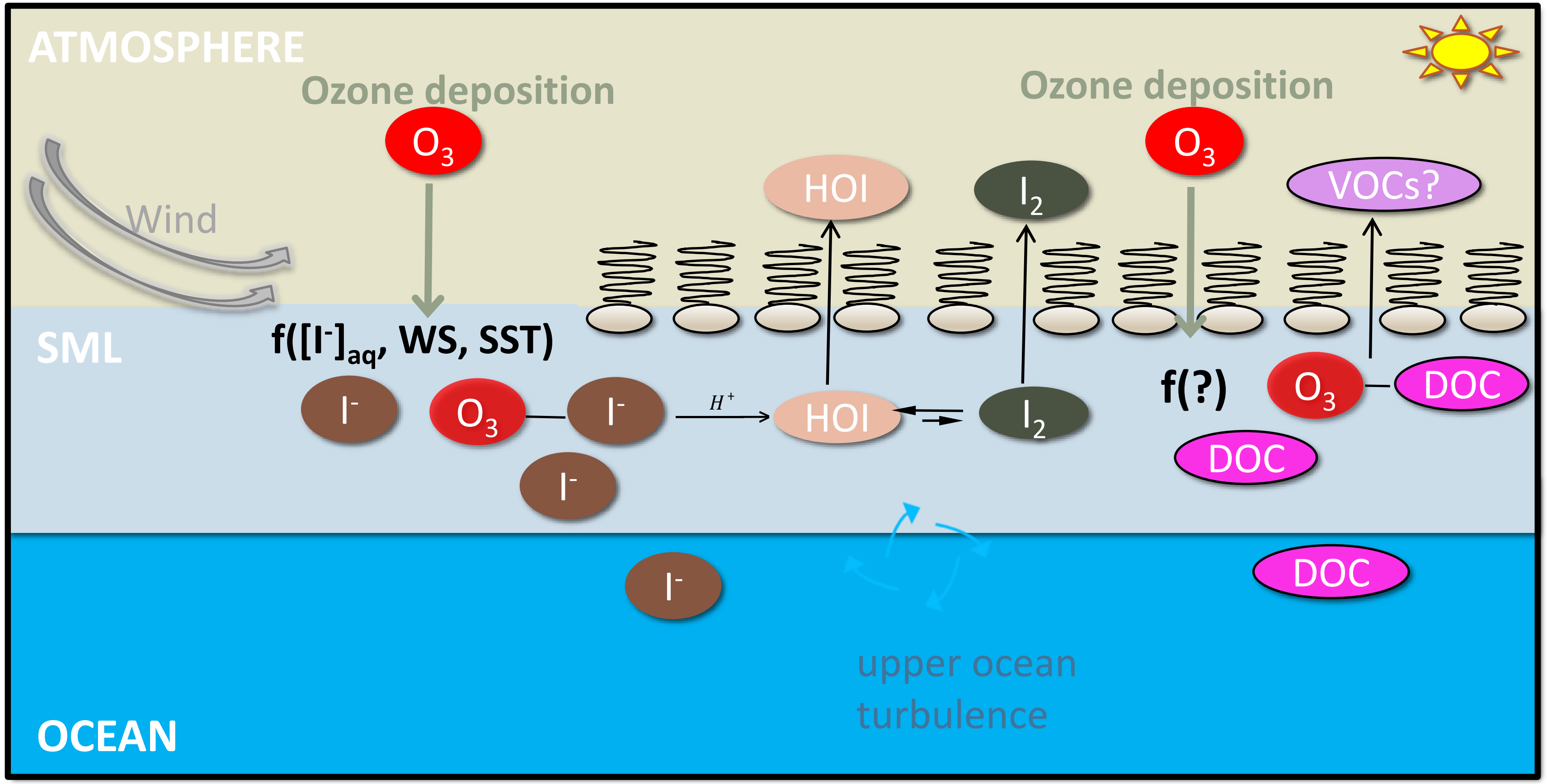
Calculating O_3 oceanic v_D





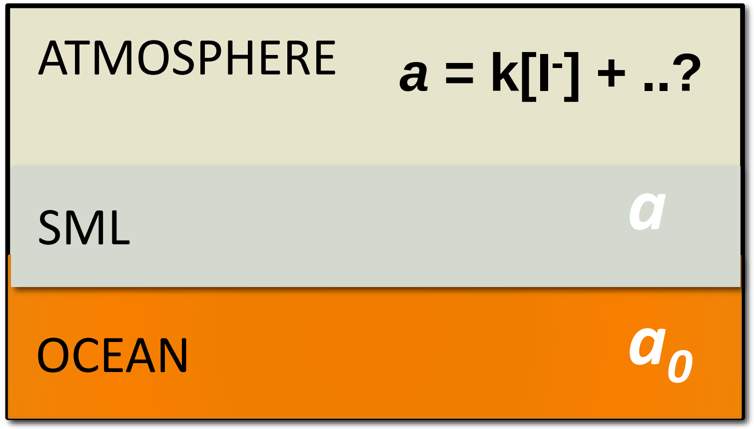
Ozone oceanic dry deposition



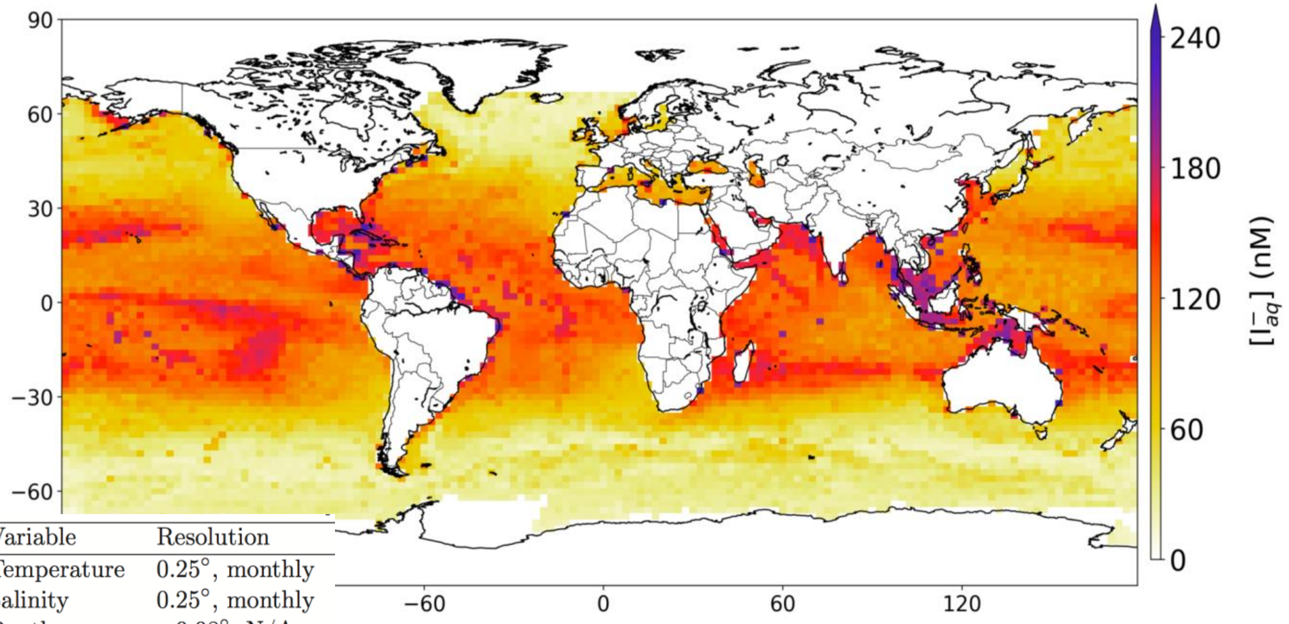
With chemistry and turbulence

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

Fairall et al., 2007; Luhar et al., 2017



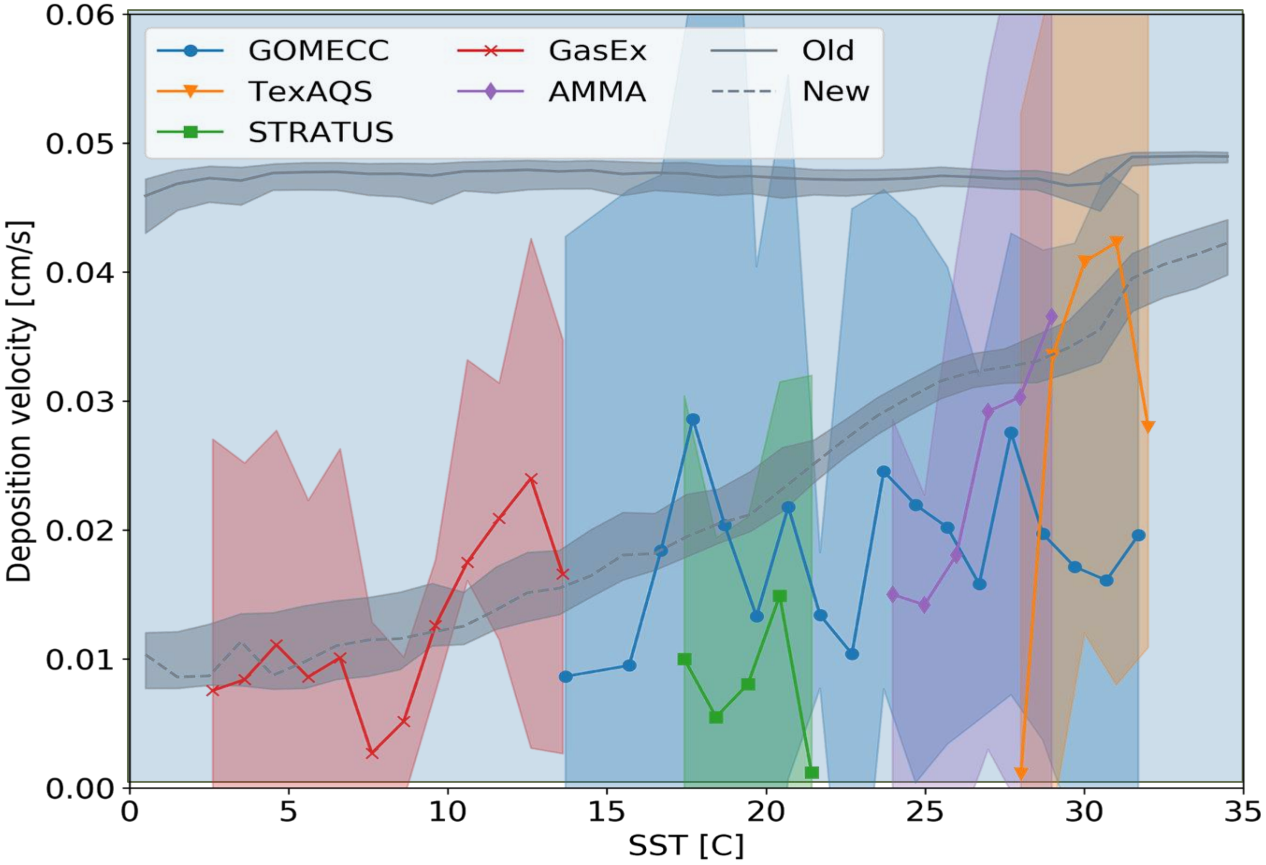
Surface ocean [I⁻]

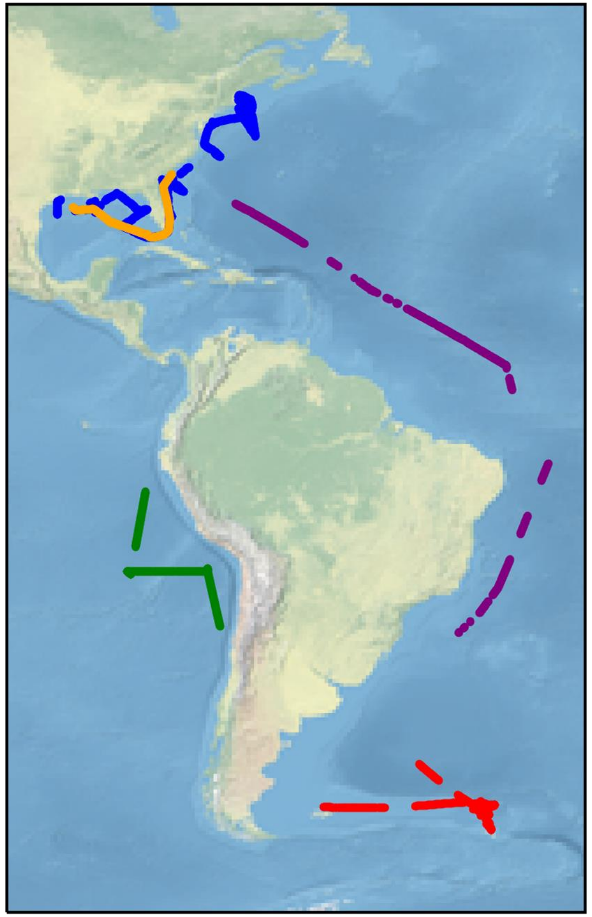


Variable	Resolution
Temperature	0.25°, monthly
Salinity	0.25°, monthly
Depth	~0.08°, N/A

Chance et al., 2014; Sherwen et al., in prep

Comparison with observations



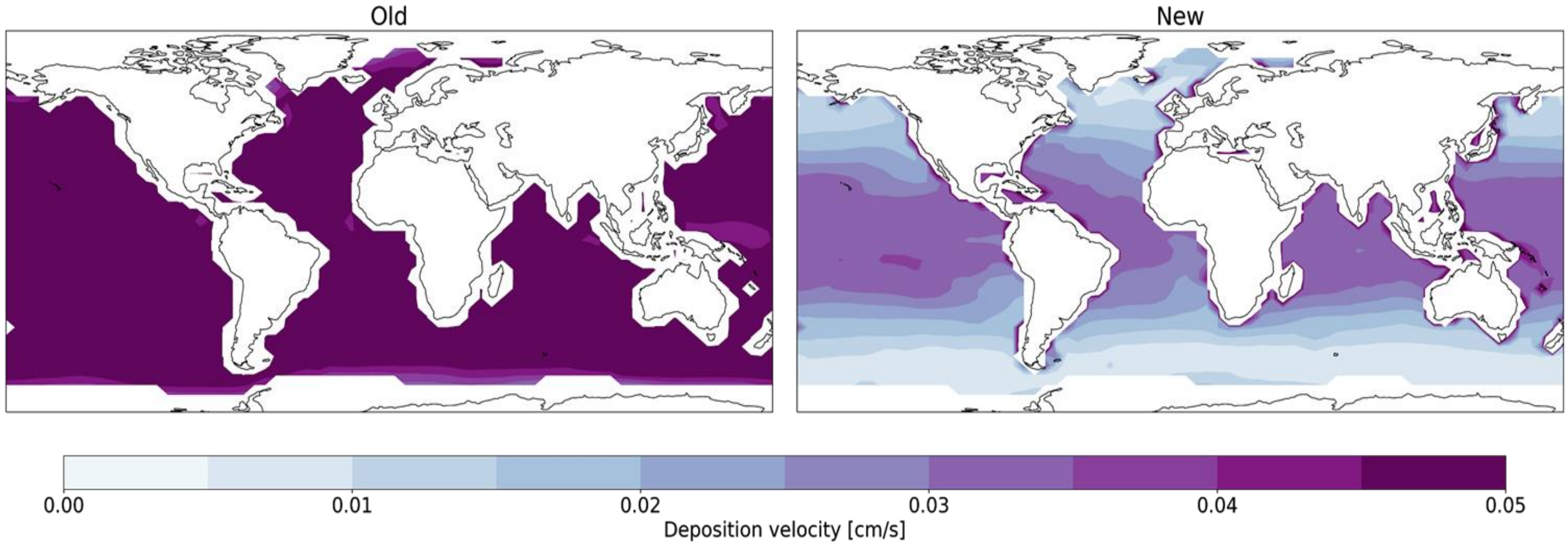


Helmig et.al 2012

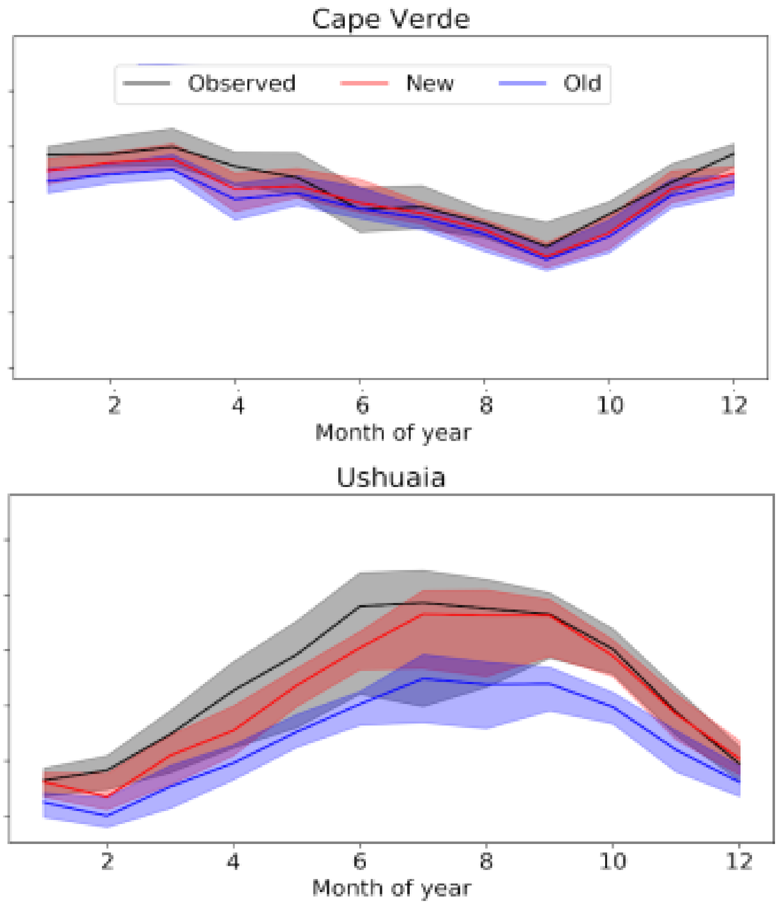
Pound et al. unpublished data

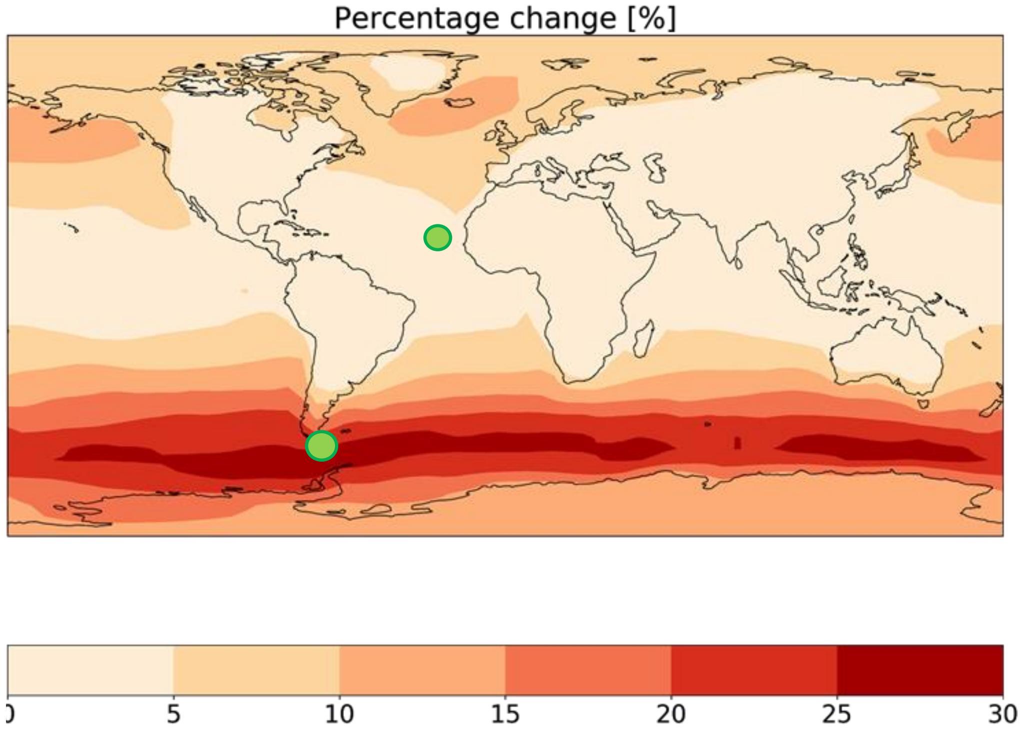
Ryan Pound (rp819@york.ac.uk)

Change in ozone v_D



Change in surface ozone predictions





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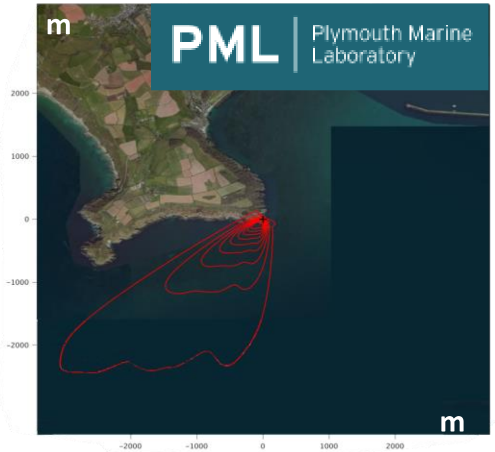
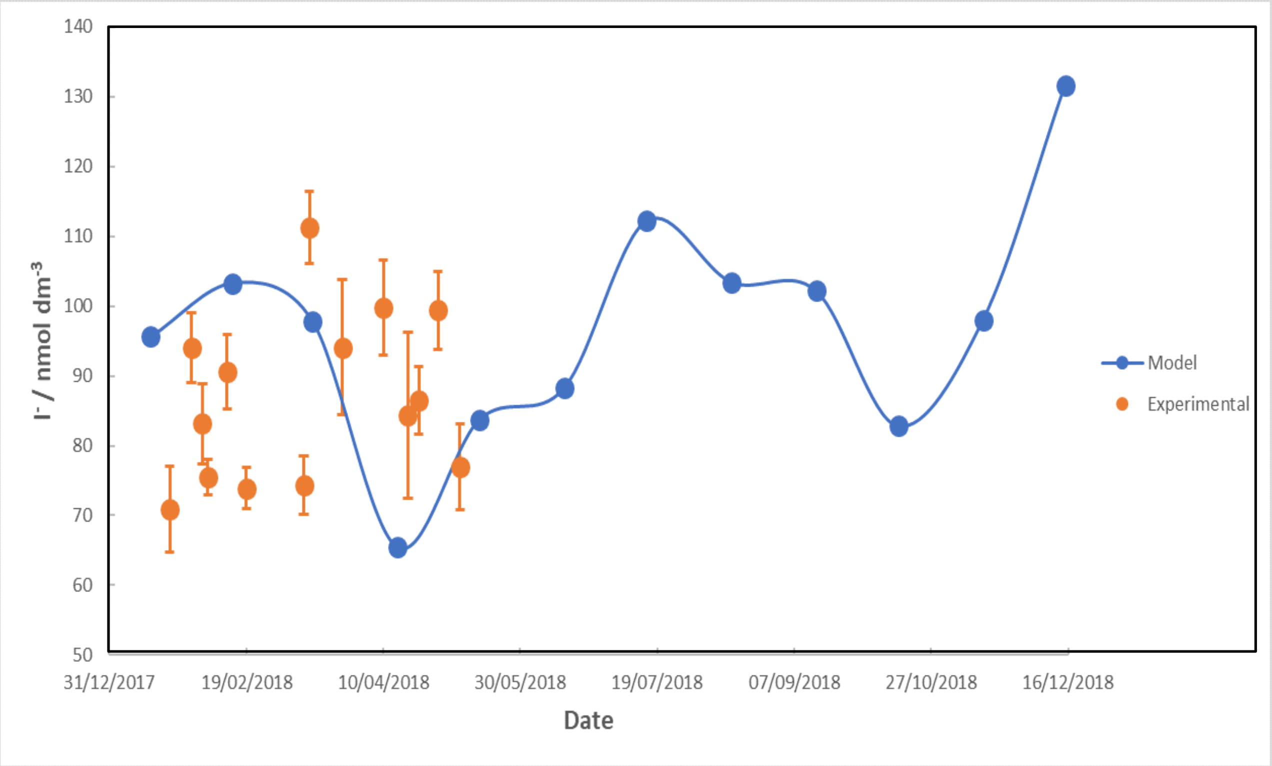
Comparison with coastal observations



Eddy covariance, 10 Hz

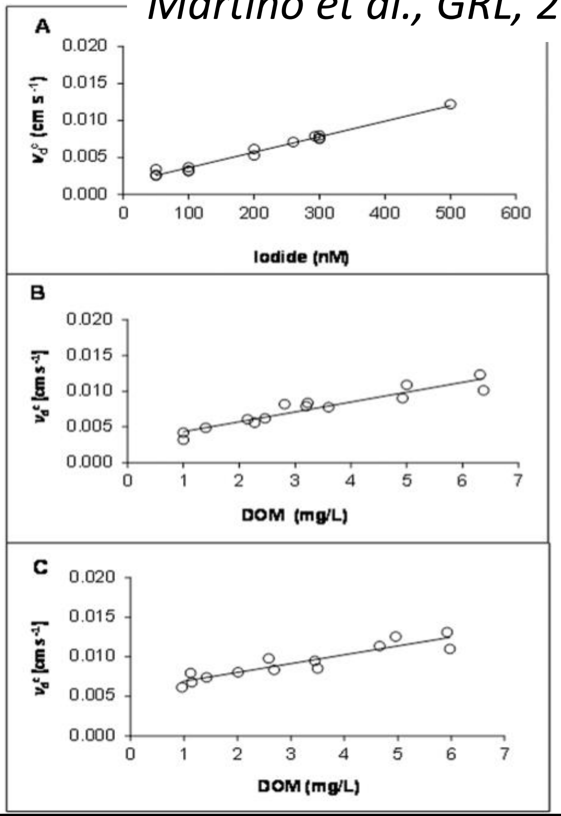
$$O_3 + NO \rightarrow NO_2^* + O_2$$
$$NO_2^* \rightarrow NO_2 + light$$

NO_2 chemiluminescence



Organic reactivity in the SML?

Martino et al., GRL, 2012



I^- only

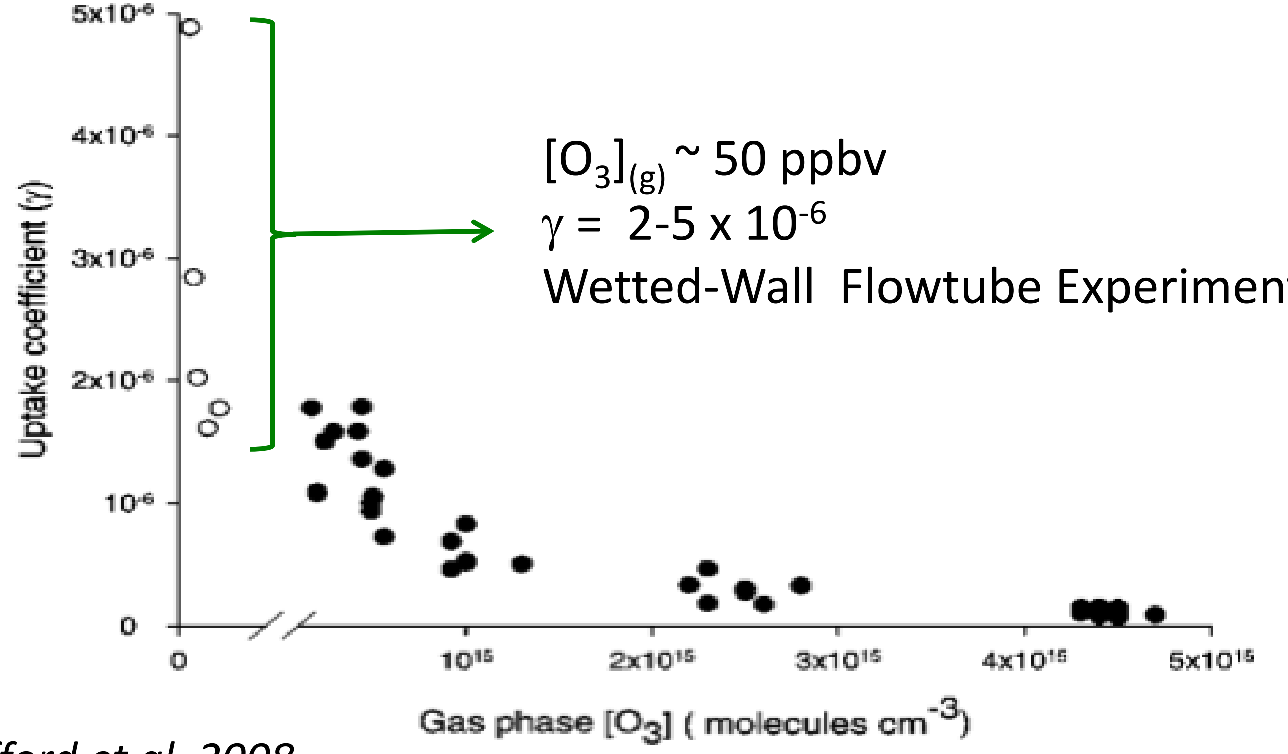
DOM only (Suwannee River NOM)

DOM and 150 nM I^-

- Equates to γ_{obs} for DOM of 1-3 x 10^{-6}

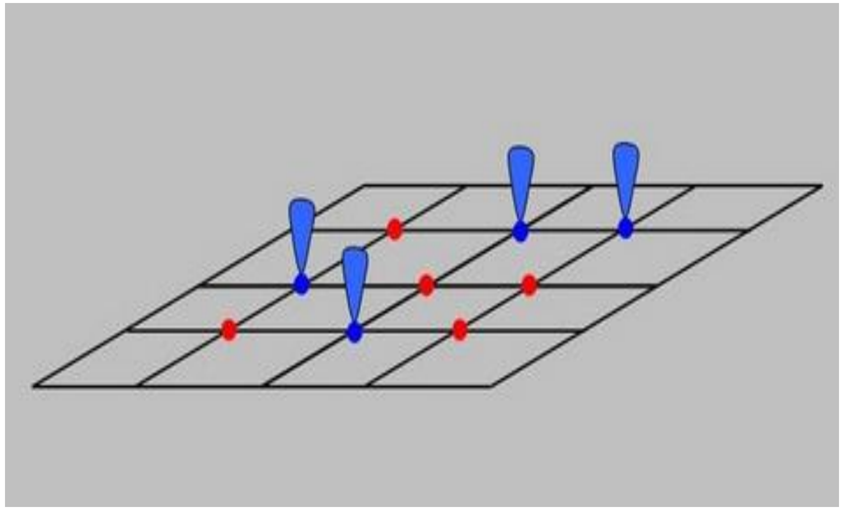
Organic reactivity in the SML?

O_3 on Chla/aqueous solution



$[O_3]_{(g)}$ ~ 50 ppbv
γ = 2-5 x 10^{-6}
Wetted-Wall Flowtube Experiments

Clifford et al. 2008

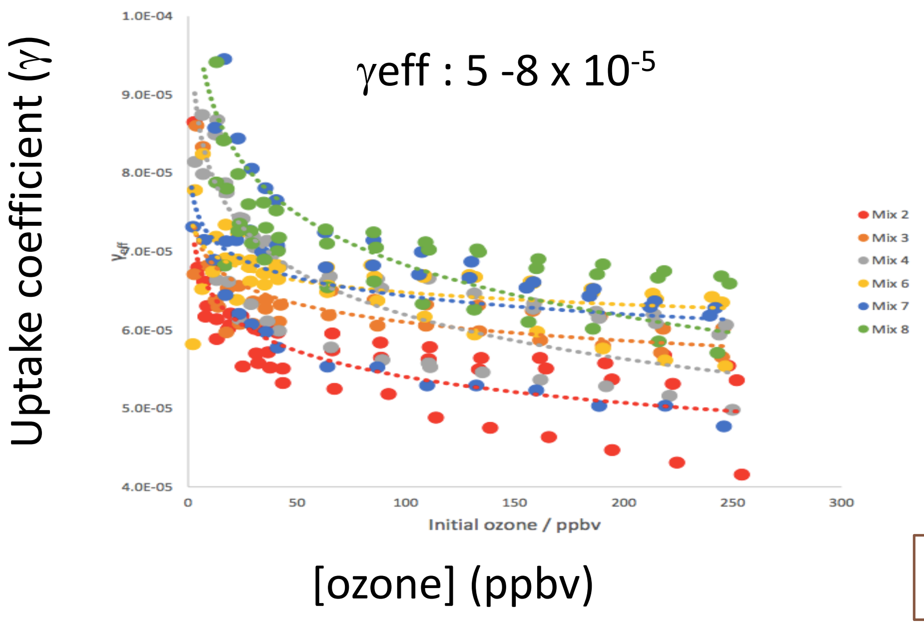


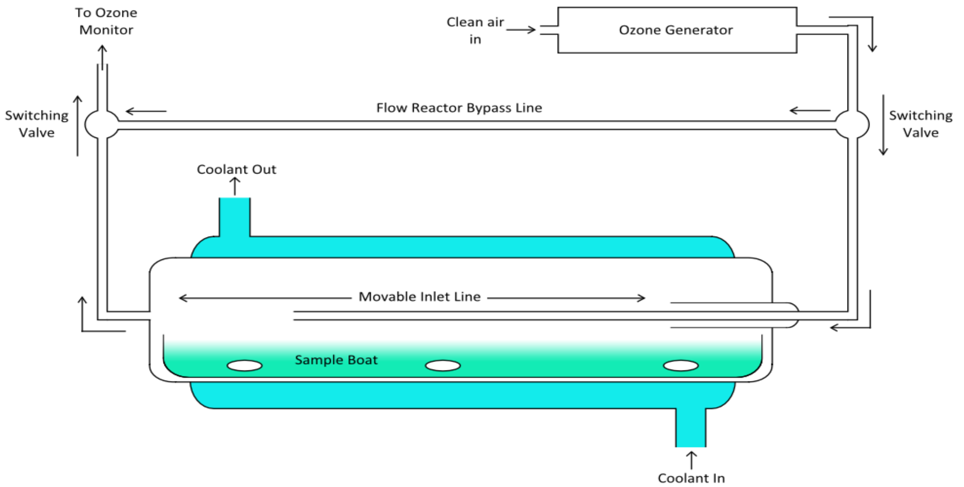
Langmuir-Hinshelwood mechanism

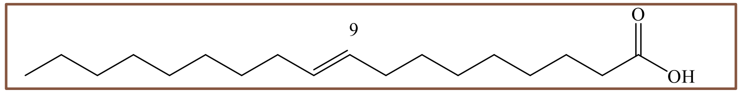
$$O_3(g) \xleftrightarrow{k_{ads}, k_{desorb}} O_3(\text{interface})$$

$$O_3(\text{interface}) + X(\text{interface}) \xleftrightarrow{k_{surf}} \text{products}$$

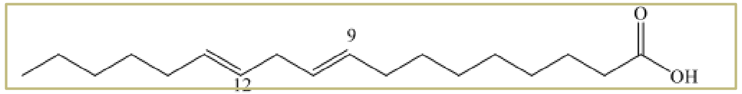
O_3 uptake on fatty acid monolayers



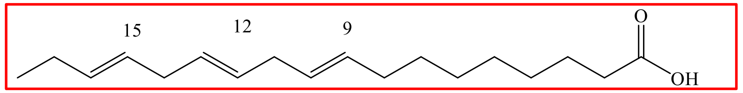




OL = oleic acid



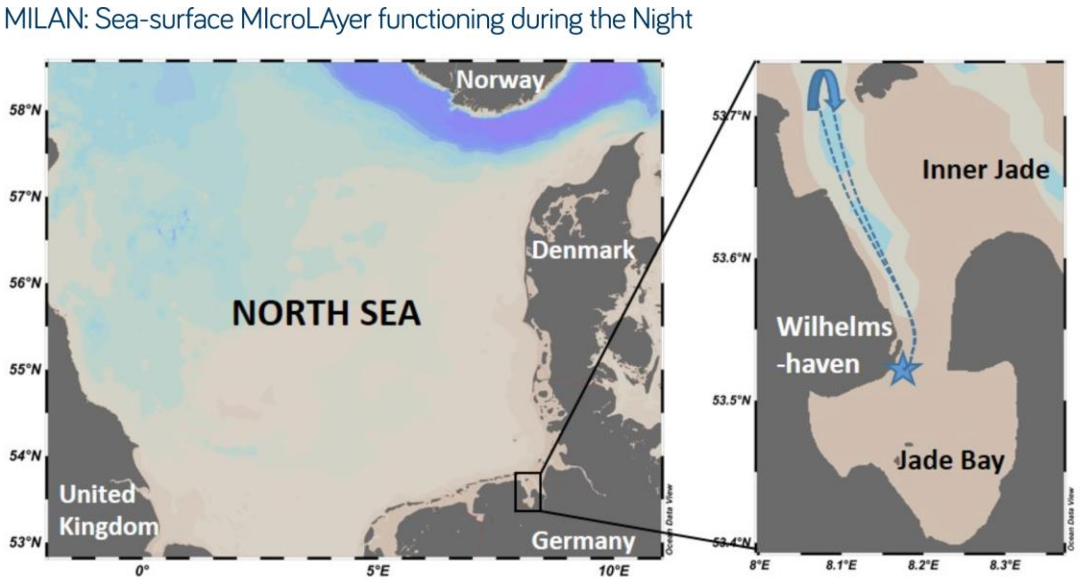
LA = linoleic acid

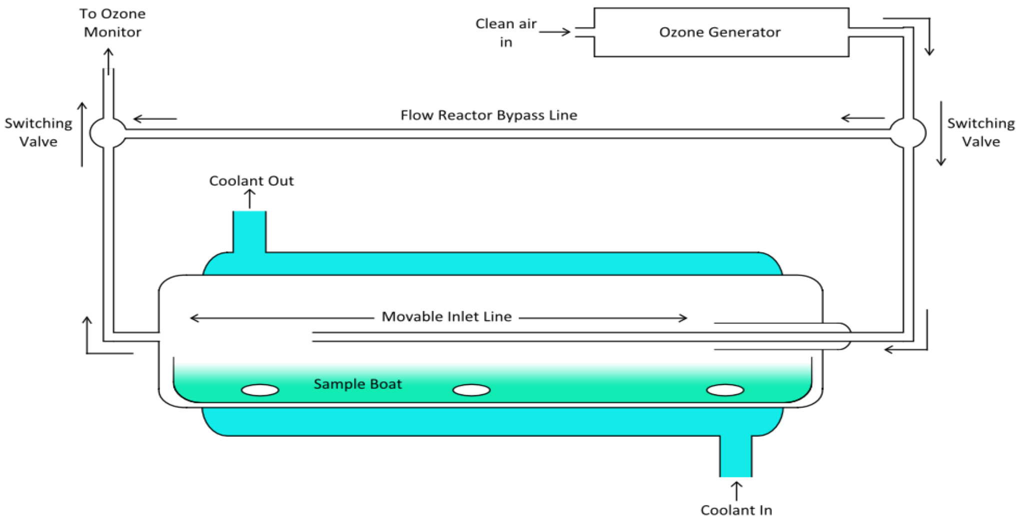


LN = linolenic acid

MIcroLayer At Night (MILAN)

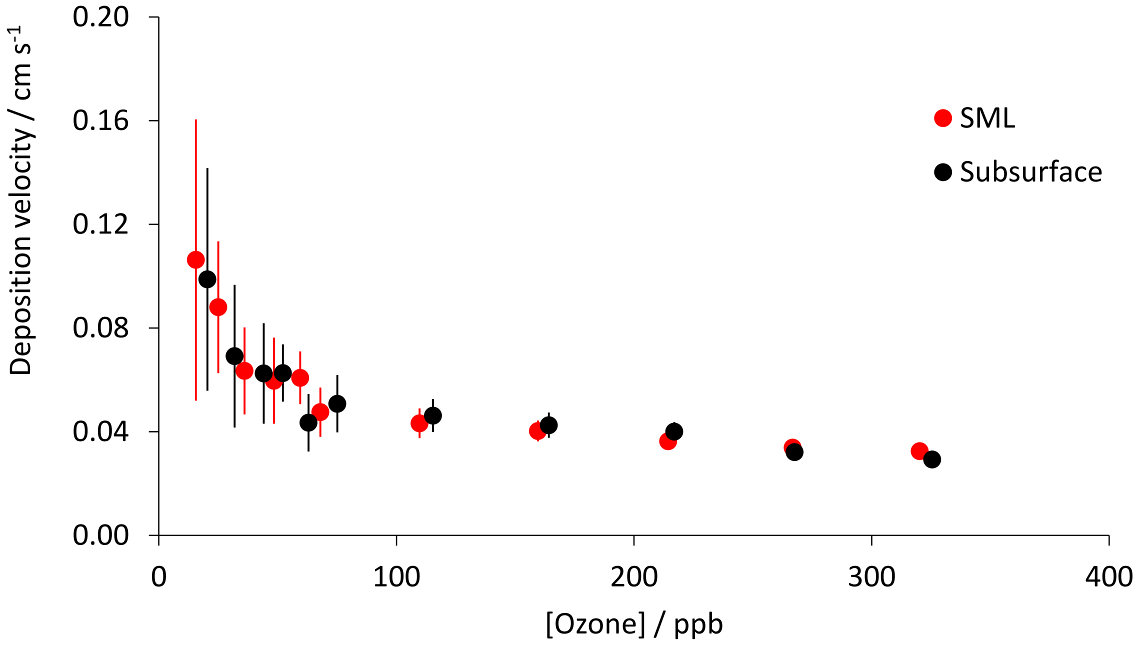
- First assessment of chemical controls of v_D in SML vs underlying water (ULW)
- Gaining an understanding of organic controls of v_D

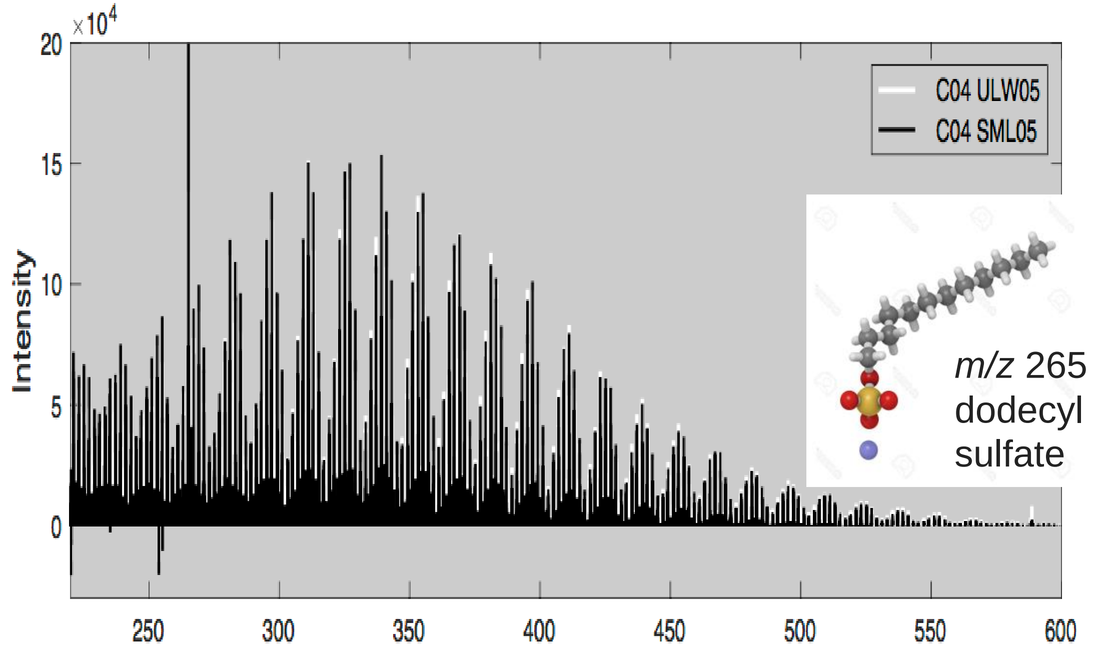




- M. Ribas-Ribas, N. I. Hamizah Mustaffa, J. Rahlff, C. Stolle and O. Wurl, *J. Atmos. Ocean. Technol.*, 2017, **34**, 1433–1448

Results from MILAN

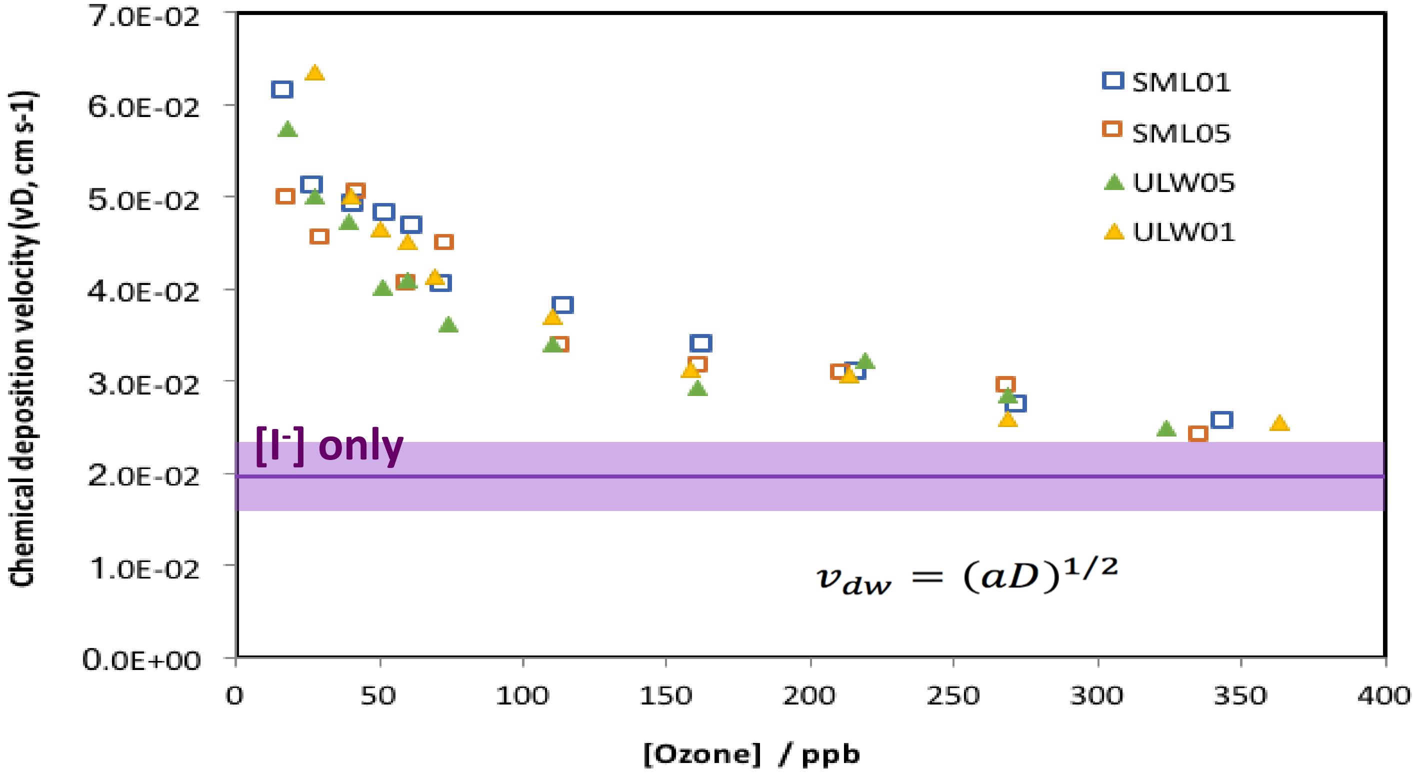




SPE-DOM (Orbitrap Q-Exactive)

- Ratios of v_D in SML/ULW of 0.2 - 1.5
  - Is the model framework of bulk reactivity correct?

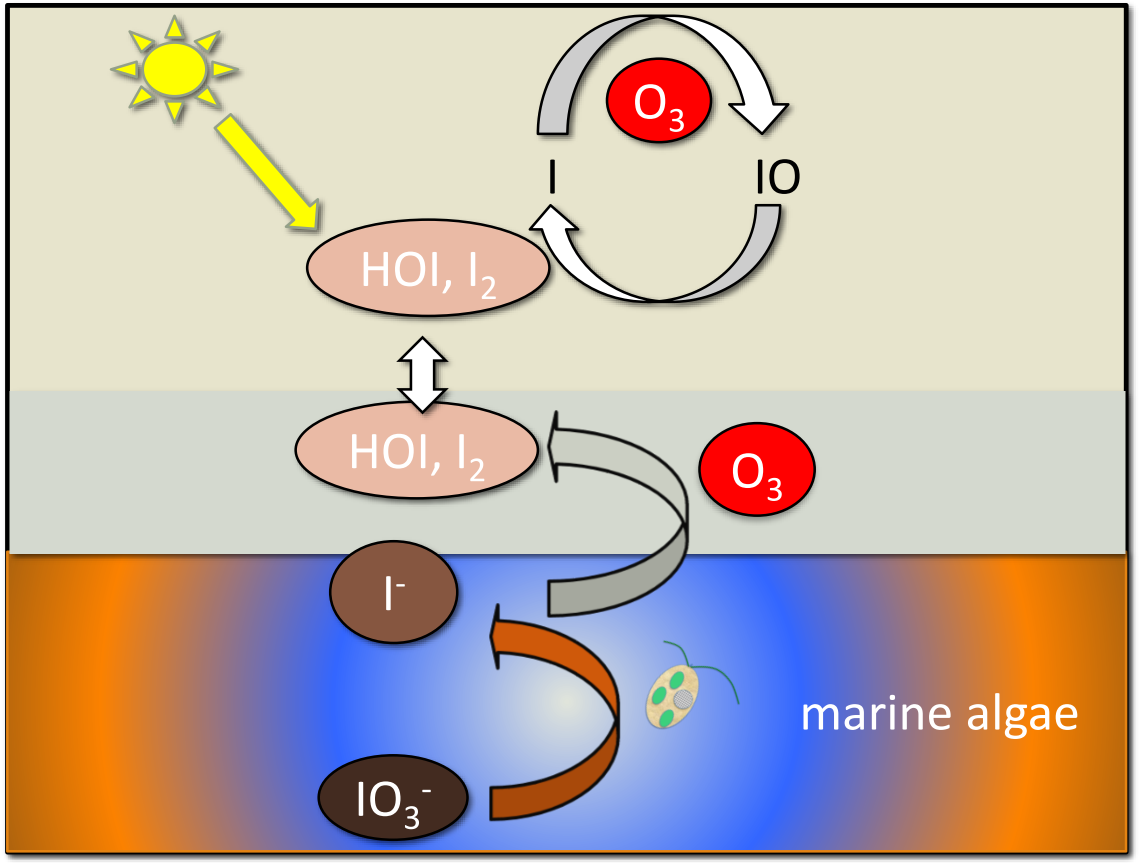
Results from MILAN



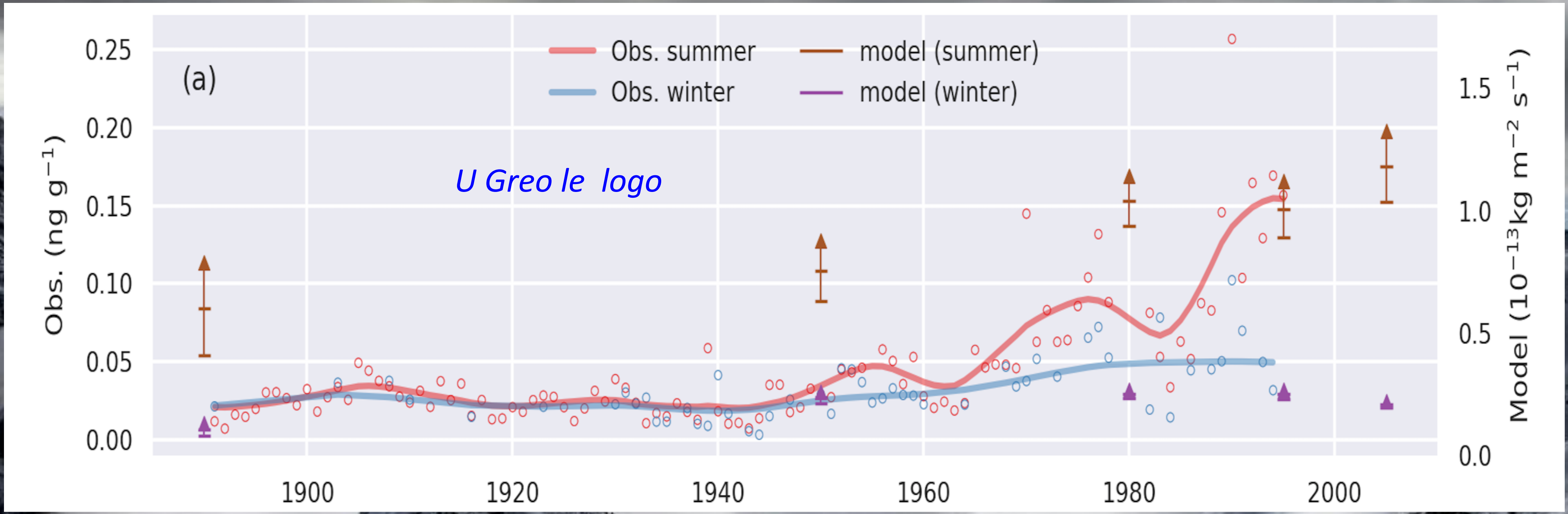
- Calculations show that [iodide] contributes 10-80% of chemical deposition velocity

Do any of these processes affect ozone trends?

- Negative feedback on O_3



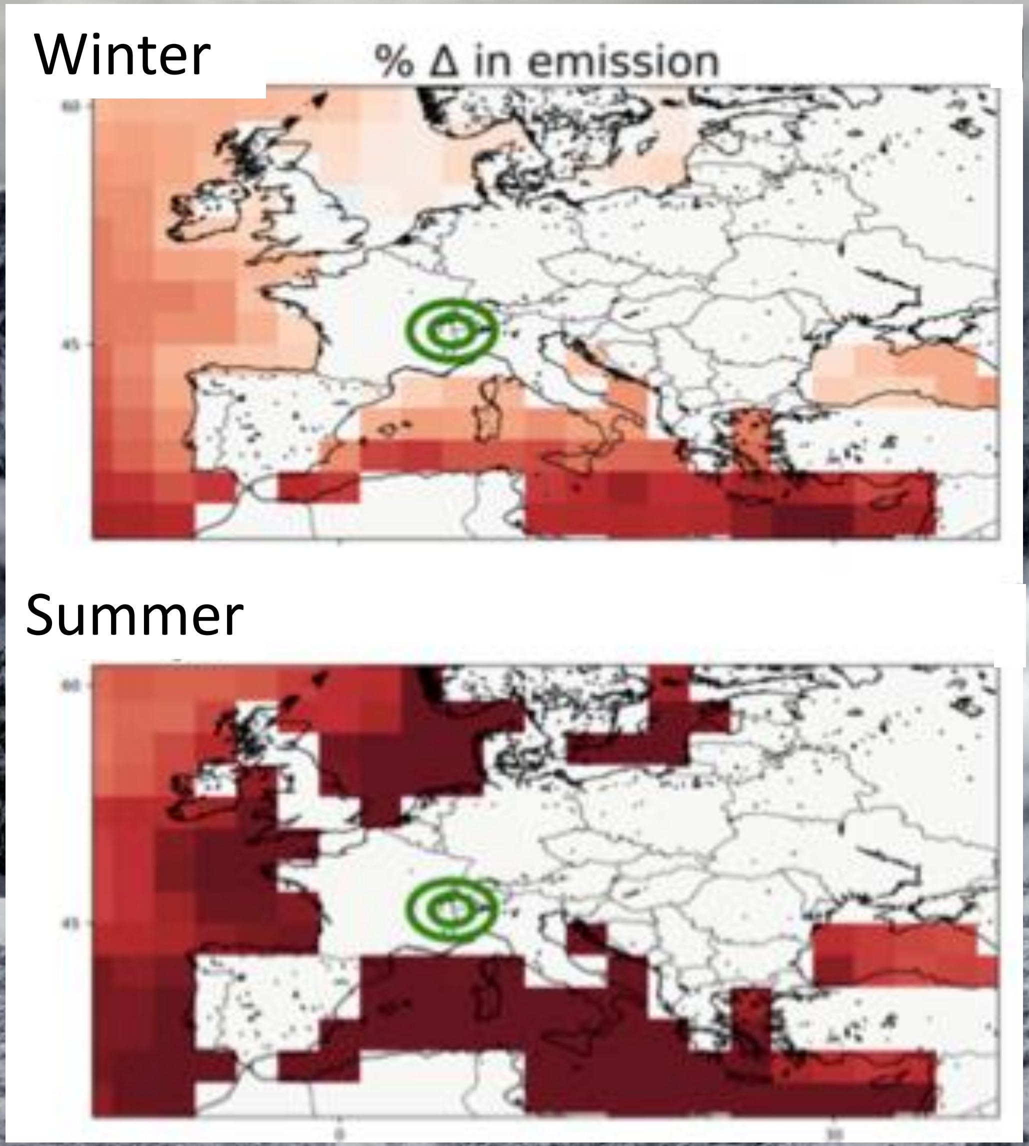
Iodine time series– new Alpine ice core record

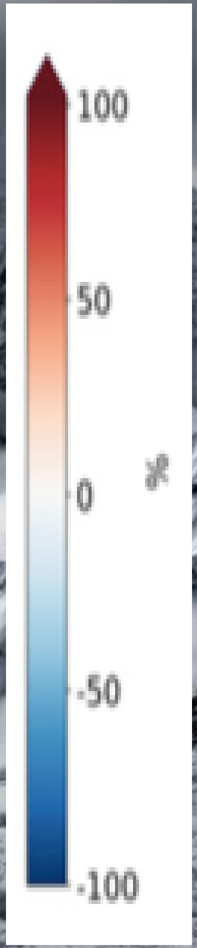


Col du Dome

Legrand et al. PNAS, 2018

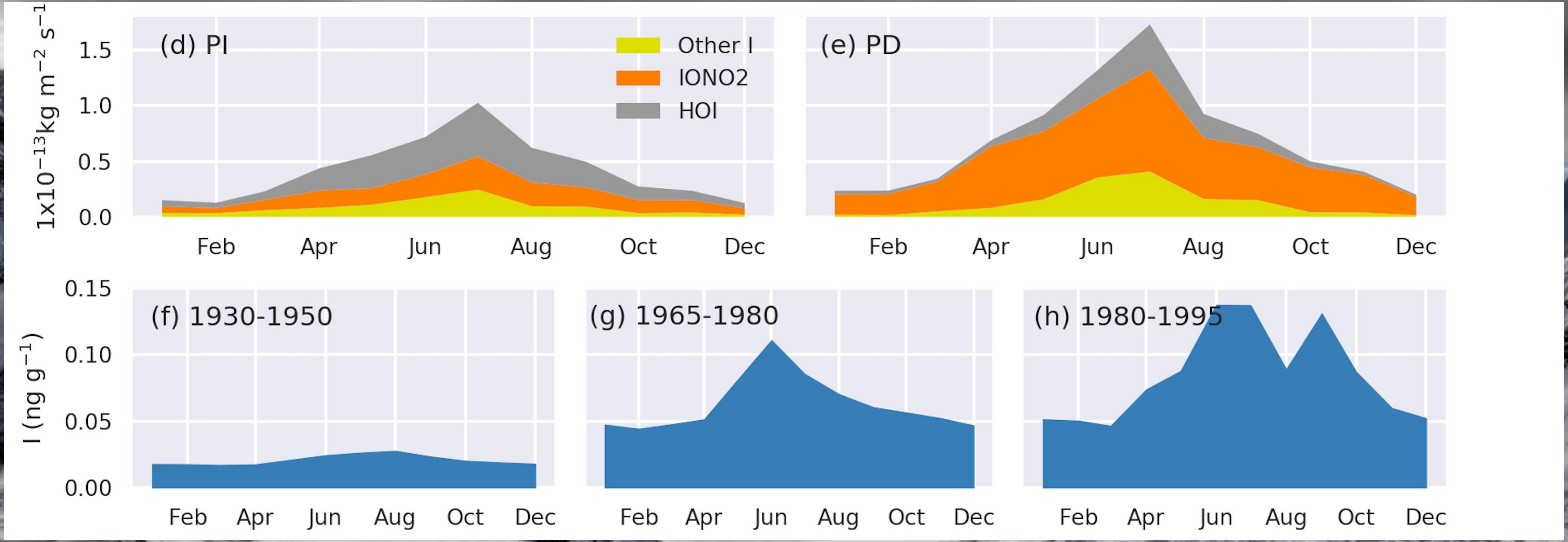
Pre-industrial -to- Present Day changes in iodine emissions





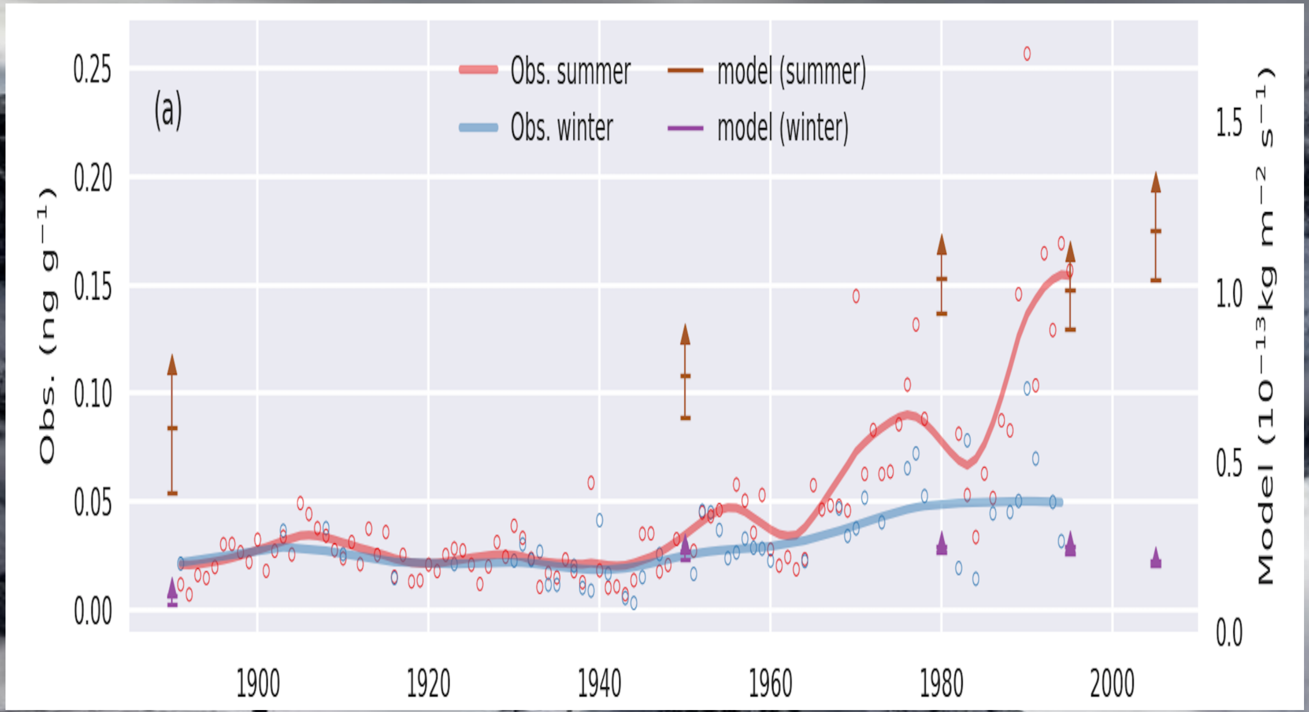
Legrand et al. PNAS, 2018

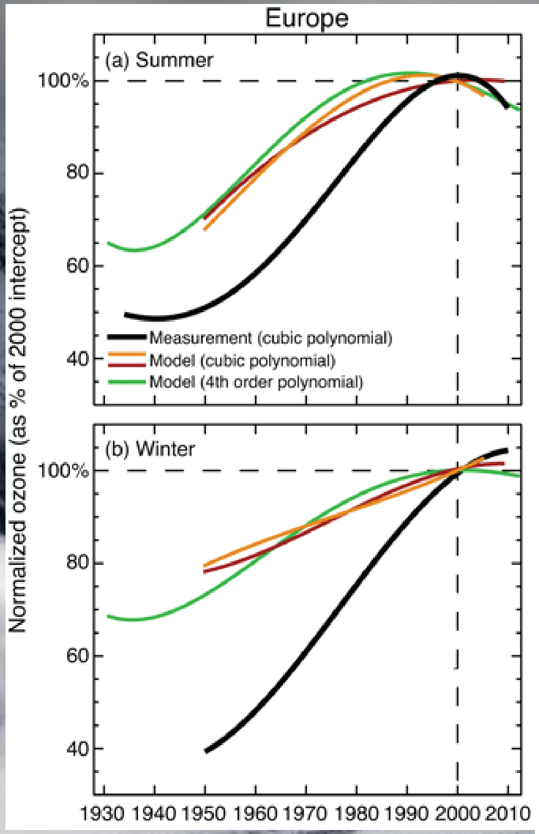
Pre-industrial and Present Day iodine deposition over Europe



Legrand et al. PNAS, 2018

Iodine time series and mid century O_3





Long-term changes in ozone at approximately baseline surface stations

Young et al. (2018) derived from Parrish et al. (2014)

Col du Dome

Legrand et al. PNAS, 2018

Summary

- Tropospheric halogen chemistry reduces both background marine O_3 and O_3 further inland.   Implications for air quality models
- Iodine has a double whammy role – atmospheric chemistry, ocean deposition
- Oceanic O_3 deposition is highly uncertain and difficult to measure, yet deserves more study
- Halogen chemistry has implications for 20th century trends in $O_{3,}$ not least due to increased oceanic iodine emissions

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THE UNIVERSITY of York

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The MILAN team:
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David Loades


Tomas Sherwen


Mat Evans


Rosie Chance


Liselotte Tinel


Adam Saint

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surface ocean solas lower atmosphere study

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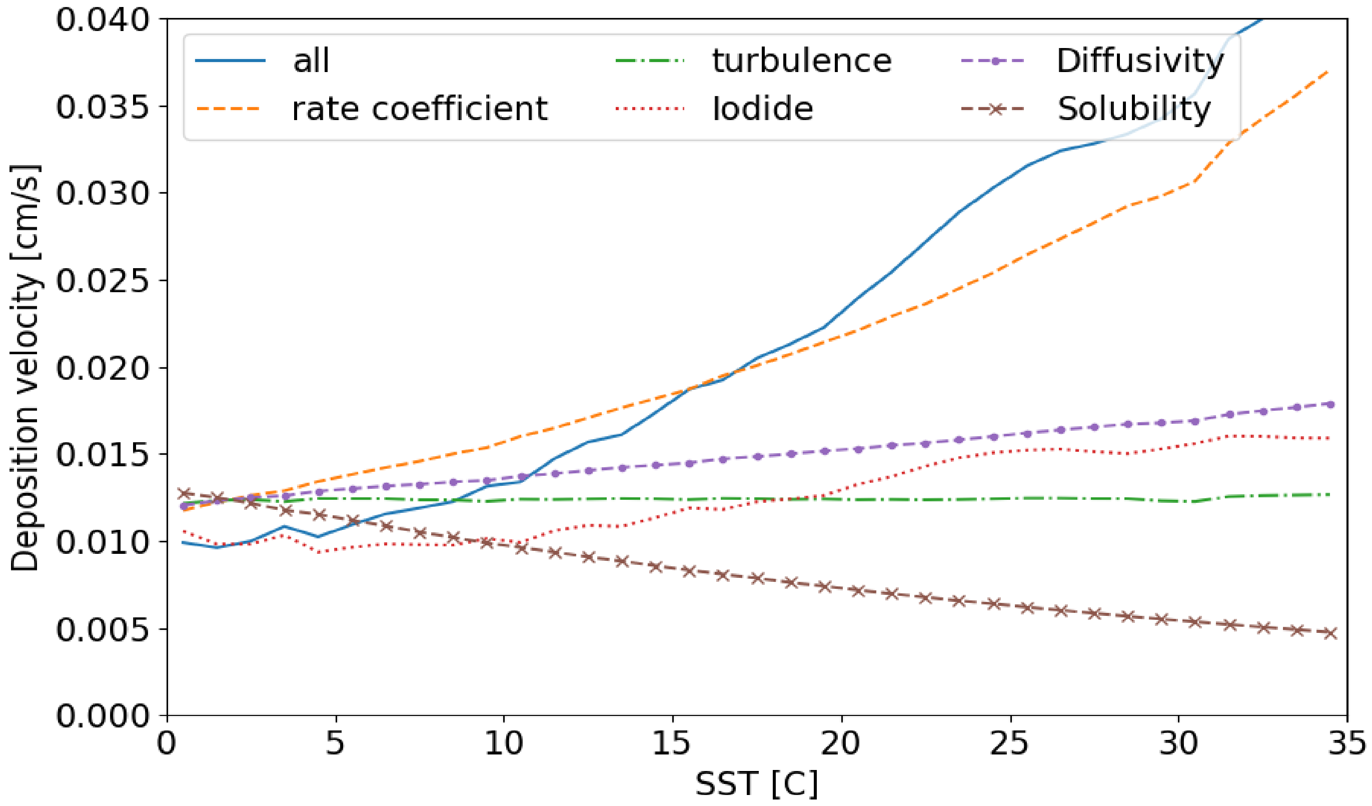
Calculated sensitivity of v_D to SST



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Cape Verde Observatory