Very short lived halocarbons (VSLH) in air and seawater

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Halocarbon air samples: TD-GCMS Unity2+CIA8-7890-5975C

- 1L sample volume
- Analysis frequency: 3-4 samples/hr

	CH_3I	$CHCl_3$	CHBrCl2	CH_2Br_2	CH_2ICl	$CHBr_2Cl$	CH_2IBr	$CHBr_3$	CH_2I_2
LOD (ppt)	0.014	0.102	0.114	0.019	0.007	0.015	0.018	0.018	0.007
LOQ (ppt)	0.024	0.169	0.190	0.032	0.012	0.026	0.030	0.031	0.011
%RSD	1.8	10.5	4.1	1.8	1.6	1.7	3.0	1.9	4.7

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Halocarbon seawater samples: AutoP&T-TD-GCMS Unity2+CIA8-6850-5975C

- Portable instrument can be operated from flight case
- Approx. 150kg
- Fully automated purge and trap system analyses 1-2 seawater samples/hr
- Fully automated from seawater inlet or semi-automated sampling from CTD samples
- Both instruments calibrated using NOAA SX-3570 cylinder and York permeation system (both ppt levels VSLH). See Jones et al., AMT, 2011.

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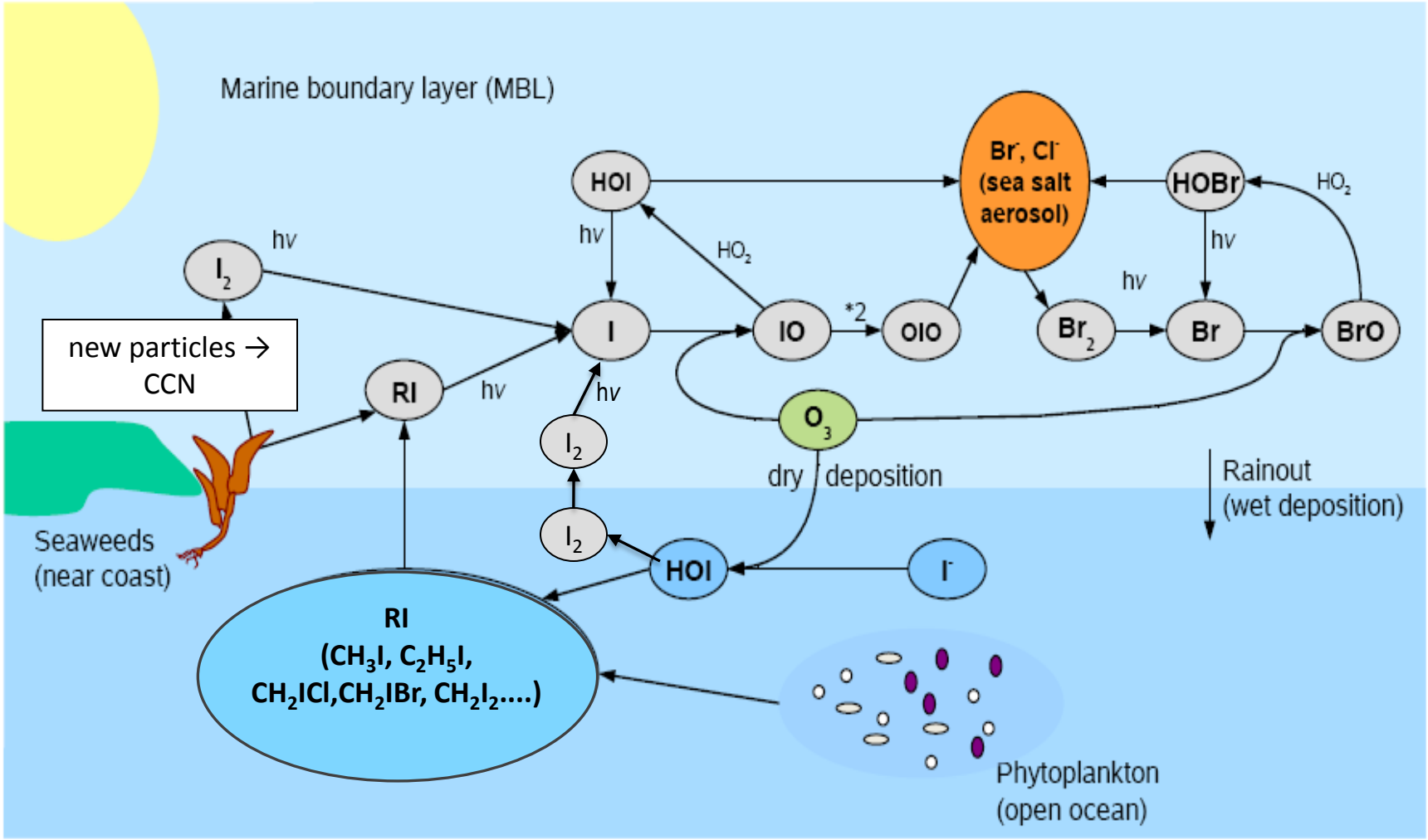
Marine boundary layer halogen chemistry



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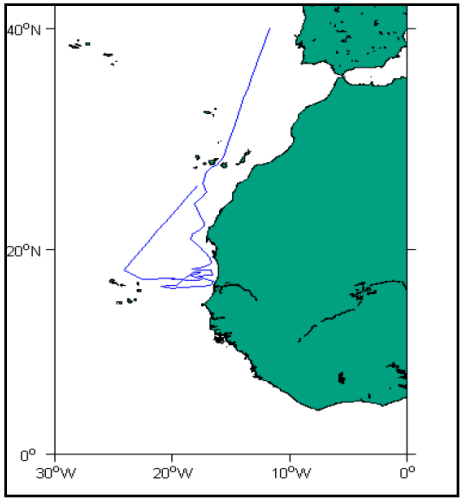
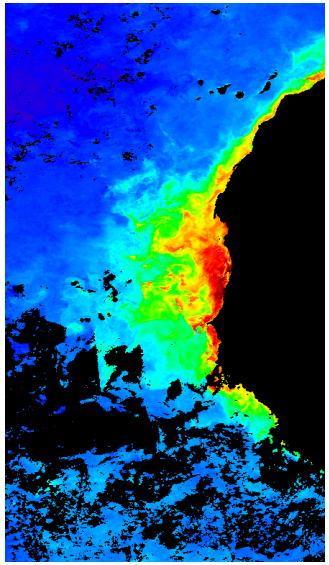
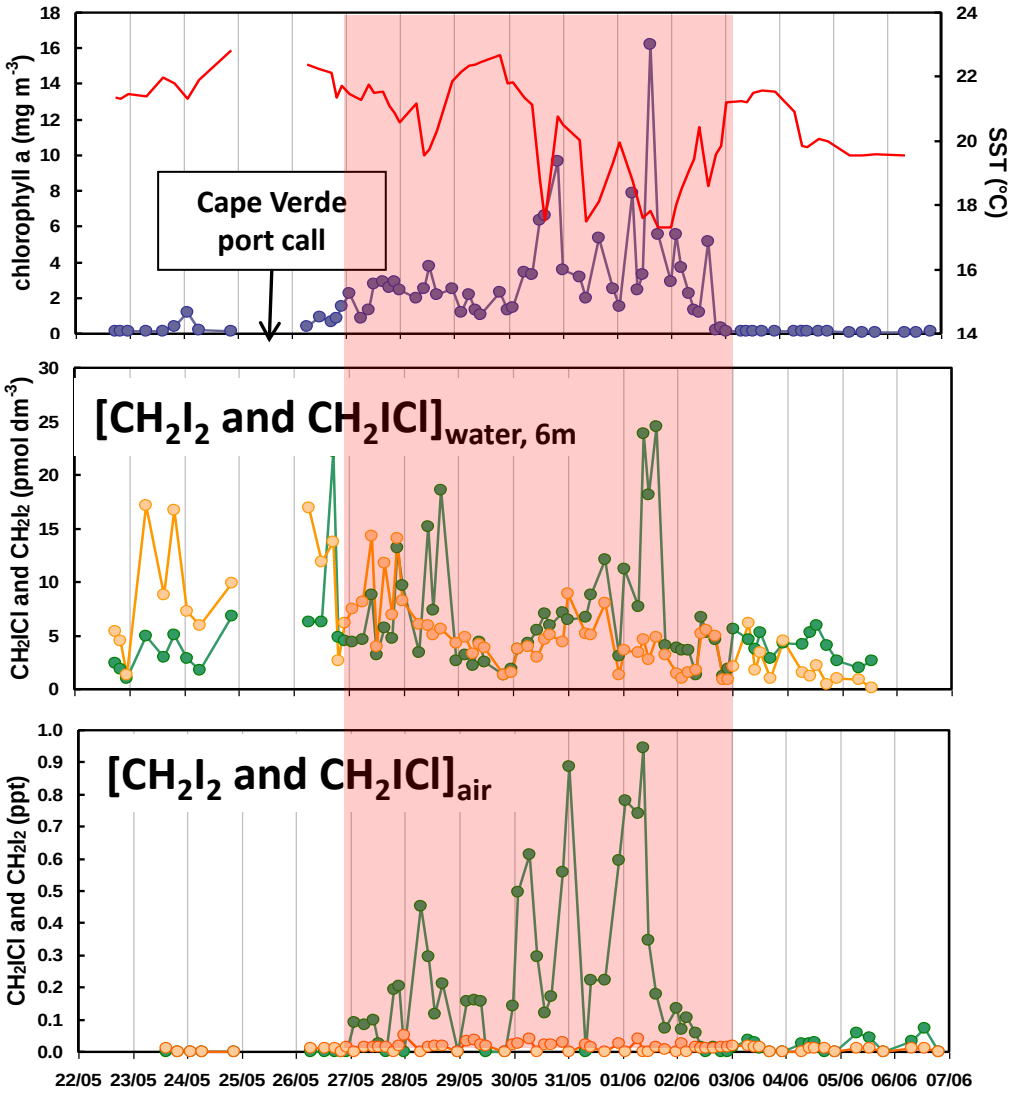
RHaMBLe: Dihalomethane concentrations in seawater and air

RHaMBLe Cruise: open ocean & Mauritanian upwelling

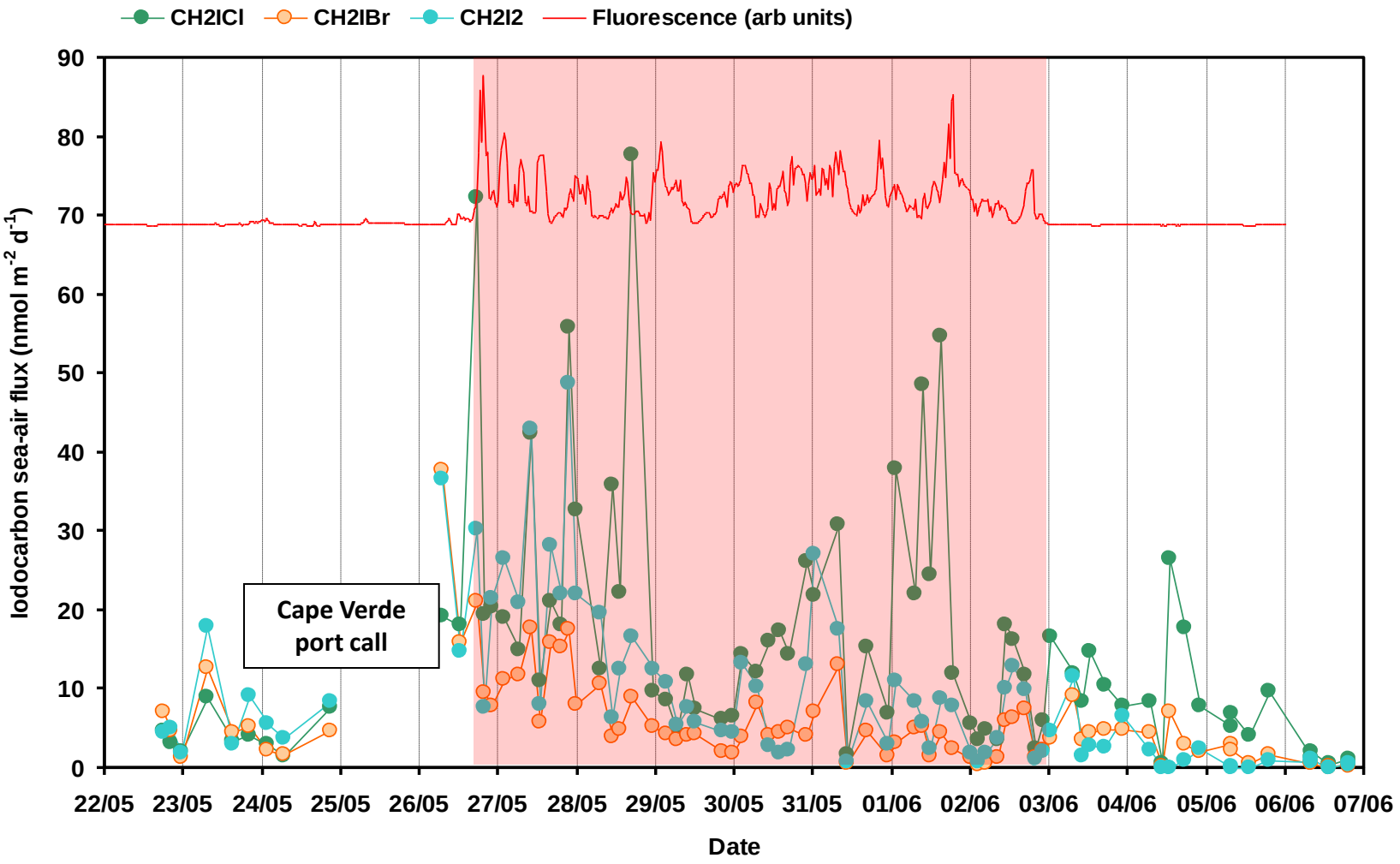




upwelling



Dihalomethane sea-air fluxes from RHaMBLe cruise



Fluxes calculated using the Nightingale 2000 approximation for the transfer velocity *k*w & the McGillis 2000 expression for the airside resistance *k*a

Photolysis of CH_2I_2 and CH_2I_2Cl in surface waters

$$CH_2I_2\ (aq) + h\nu + Cl^- \rightarrow 0.3\ CH_2ICl$$

τ ~ 10 mins at midday 53^{o}N at surface

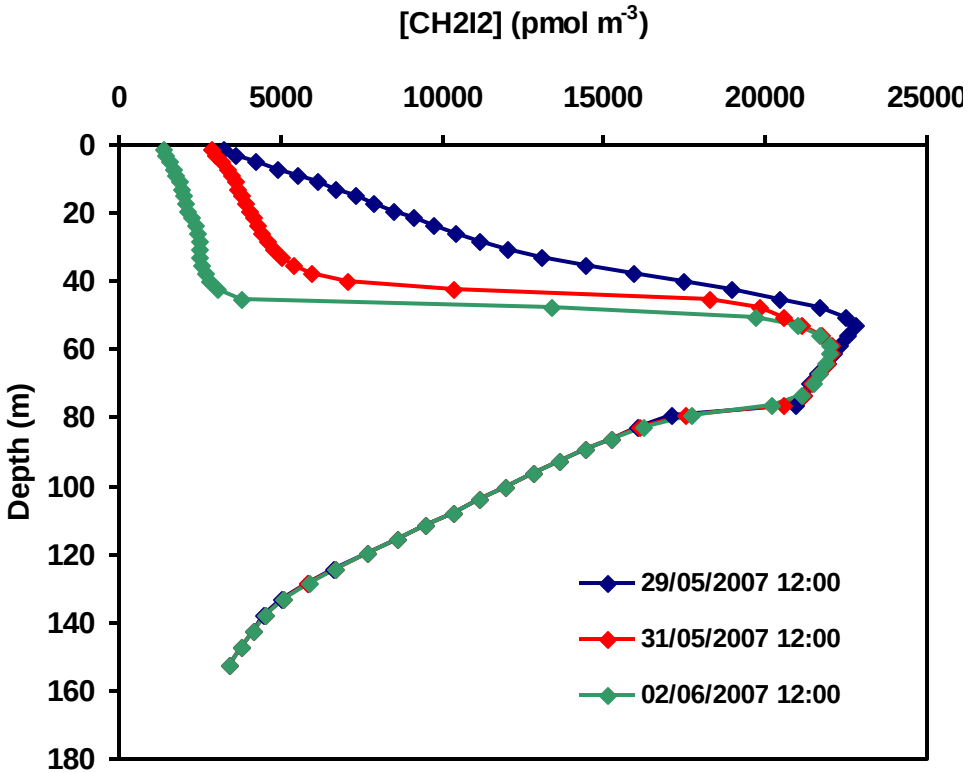
$$CH_2ICl\ (aq) + h\nu + Cl^- \rightarrow CH_2Cl_2$$

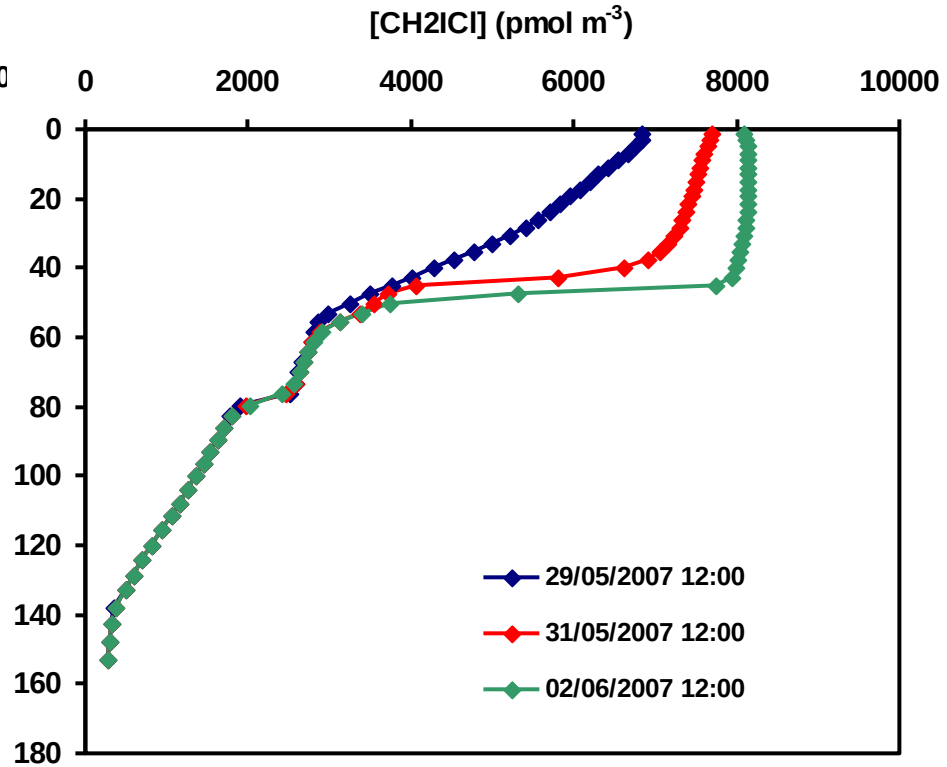
τ ~ 10 hrs at midday 53^{o}N at surface

1-D Model of Turbulent Vertical Mixing in the Oceanic Boundary Layer

- used to correct sub-surface [CH_2ICl] & [CH_2I_2] into equivalent surface concentrations

-model generates time-resolved depth profiles of CH_2I_2 & CH_2ICl within the top 150 m of the water column as a function of meteorological, biological & physical parameters





Absorption cross sections & photolysis quantum yields from Jones and Carpenter, *Environ. Sci. Technol.*, 2006.

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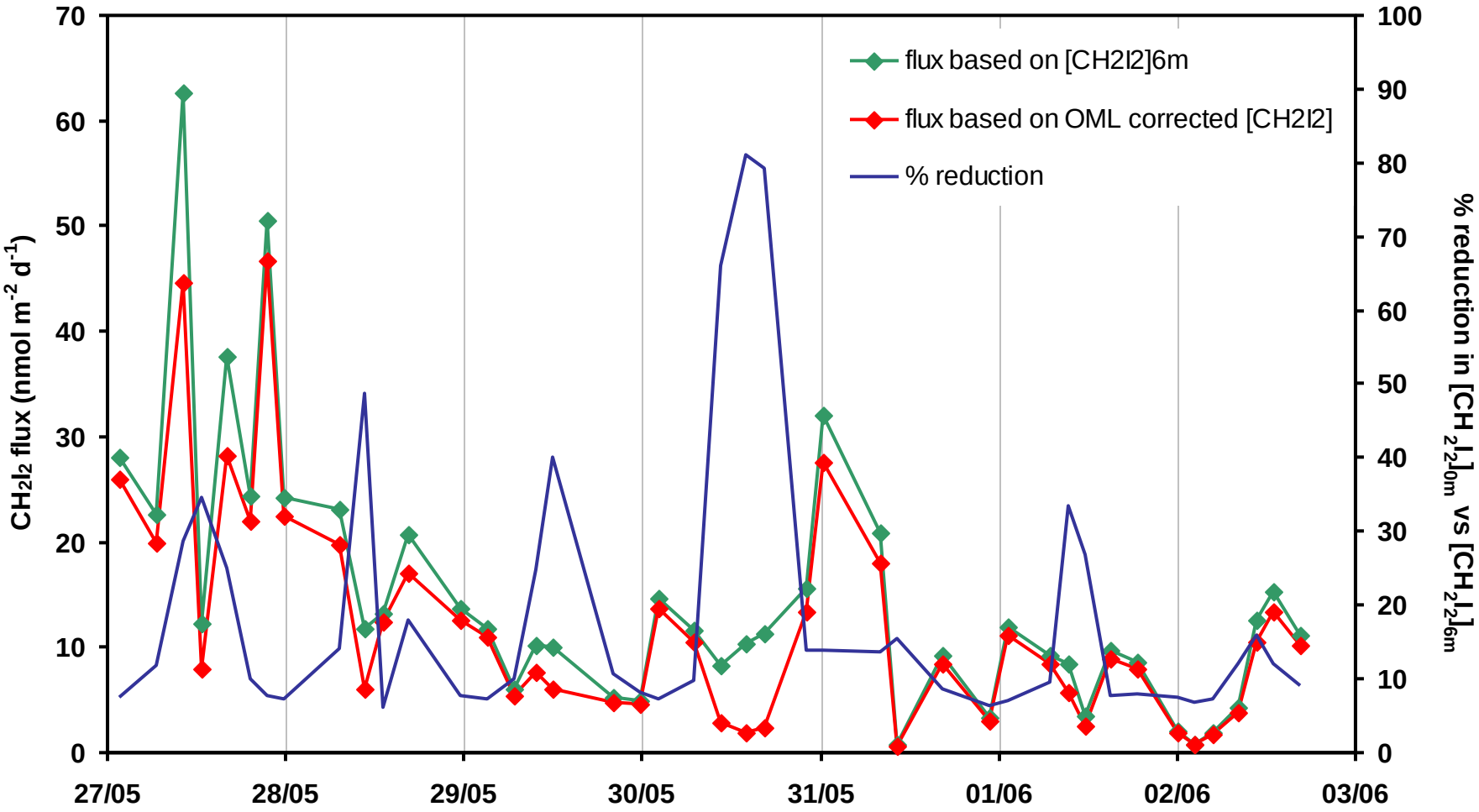
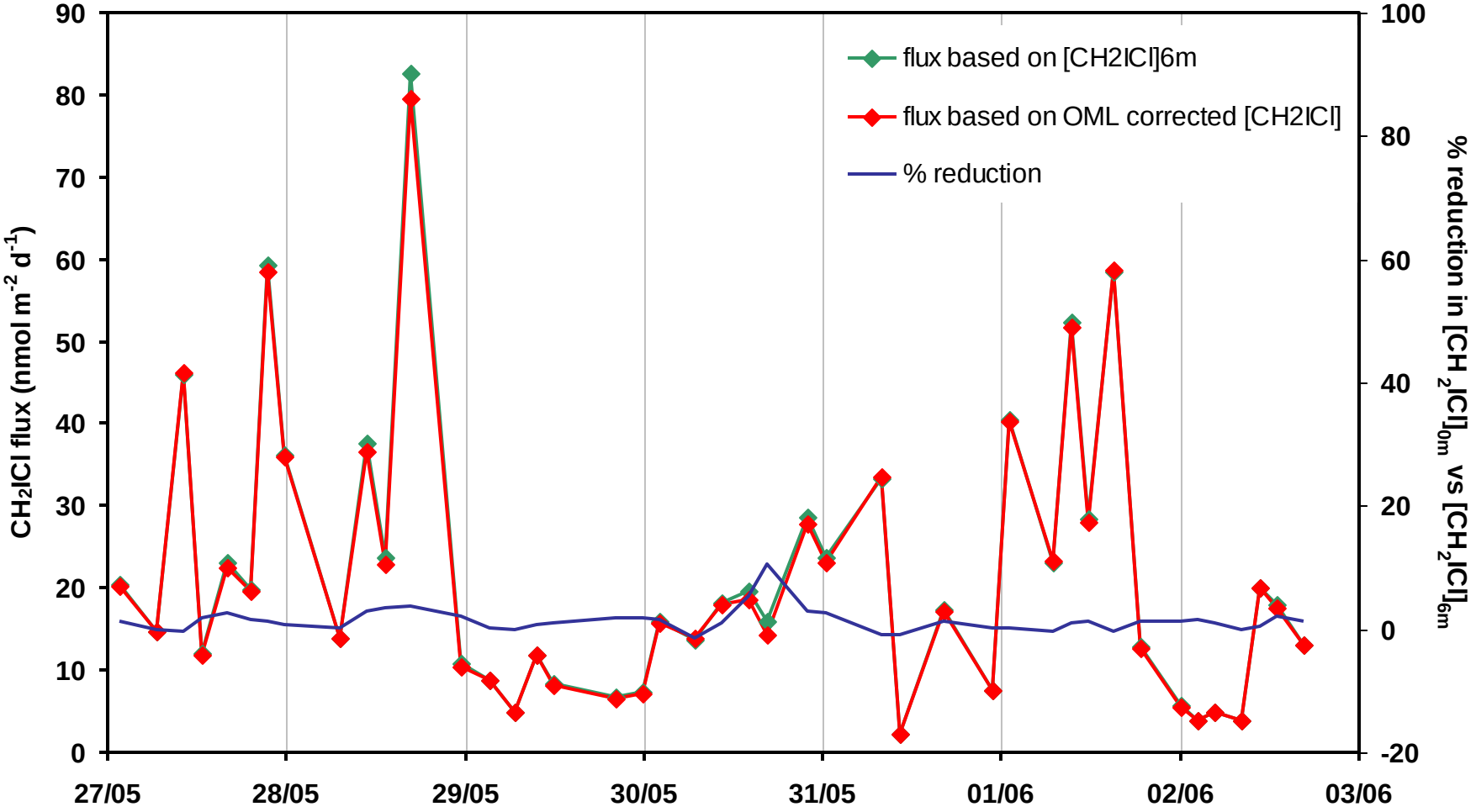
CH_2I_2 sea-air fluxes from the Mauritanian upwelling region



- Original mean CH_2I_2 flux from upwelling waters = 20.4 nmol m^{-2} d^{-1}
- Mean CH_2I_2 flux after correcting surface seawater [CH_2I_2] = 16.5 nmol m^{-2} d^{-1}

i.e. using sub-surface seawater [CH_2I_2] leads to an over-estimation of the CH_2I_2 flux of ~25%

CH_2ICl sea-air fluxes from the Mauritanian upwelling region



- Original mean CH_2ICl flux from upwelling waters = 21.6 nmol m^{-2} d^{-1}
- Mean CH_2ICl flux after correcting surface seawater [CH_2ICl] = 21.3 nmol m^{-2} d^{-1}

i.e. in the Mauritanian upwelling waters using sub-surface seawater [CH_2ICl] to calculate the sea-air flux does not lead to significant over- or under- estimation of the flux when averaged over a few days

Contribution of iodocarbons to the global iodine budget

Halocarbon	Open ocean flux (Gg I yr^{-1})	Shelf flux (Gg I yr^{-1})	Coastal flux (Gg I yr^{-1})	Upwelling flux (Gg I yr^{-1})	Total global Iflux (Gg I yr^{-1})	Mean sea-air flux (µmol I m^{-2} yr^{-1})
CH_2ICl	93.0	87.1	12.2	10.6	213	
CH_2I_2	169.0	34.8	6.3	12.8	221	
CH_2IBr	68.7	6.4	0.9	3.3	79	
Total (from CH_2IX)	**331**	**128**	**19**	**27**	**513**	
CH_3I	460	47	4	20	**531**	

Jones et al., GRL, 2010

Bell et al. 2002, Butler et al., 2007

272-546

Total (all iodocarbons)

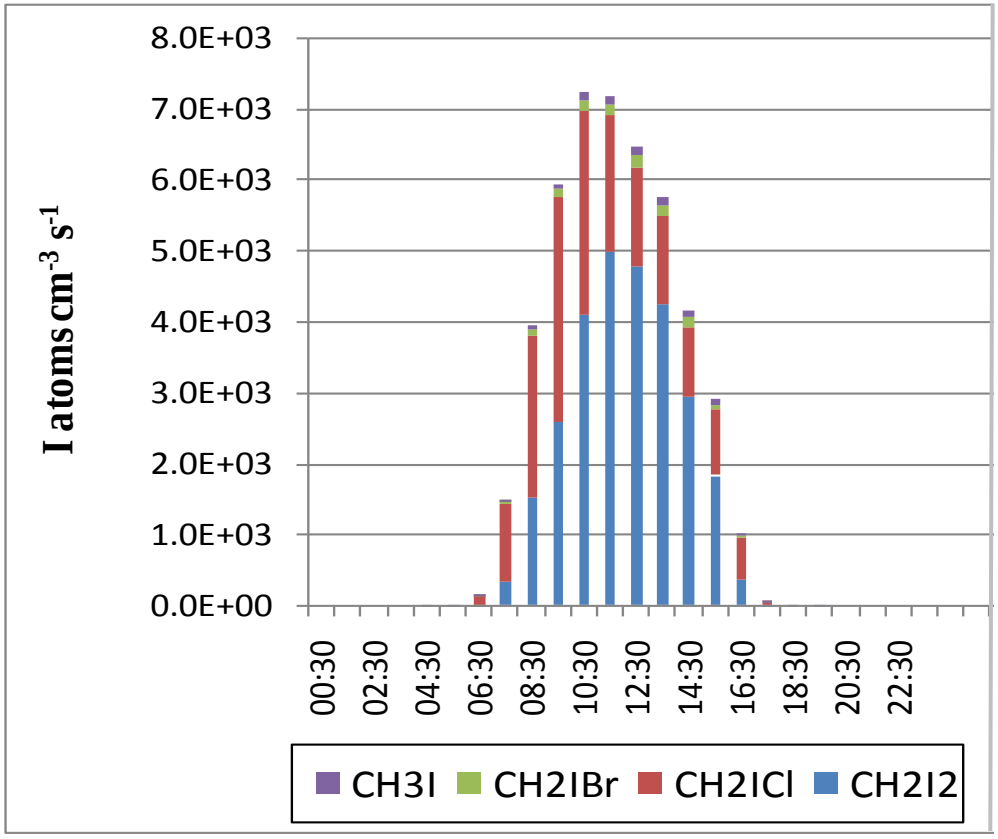
785-1060

17-23

Deposition in rain and aerosol () are the major routes for removal of iodine from the marine atmosphere[2] - total of **6.3 – 9.2 µmol I m^{-2} yr^{-1}** I^- and IO_3^-

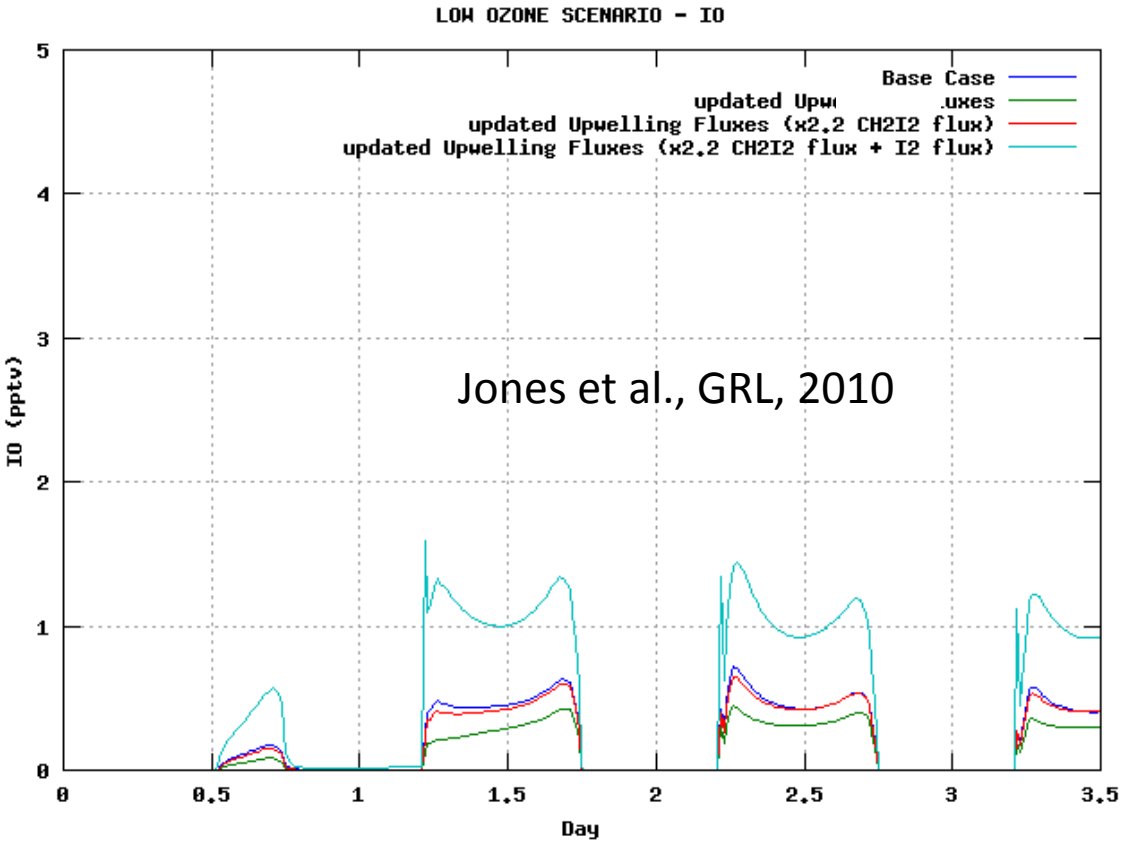
[2] Baker et al., JGR, 2001 results from southern North Sea

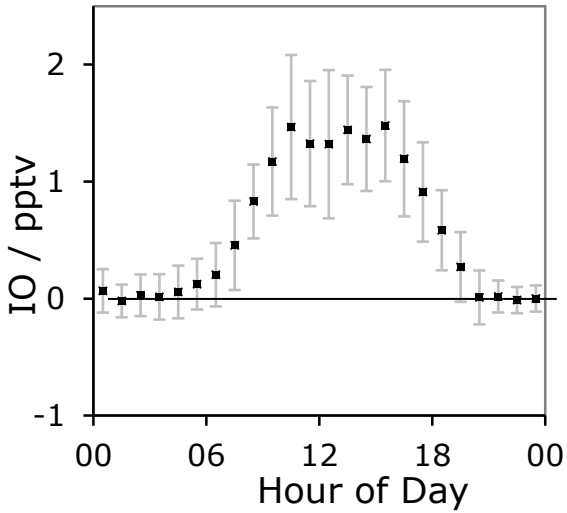
Contribution of iodocarbons to I atom production



- Instantaneous source rate of iodine atoms ~0.7 x10^4 atoms cm^{-3}

MISTRA results – R. von Glasow and R. Sommariva





- LP-DOAS results

J. Plane group

"Base Case" – Vogt et al. (1999) organoiodine fluxes

Upwelling fluxes

To match CH_2I_2 in air observations

x 2.2 CH_2I_2 flux + 80 µmol I m^{-2} yr^{-1} (as I_2)

U York contributions to TORERO

Data outputs:

- Underway seawater and air sampling of a range of VSLH: $CHCl_3$, $CHBrCl_2$, CH_2Br_2, $CHBr_2Cl$, $CHBr_3$, CH_3I, C_2H_5I, CH_2IBr, CH_2ICl, CH_2I_2
- Depth profiles of VSLH concentrations in seawater collected via CTDs
- Net sea-air fluxes of VSLH

Science outputs:

- Horizontal gradients in [VSLH] from open ocean to coastal upwelling
- Vertical gradients in [VSLH]. Comparison with Chl a fluorescence would allow an evaluation of the role of biological production in VSLH production
- Variation in chemical speciation of [VSLH] in different environments
- Comparison of Pacific with Atlantic VSLH sea-air fluxes

VSLH intercalibration:

- We can ship a 3L Silco can of pptv level VSLH (ca. 30 psi, previous tests show stable for months) to Elliot Atlas and Eric Apel for intercomparison purposes

U York questions for TORERO

Logistical:

ACCESS to Joint Base Pearl Harbor-Hickam

Lab space. We need approx 1.1 x 1 m floor space and 1.5 m x 25" bench space in wet lab (for latter, looks like fixing pins are in the way). Please confirm space is available and for bench space, that pins can be removed.

Where can we put gas cylinders? What length of gas lines will we therefore need?

Air sampling line. We need a good approximation (+/- 2 m) of length required for air sampling line from air inlet at bow of ship to wet lab (incl. round corners etc.)

What load can we put on ship's UPS?

We'd like to maintain air measurements from Costa Rica – Hawaii. Requires access to GC-MSs over internet. What internet access is available?

Other:

A measurement of Chl a fluorescence (calibrated) at least in CTD samples, ideally also within underway seawater samples, would be highly beneficial to the project. Is anyone going to be doing this?