TORERO 2012 – KA'IMIMOANA

Ocean/MBL dynamics and distribution of very short-lived organic halogen species

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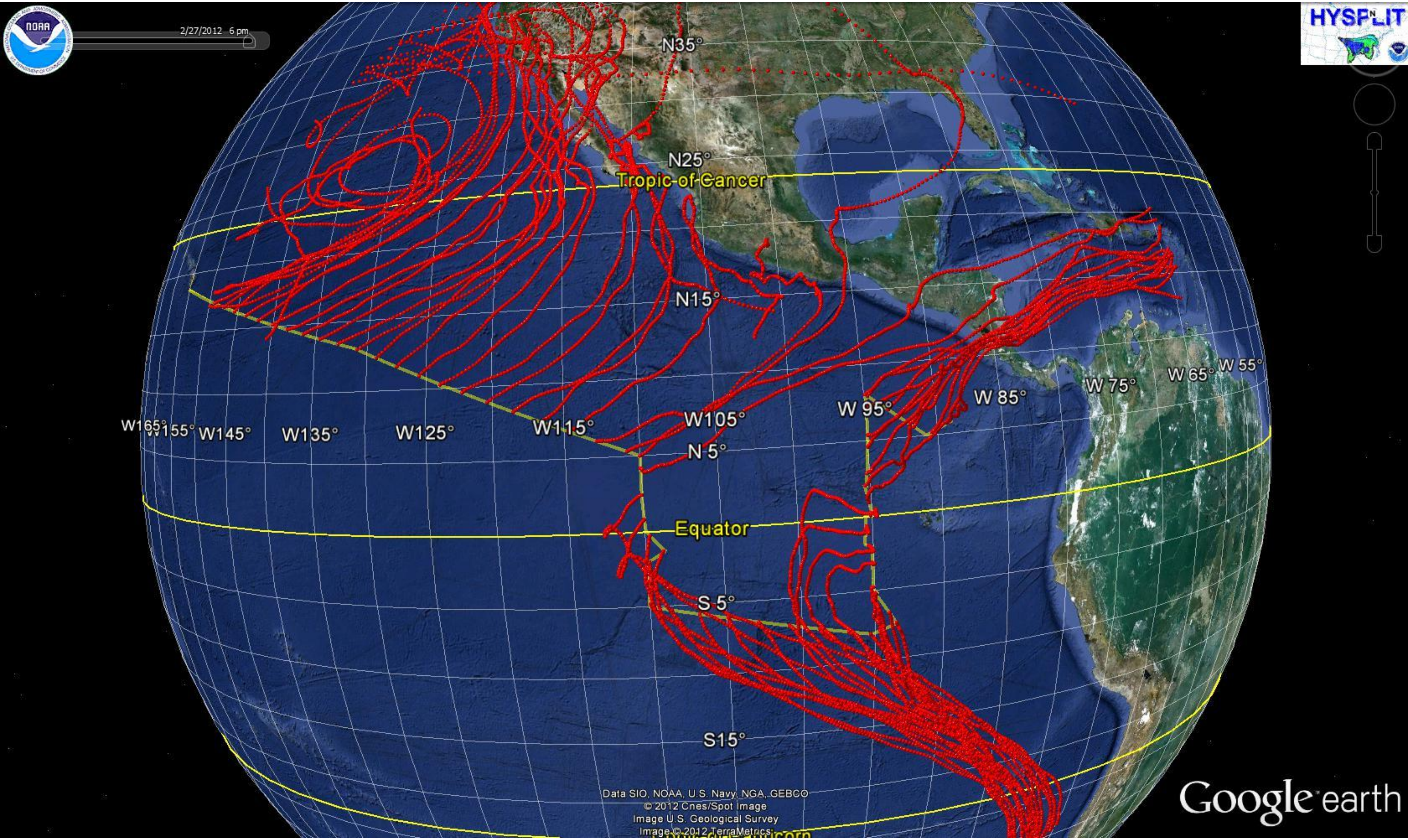
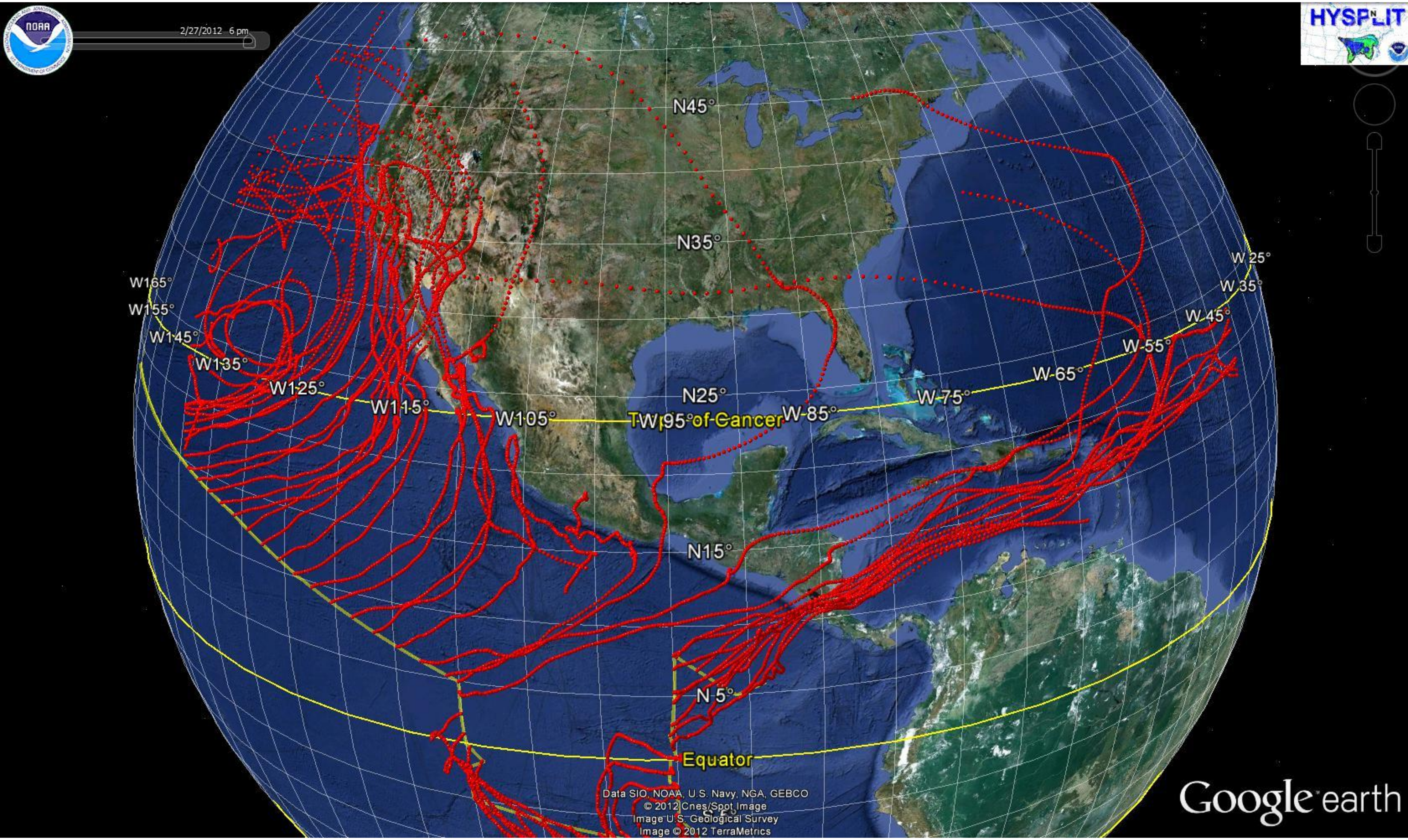
NATURAL ENVIRONMENT RESEARCH COUNCIL

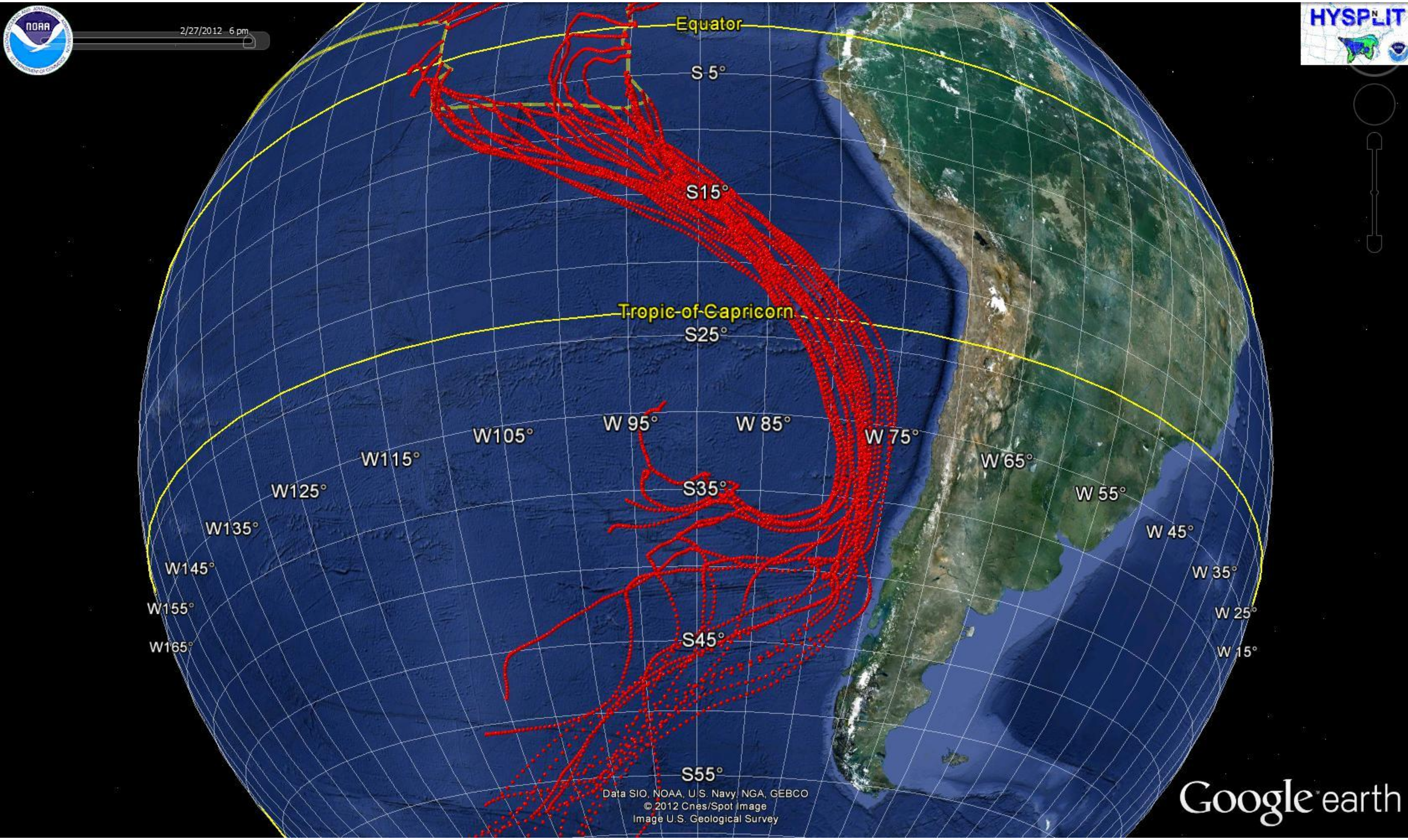
NOAA HYSPLIT modelled backward trajectories



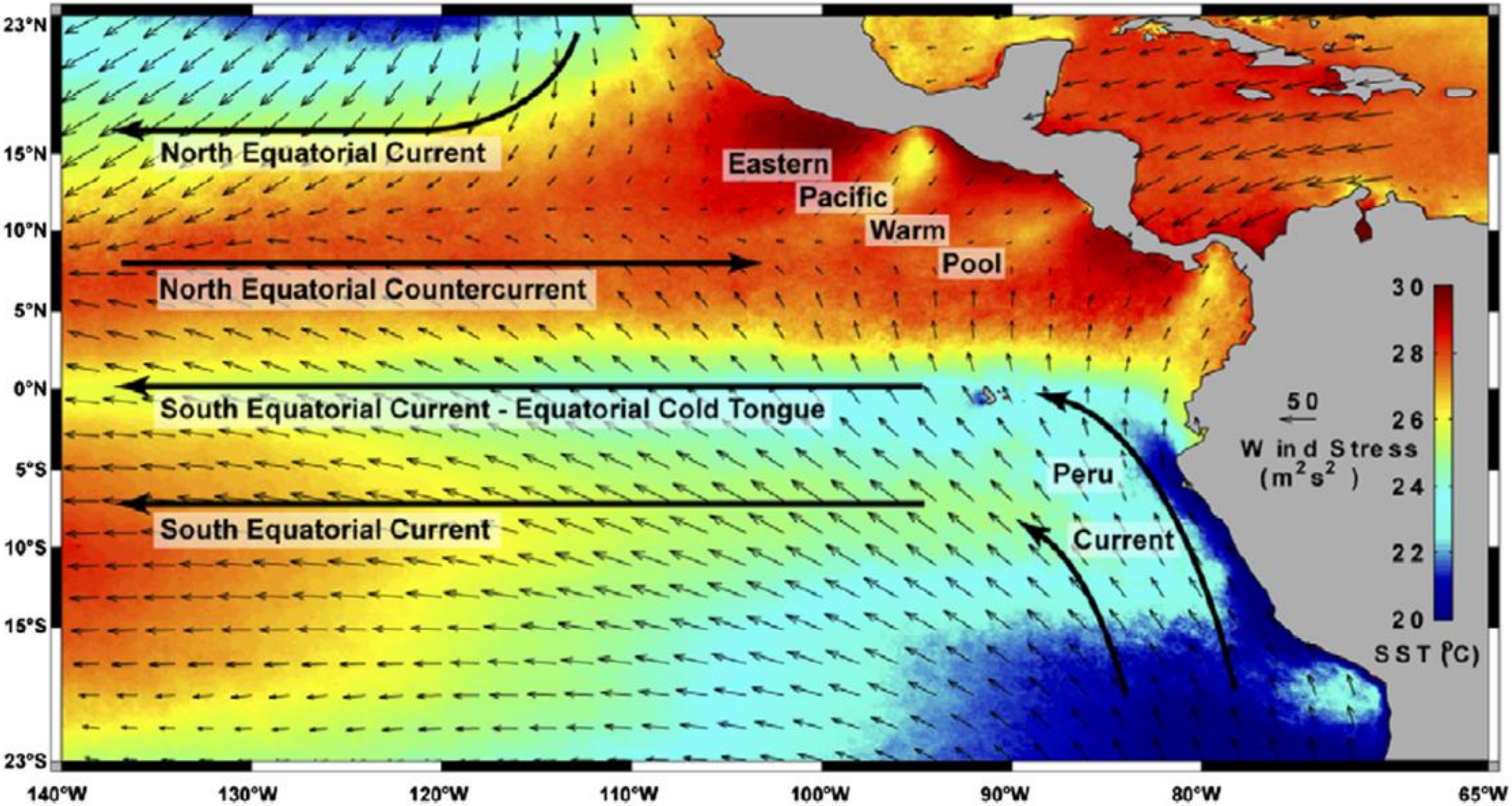
Northern Hemisphere back trajectories



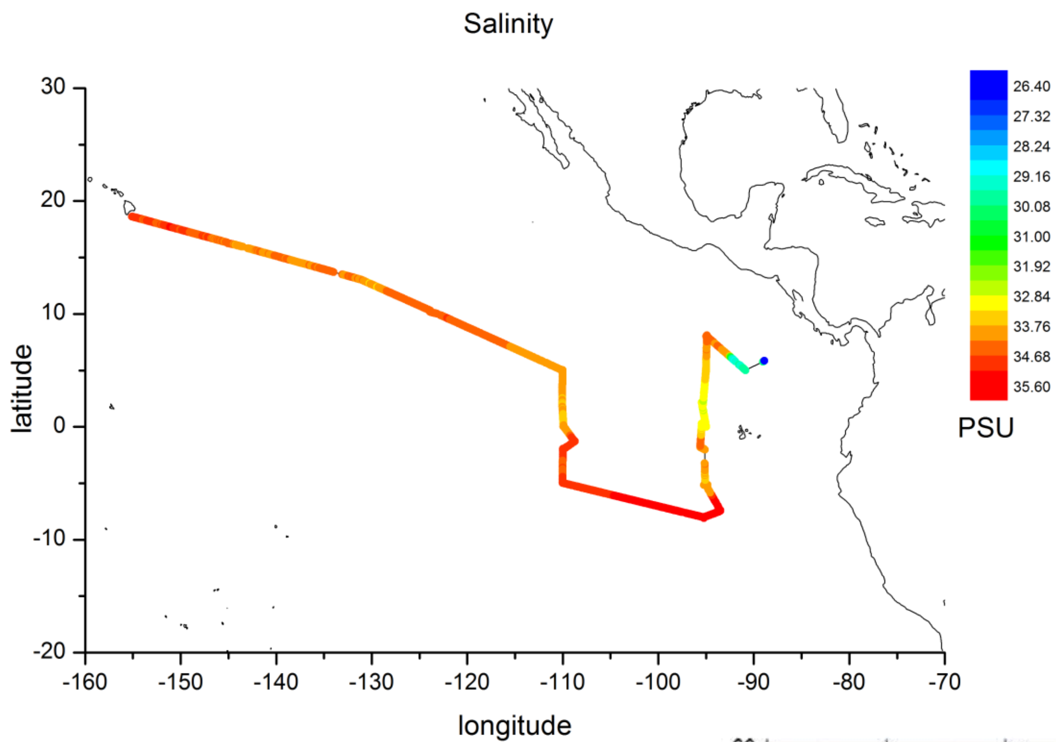
Southern Hemisphere back trajectories



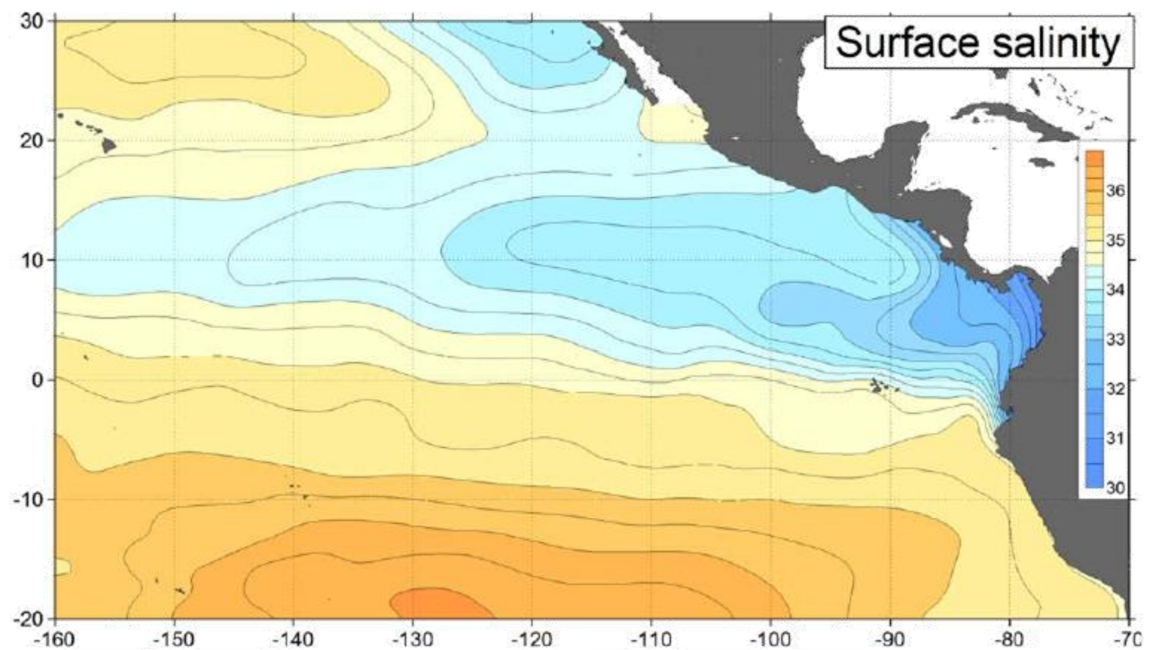
East Tropical Pacific - Ocean regimes



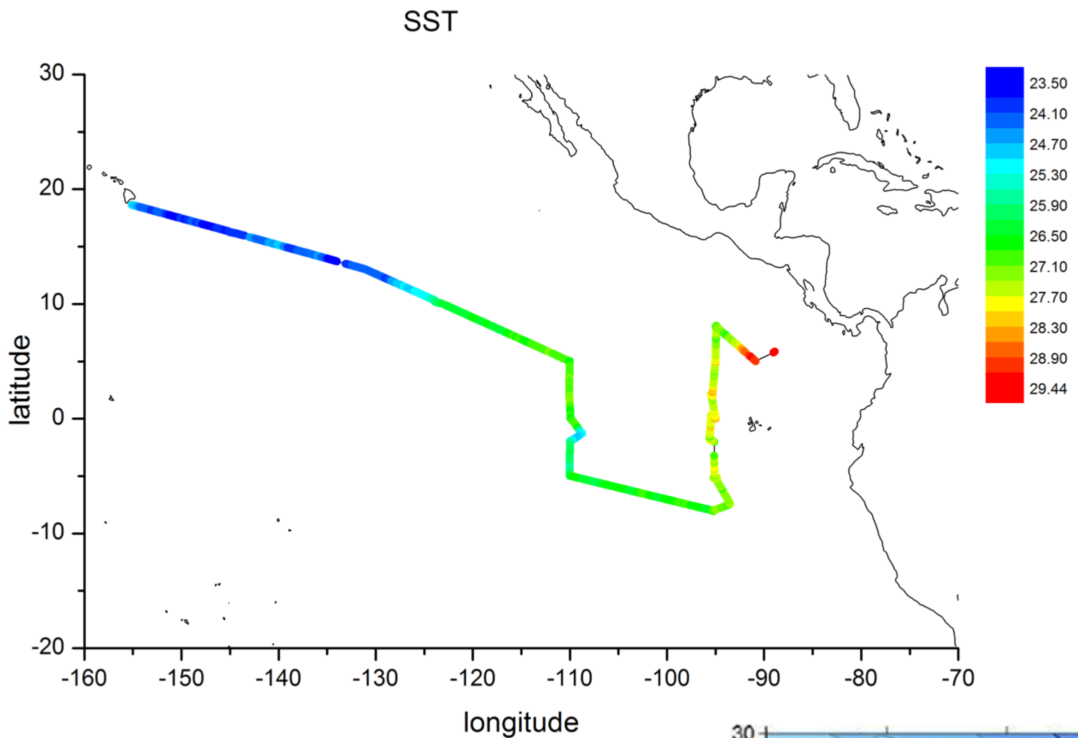
Fiedler et al. 2006, Penington et al. 2006

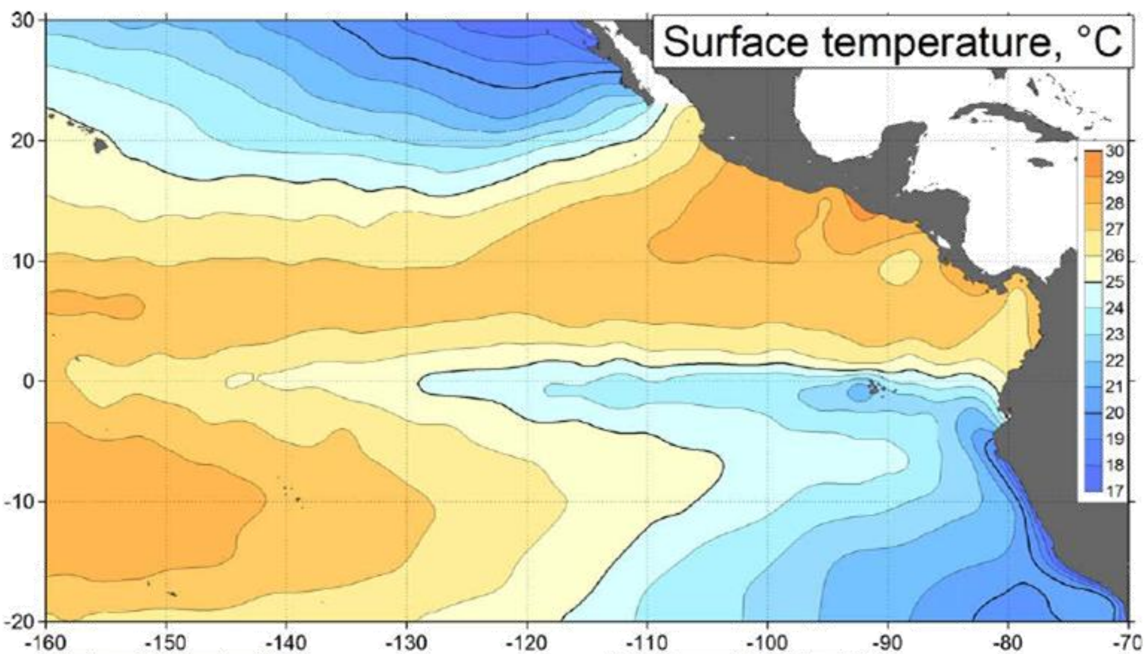


Salinity
30
20
10
0
-10
-20
latitude
-160
-150
-140
-130
-120
-110
-100
-90
-80
-70
longitude
26.40
27.32
28.24
29.16
30.08
31.00
31.92
32.84
33.76
34.68
35.60
PSU

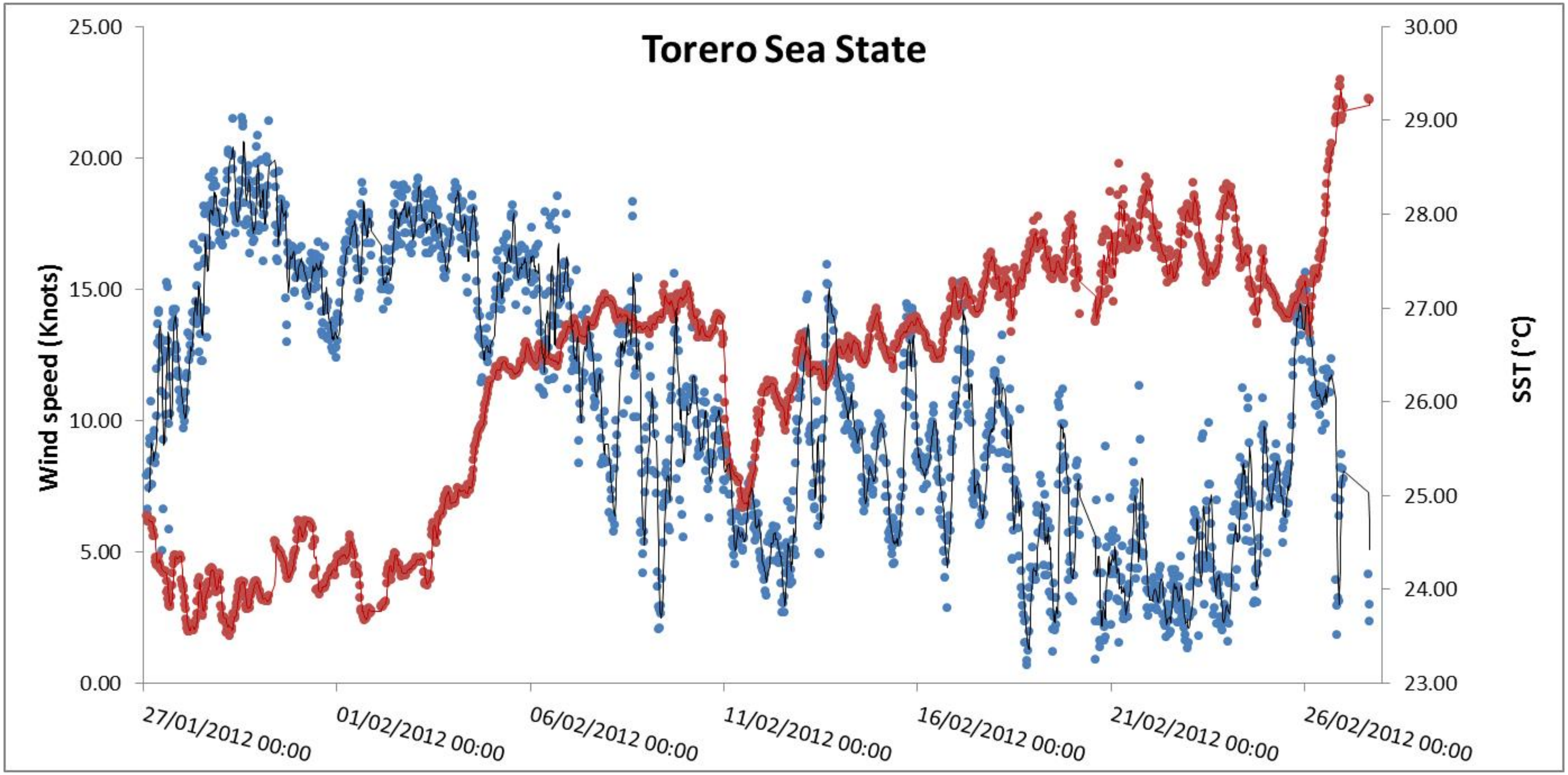


Surface salinity
30
20
10
0
-10
-20
-160
-150
-140
-130
-120
-110
-100
-90
-80
-70
36
35
34
33
32
31
30


SST
latitude
longitude
23.50
24.10
24.70
25.30
25.90
26.50
27.10
27.70
28.30
28.90
29.44

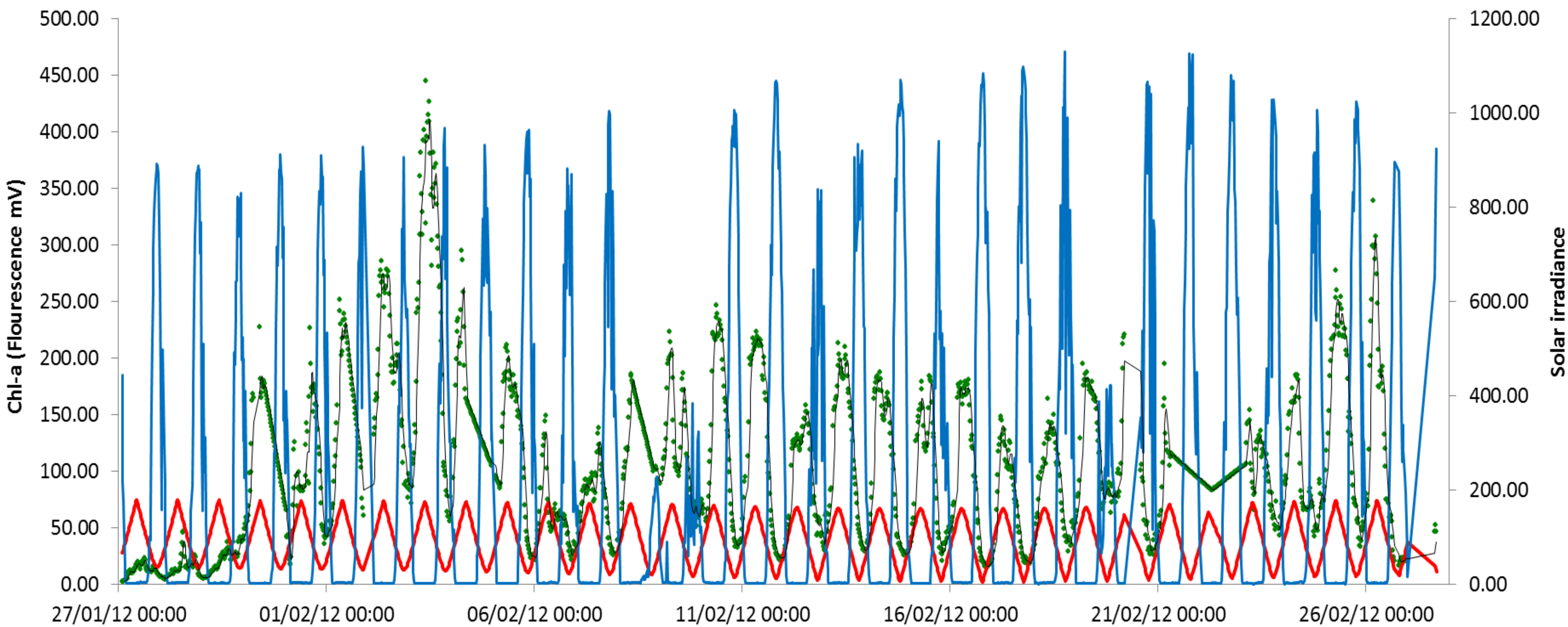

Surface temperature, °C

Wind speed and Sea surface temperature



- Wind speed was highest at the beginning of cruise and decreased as we sailed east
- Sea state went from 10ft+ waves to millpond flat toward the Duldrums

In-situ Chl-a Vs satellite retrieval

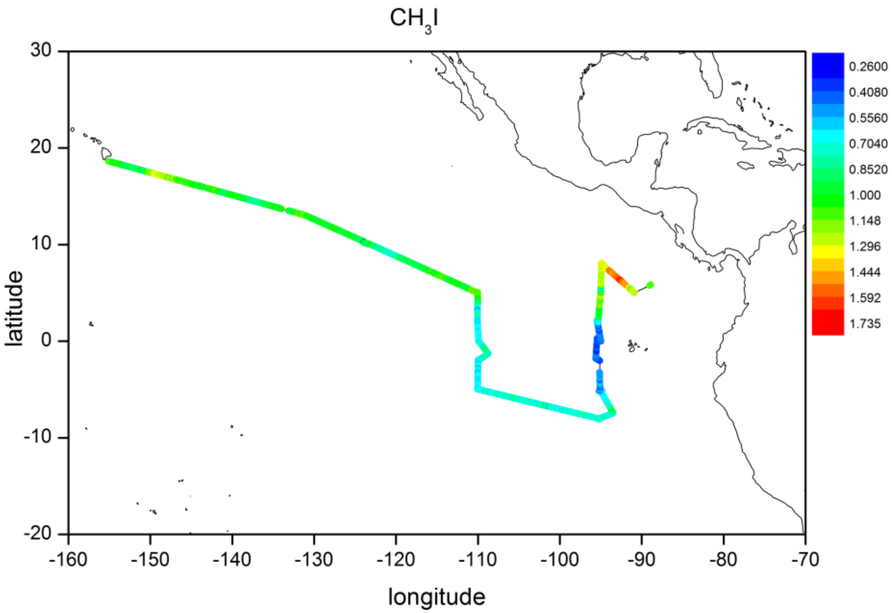


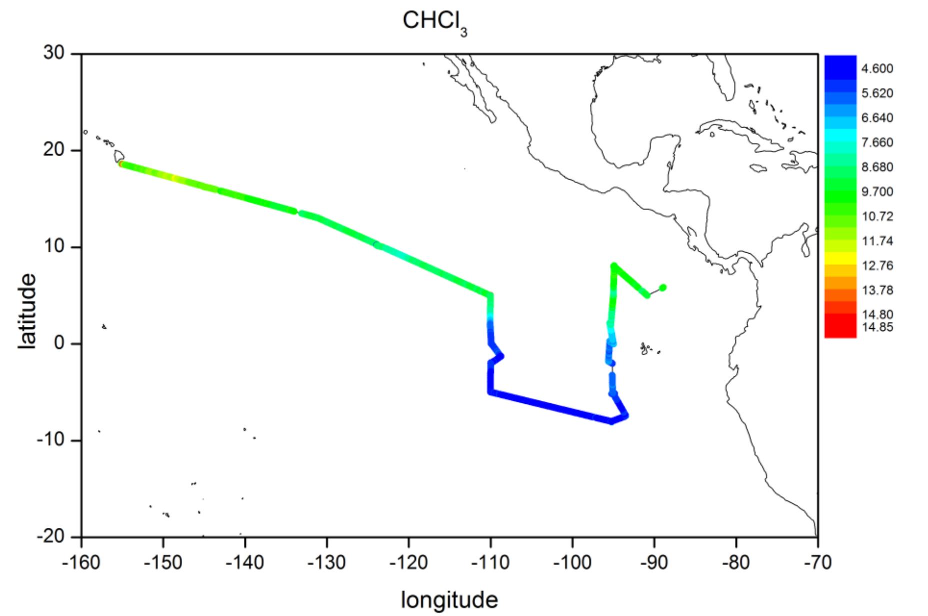
- Strong diurnal cycle could be due to greater mixing of cold nutrient rich water at night as surface cools which could be missed by averaging of remote sensing data

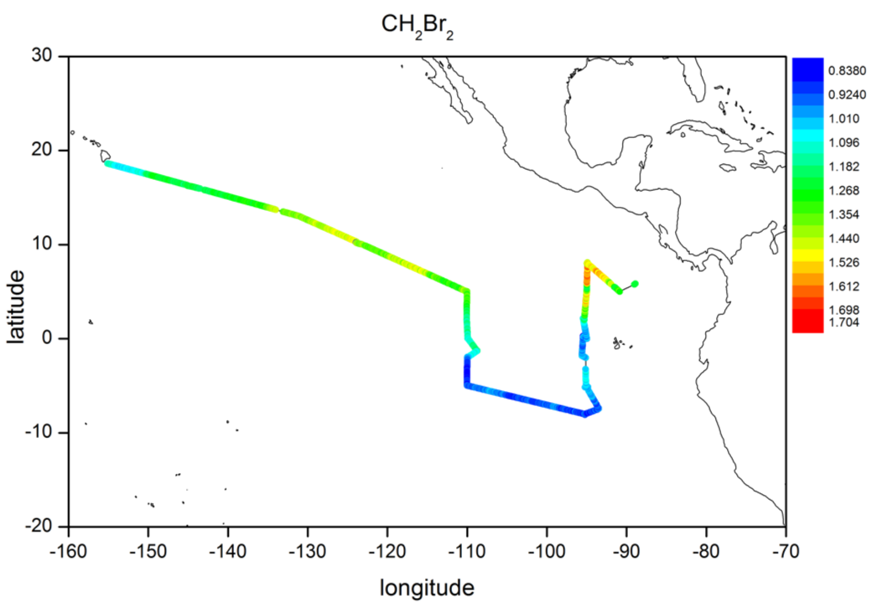
Or…

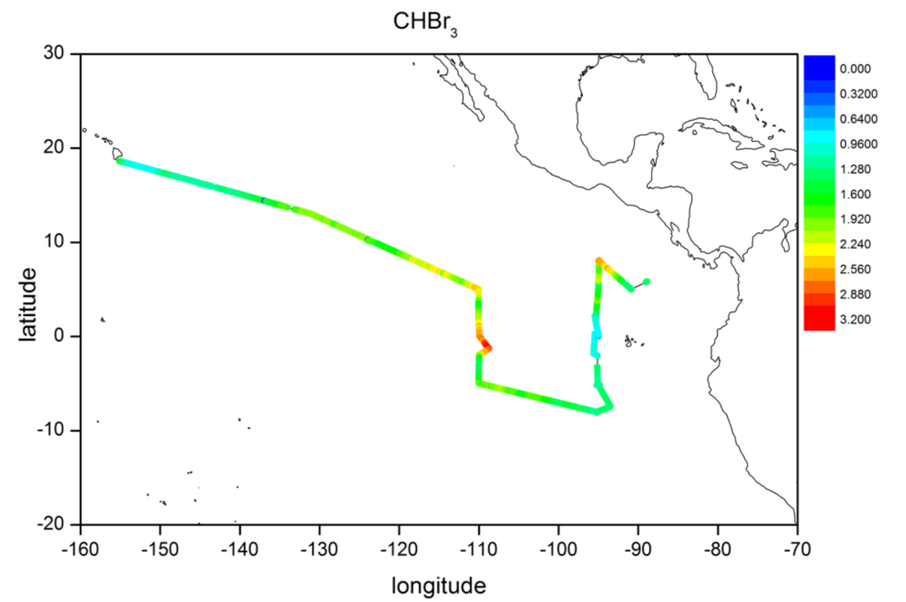
- Phytoplankton response to sunlight is to temporarily reduce their in vivo fluorescence per unit of extractable chl-a as a means of dissipating excess energy

VSLH Air concentrations

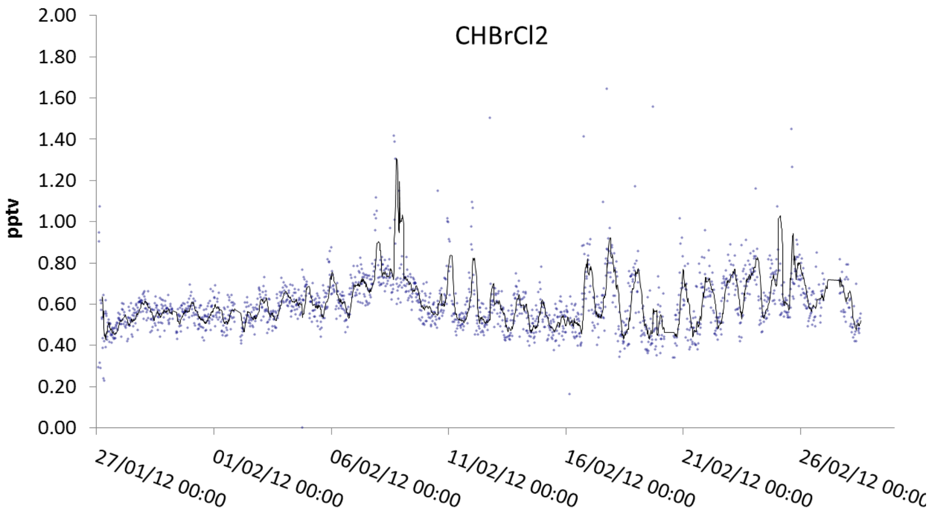


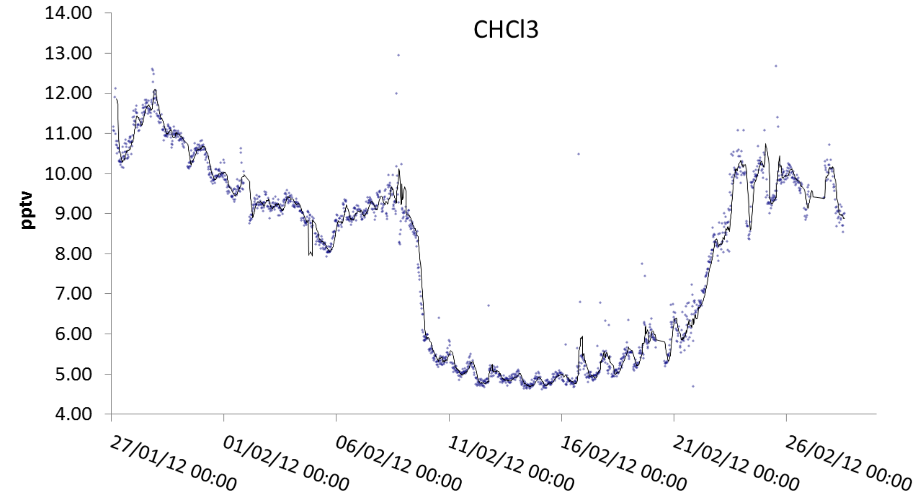


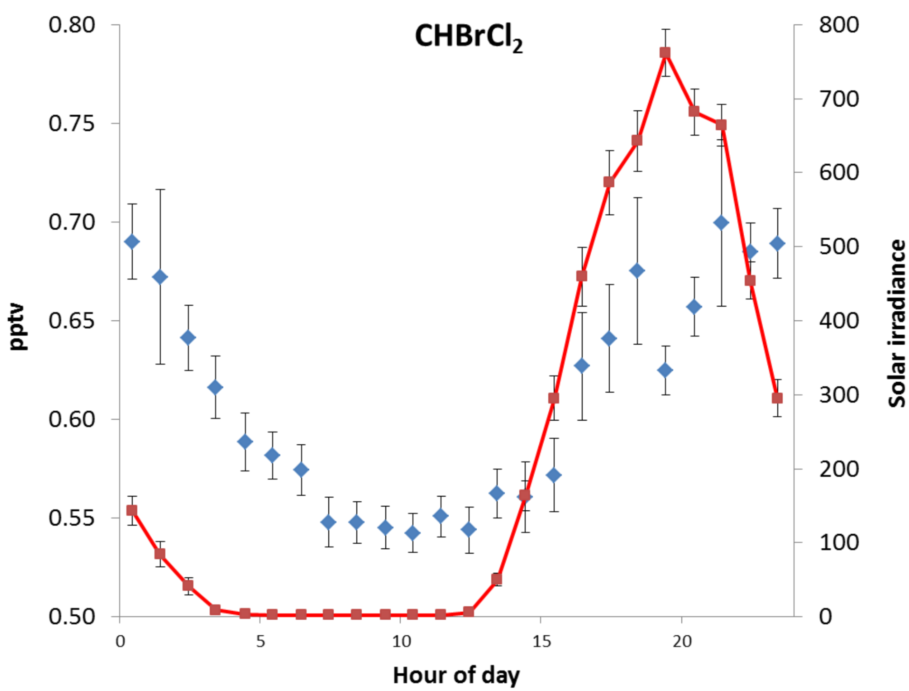




Photolytic production of bromo and chlorocarbons?

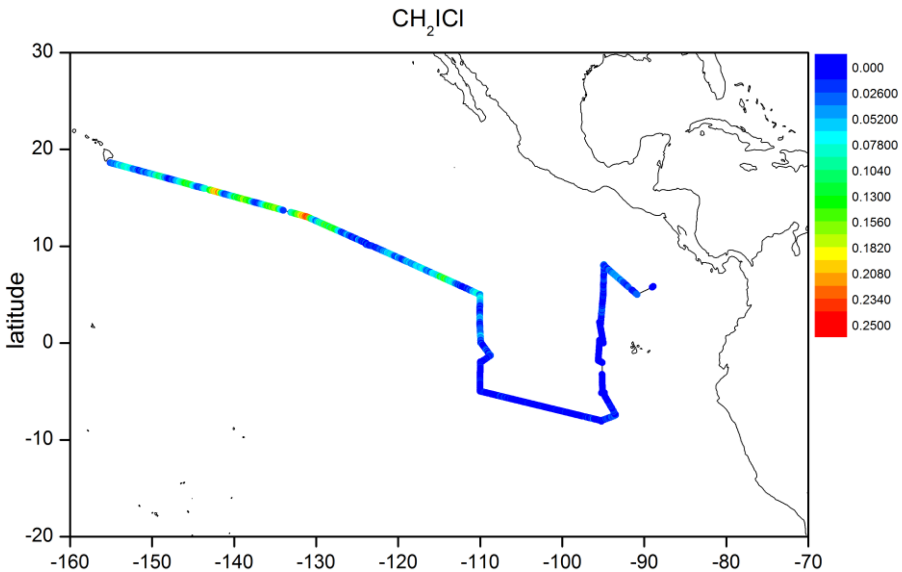


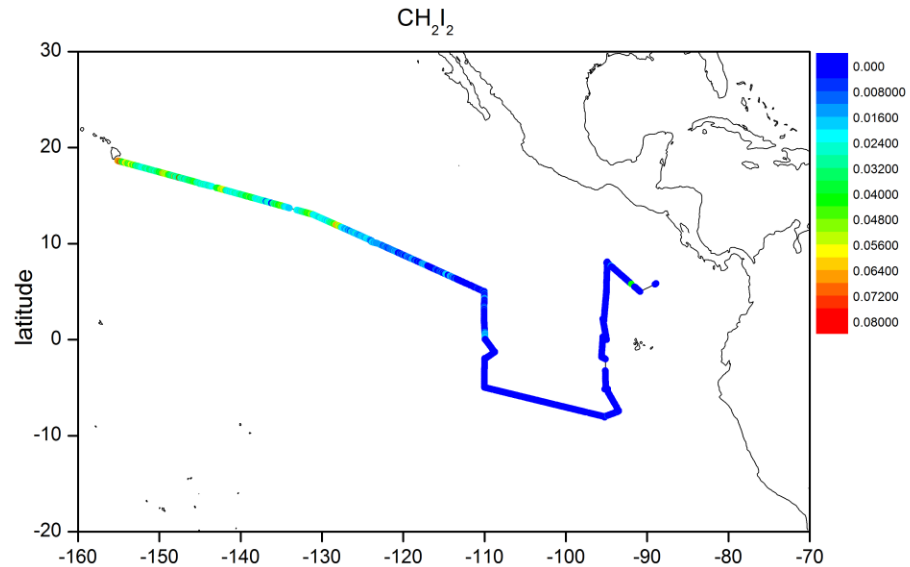


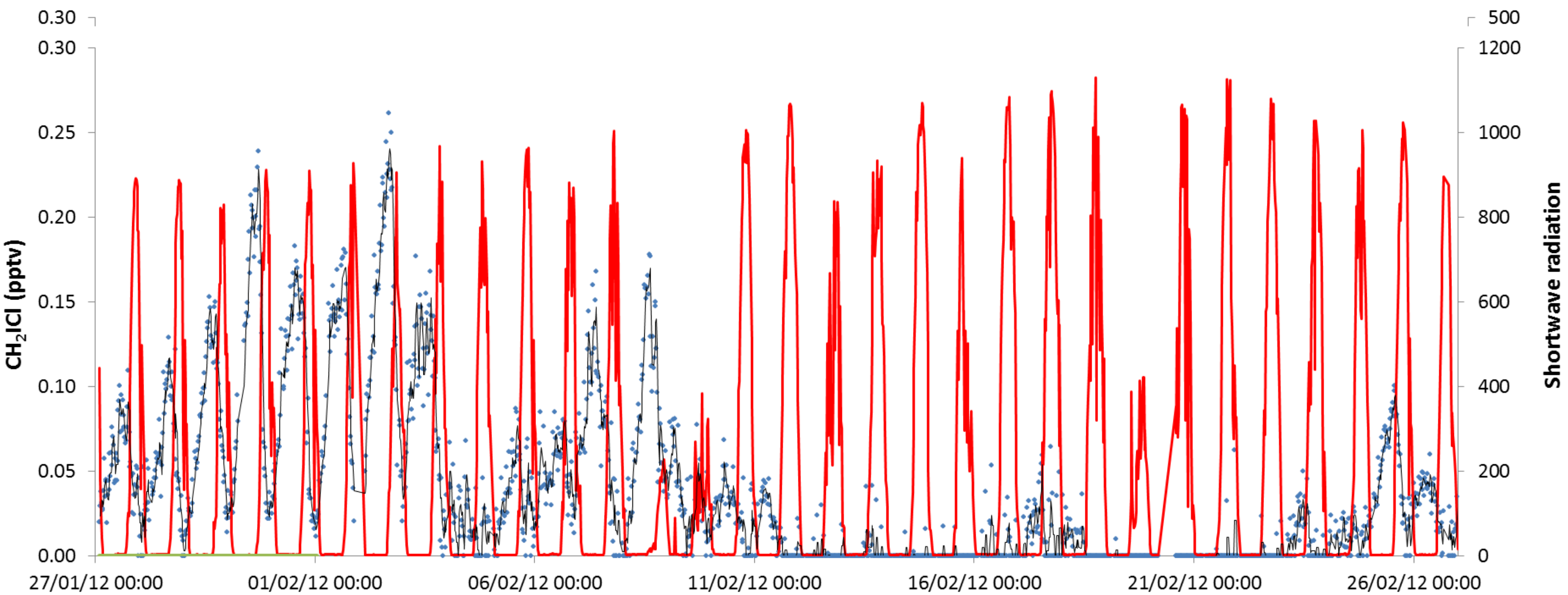


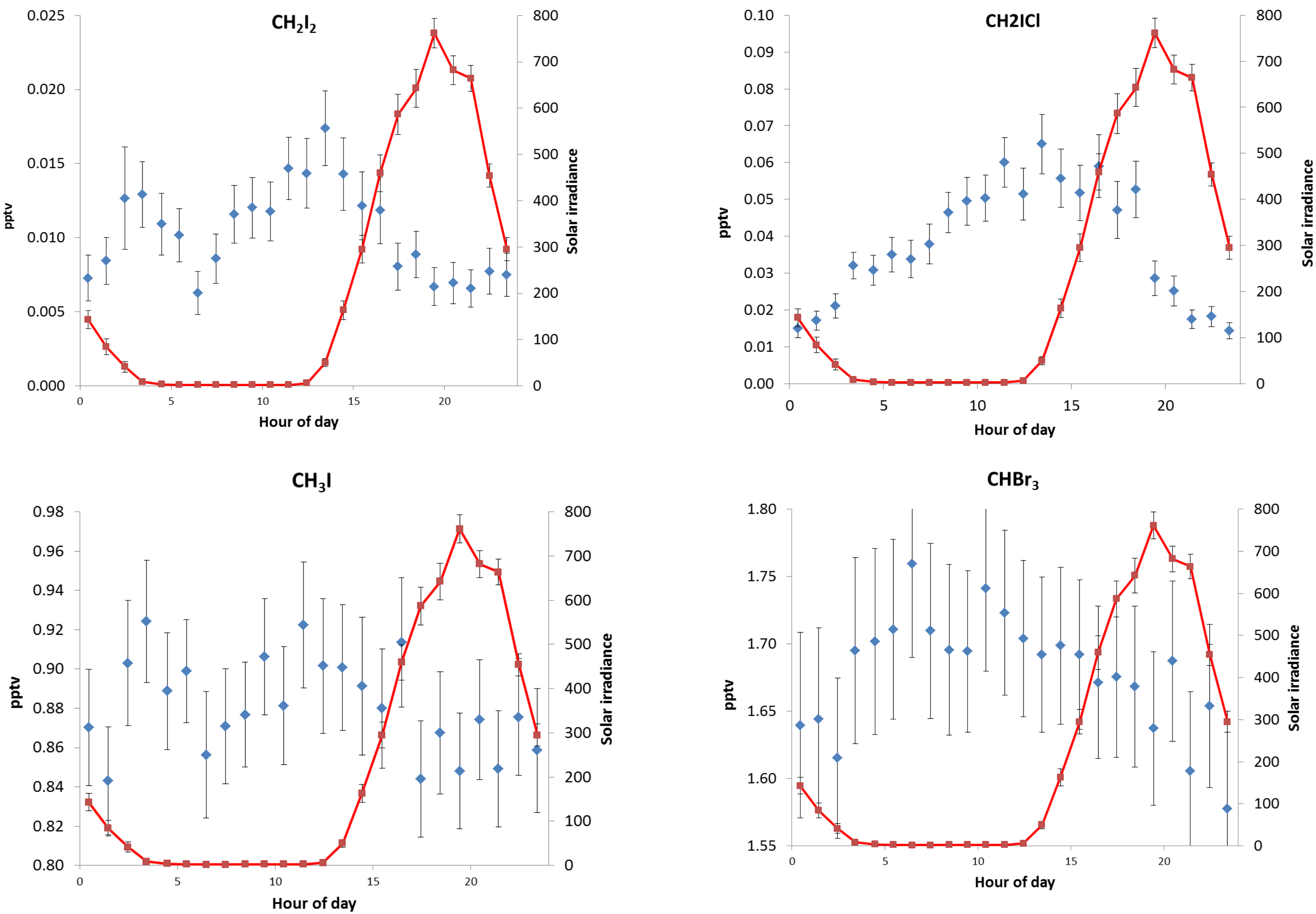
- Air concentrations show positive correlation with solar irradiance
- Possible (but unlikely) photolytic production in the air
- Diurnals are not seen in water data but maybe be too noisy to detect

VSL Iodocarbons photolytic diurnal cycle



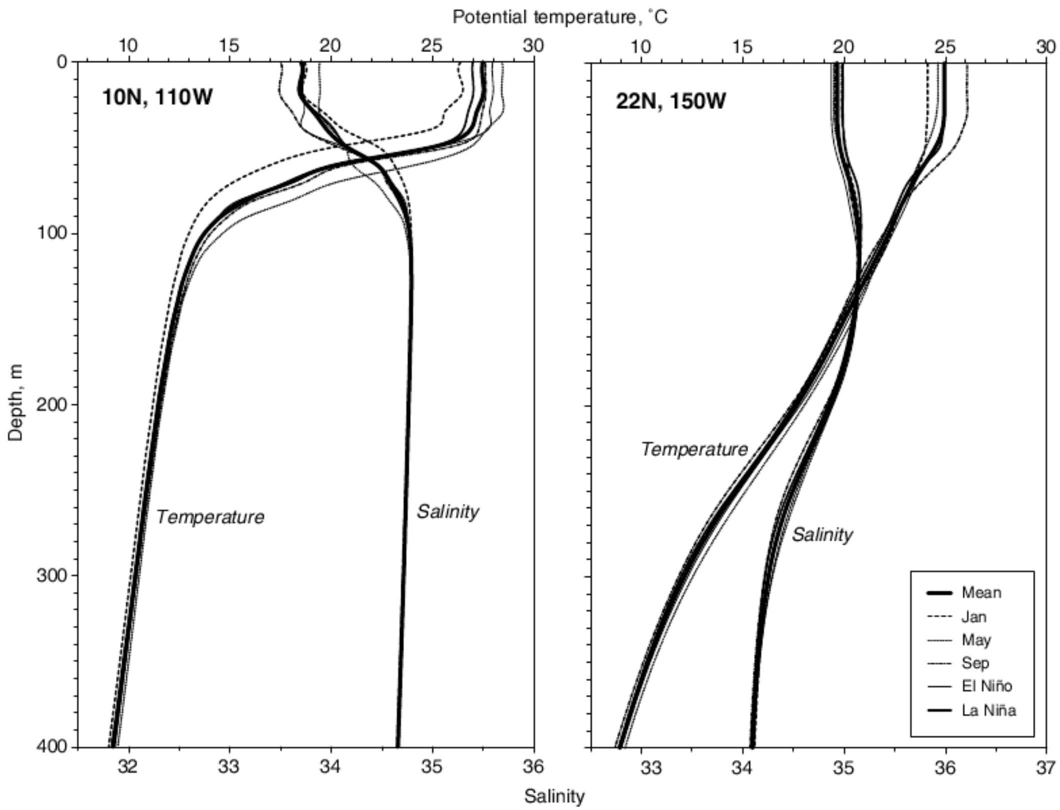


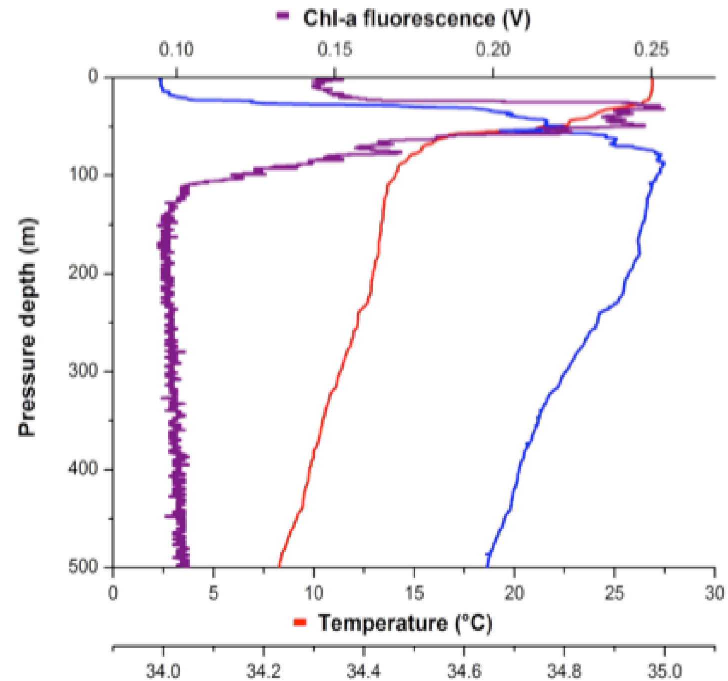




Strong averaged diurnal cycles for short-lived species showing rapid photolysis in MBL

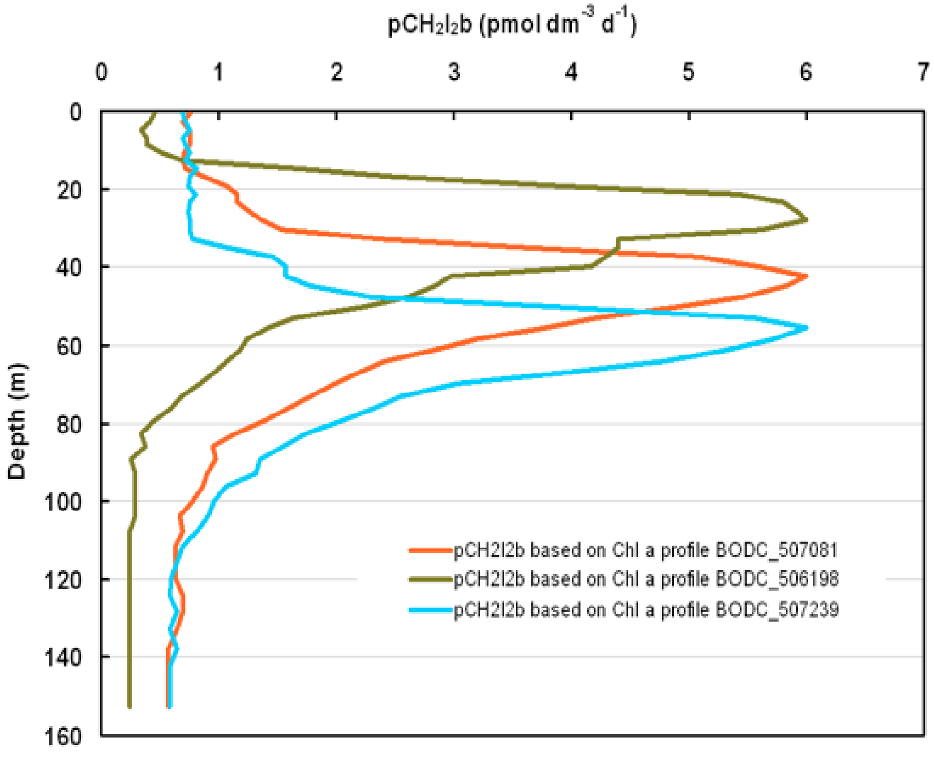
Mixed layer depth variability

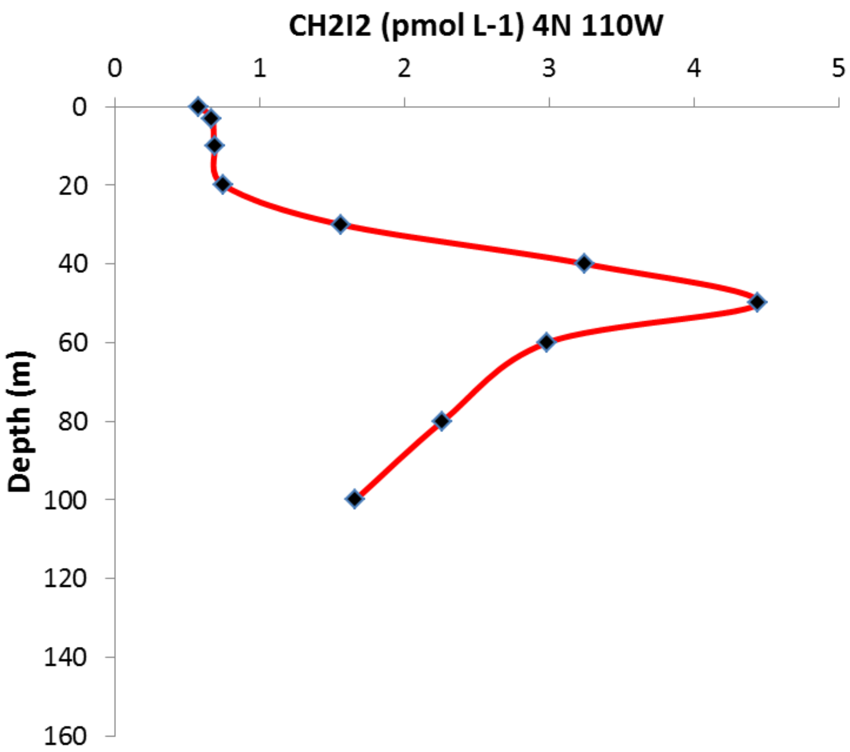




- Deeper mixed layer depth in North equatorial current region during first part of the cruise perhaps bringing CH_2ICl and CH_2I_2 to the surface when coupled with the high wind speeds

CTD profiles along the 110W TOA Buoy line



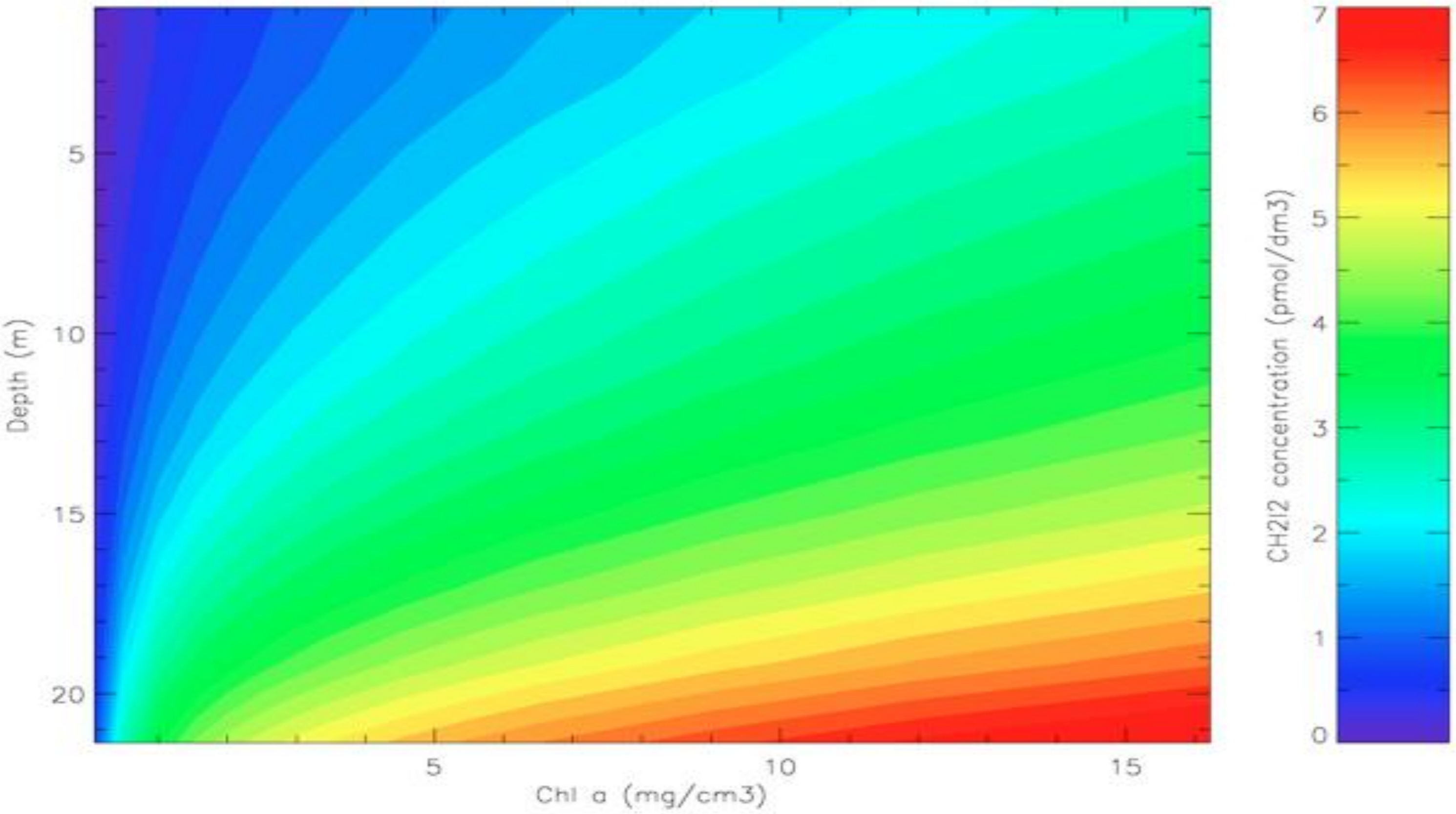


- Max rate of biological CH_2I_2 production (pCH_2I_2b) fixed at 6 pmol dm^{-3} d^{-1}

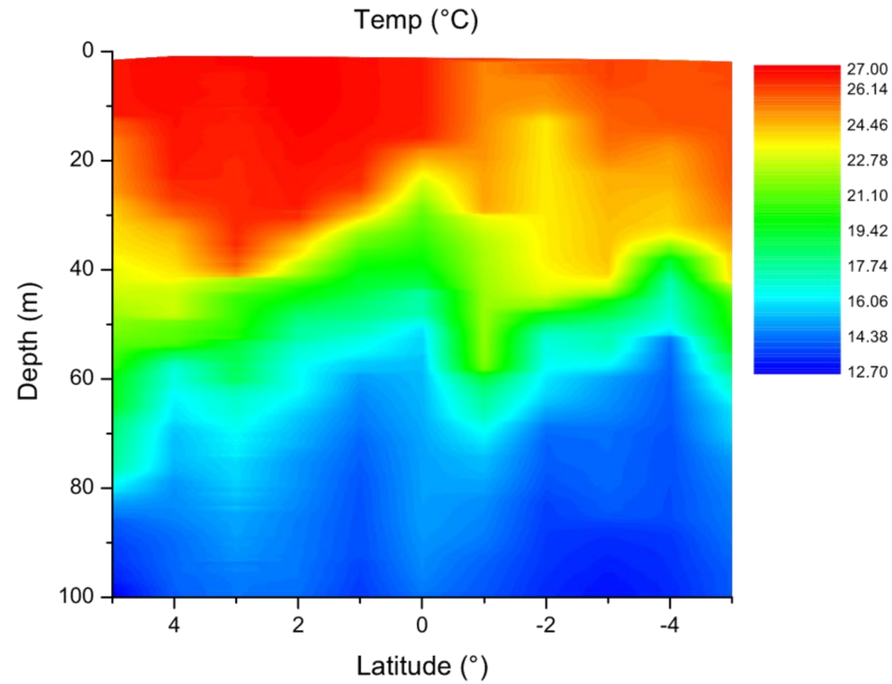
- Measured profile in good agreement with modelled data

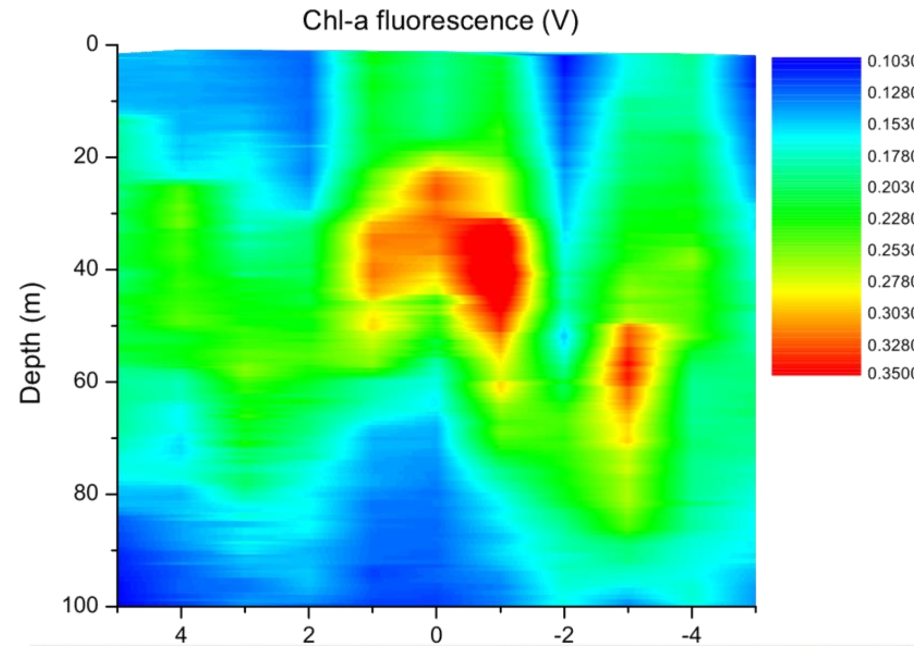
Dependence of water column $[CH_2I_2]$ on light attenuation/Chl-a

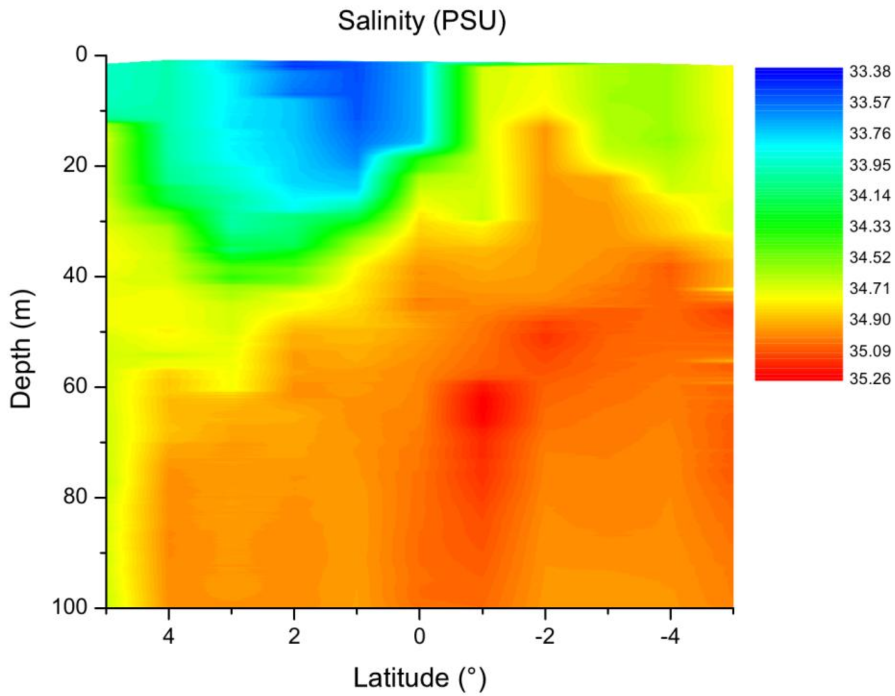
- Constant CH_2I_2 biological production profile
- Wavelength-dependant attenuation coefficients as a function of Chl-a determined from the NOAA COARRT model

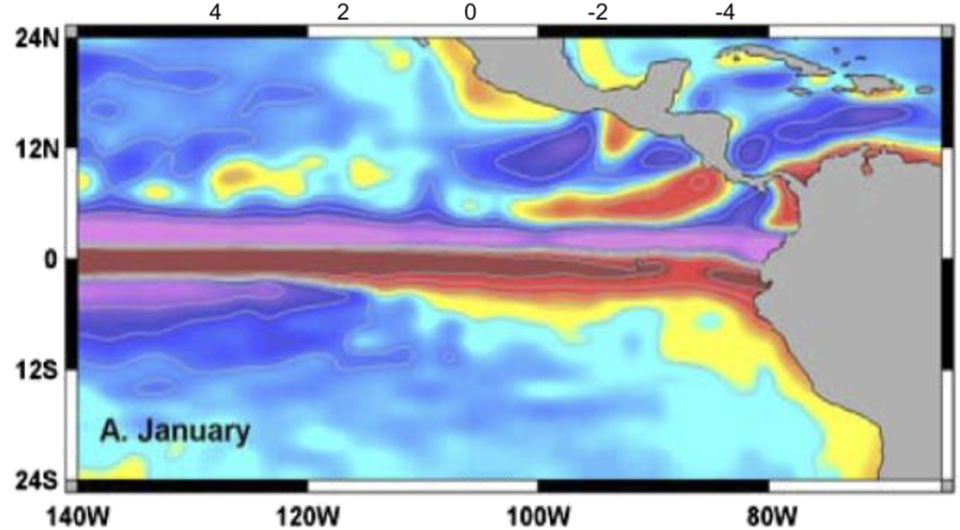


- Positive correlation of surface $[CH_2I_2]$ with Chl-a can be indicative purely of photolysis!

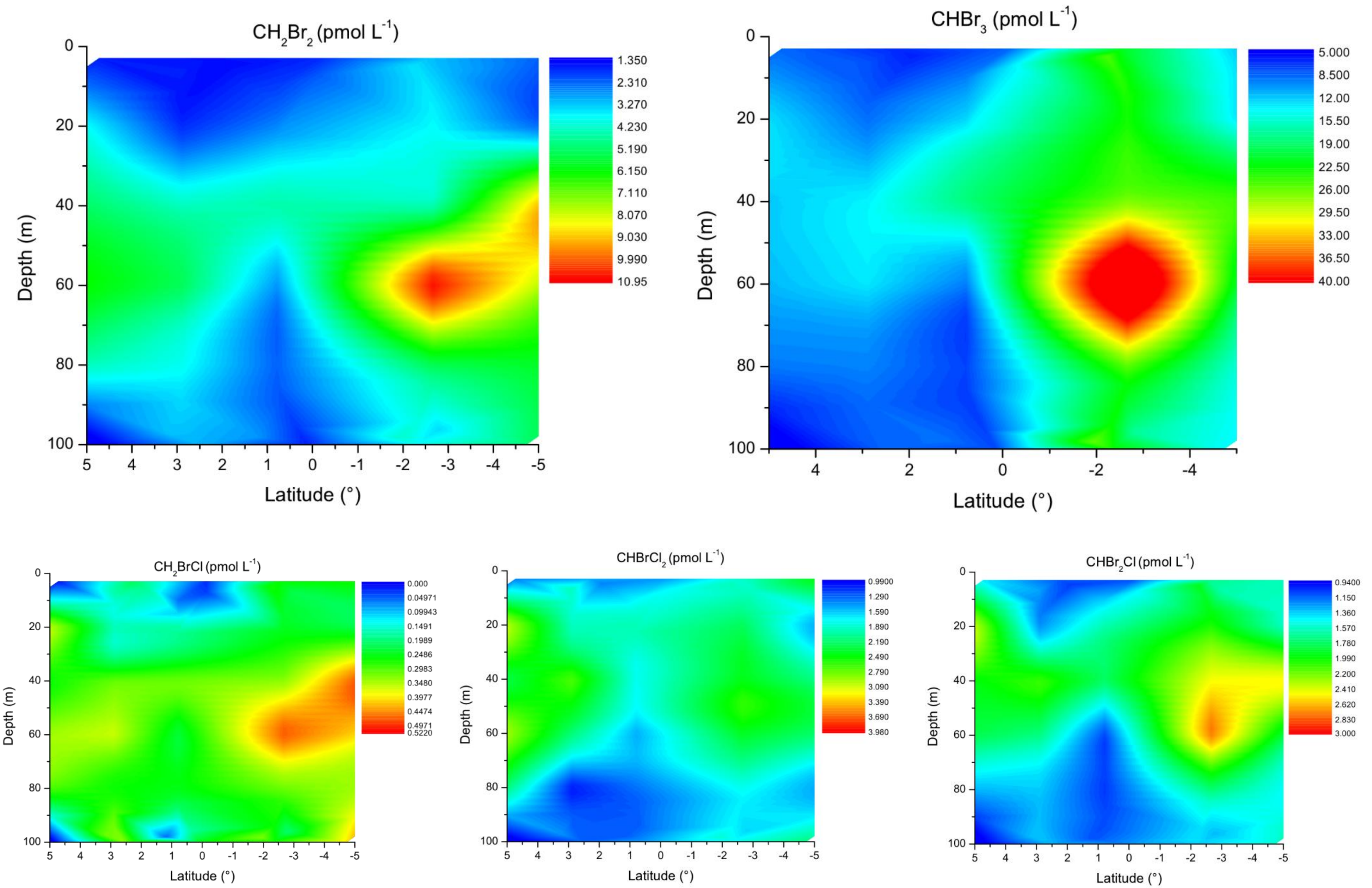




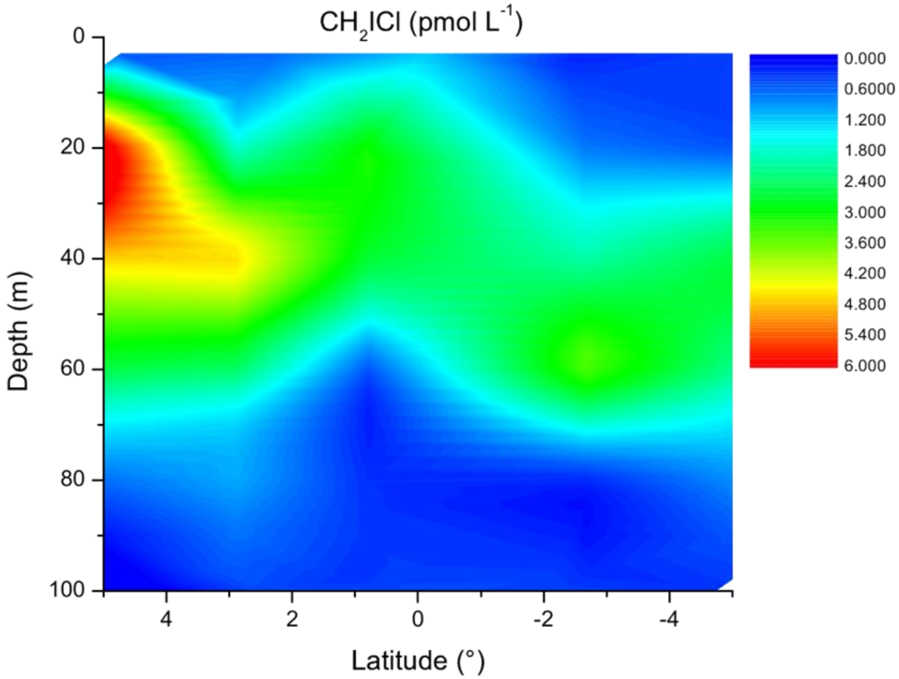


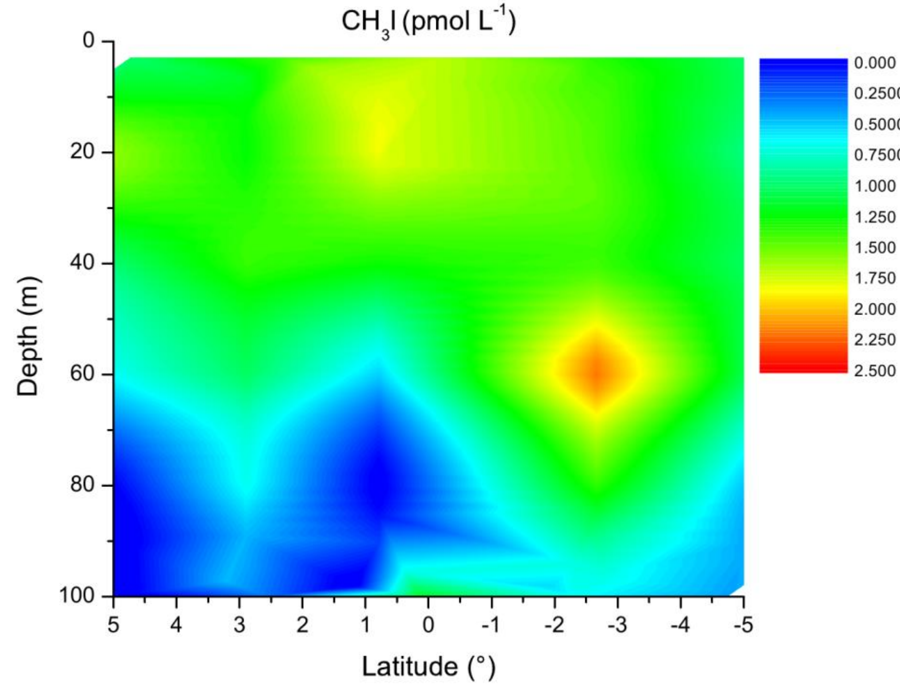


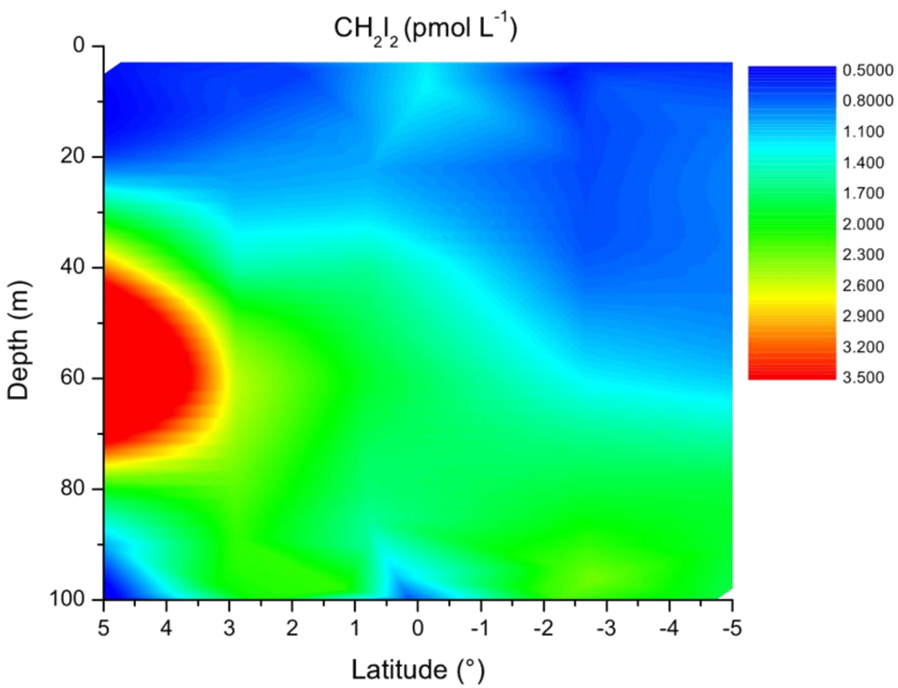
- Chl-a maximum around 30-60m
- Chl-a concentration greatest at the equator



- CH_2BrCl production from CH_2Br_2
- $CHBr_2Cl$ & $CHBrCl_2$ production from $CHBr_3$





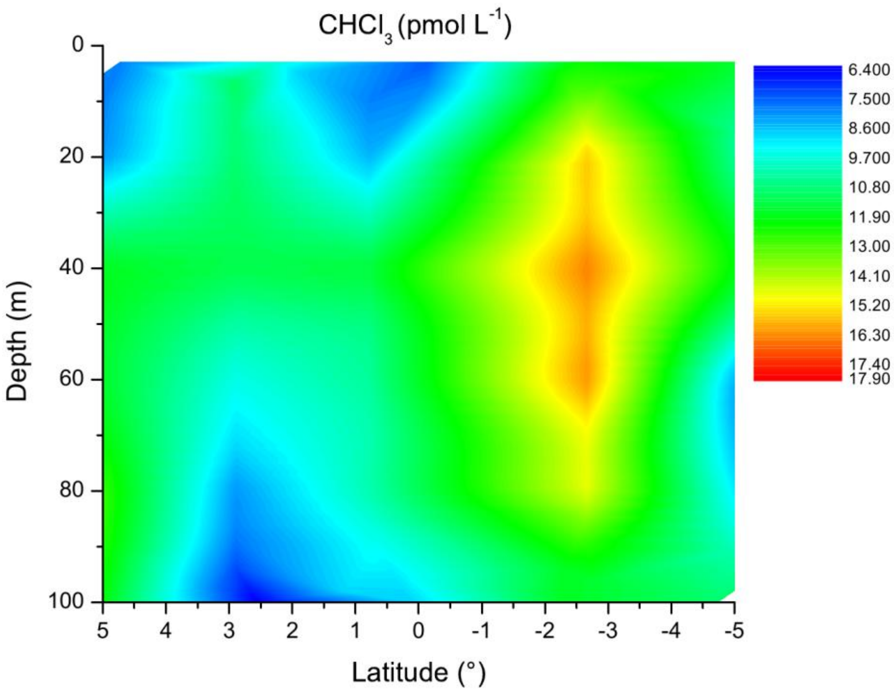


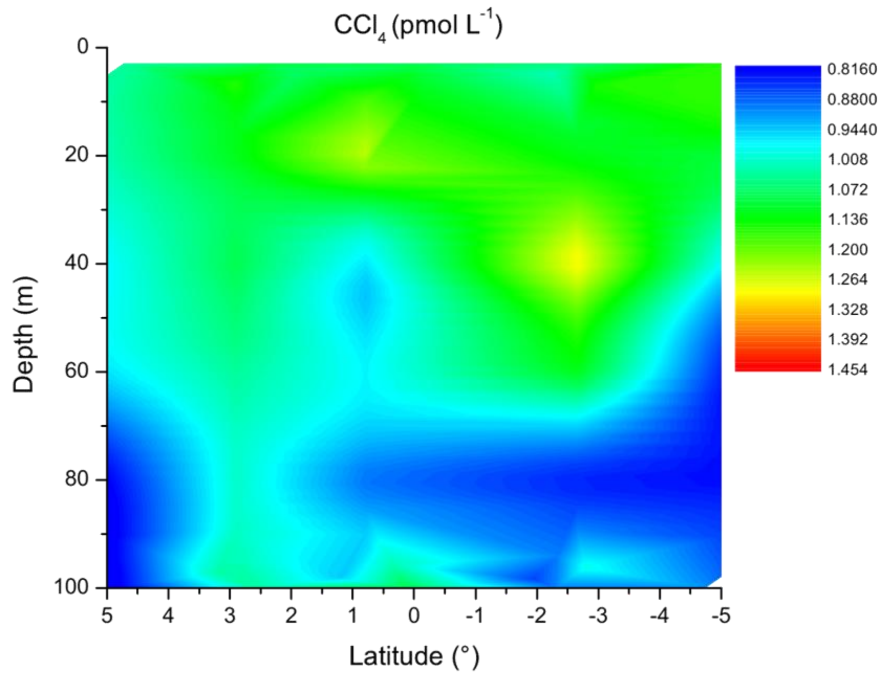
- CH_3I appears to have a surface, photolytic source plus a sub-surface biogenic source?

- $CH2_2ICl$ production from CH_2I_2 but also has its own biogenic source?

- CH_2I_2 possibly down-welled?

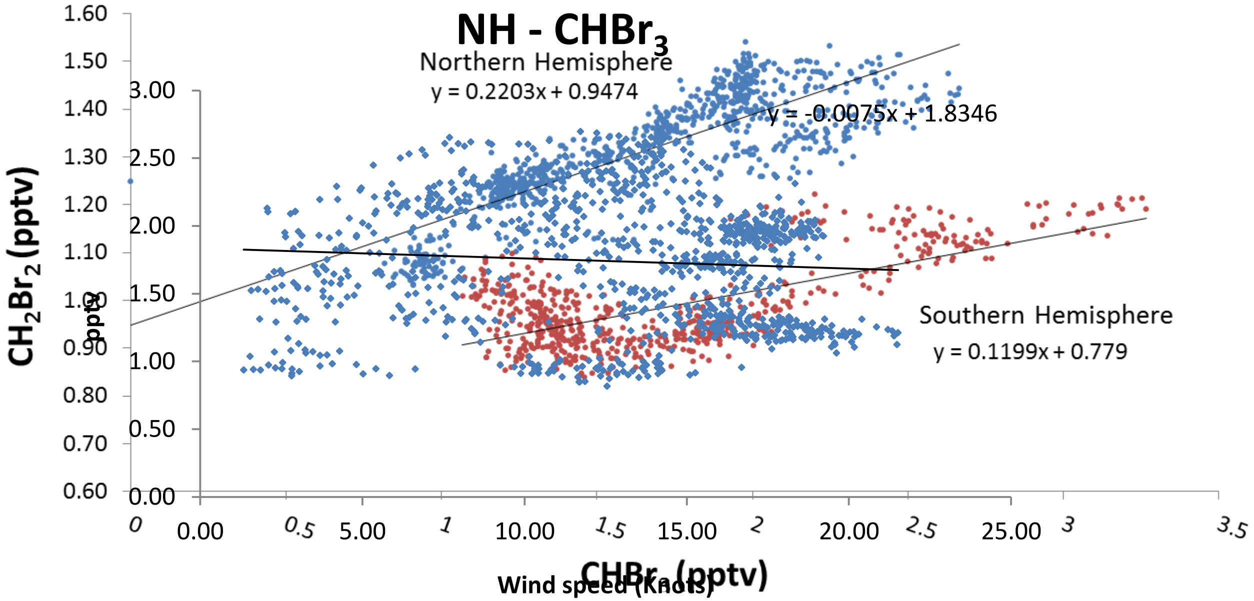
Biological production of longer-lived chlorocarbons

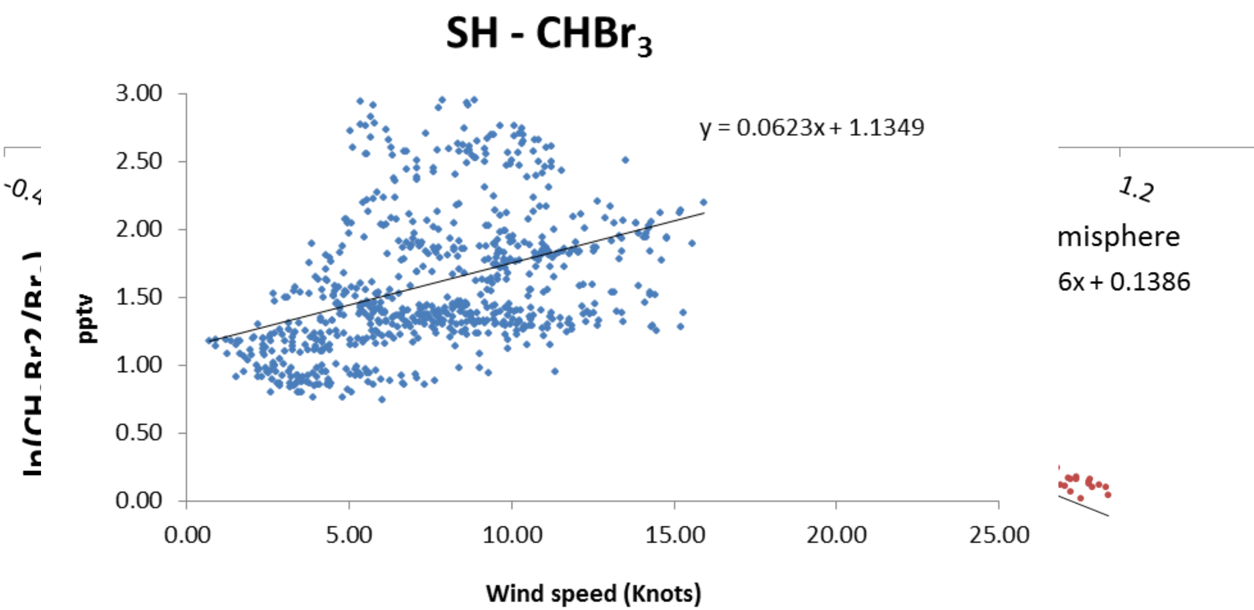




- Biogenic source of CHCl3
- Ocean sink for CCl4 but also possible biogenic production?

Halocarbon emission ratios

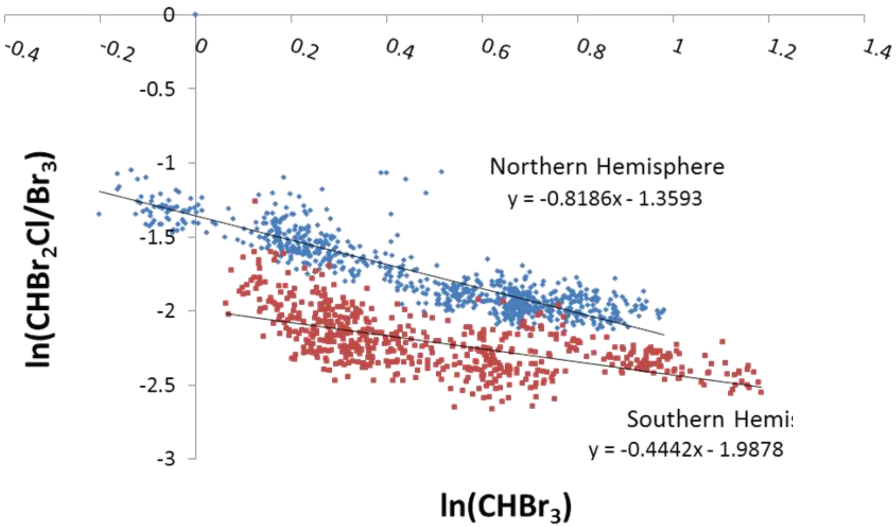




- Different sources appear to dominate from NH to SH

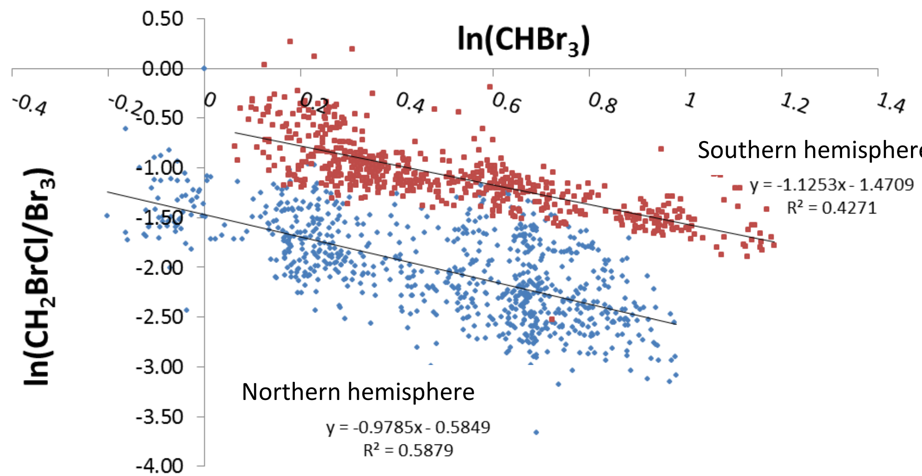
- CH_2Br_2 longer lived and destroyed predominantly via OH

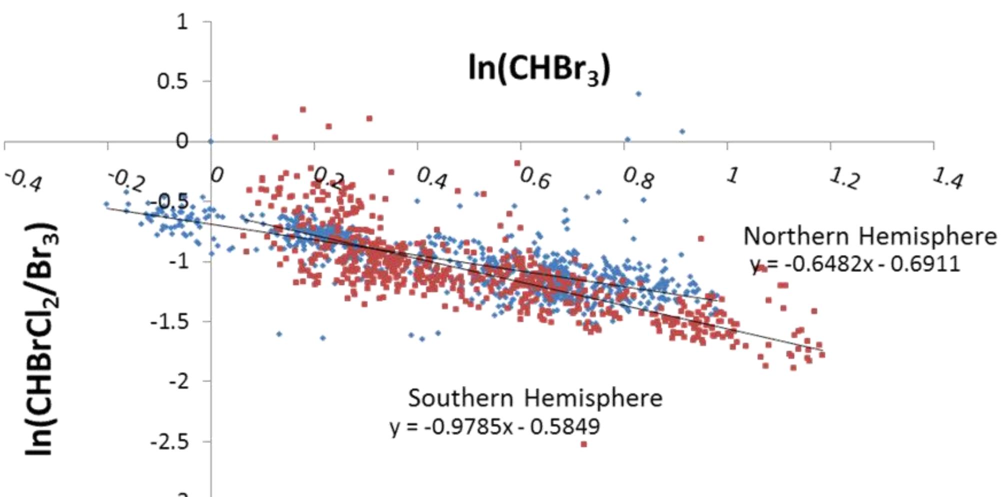
- NH-SH difference is independent of rates



- NH – greater $CHBr_2Cl$ and CH_2BrCl emissions than SH

- For $CHBrCl_2$ there is no difference NH-SH





- $CHBrCl_2$ may have a different source to the others – photolytic like mentioned earlier?

VSLH fluxes

	nmol m^{-2} day^{-1}			Tonnes $year^{-1}$		
Species	**Mean Flux**	**NH mean flux**	**SH mean flux**	**Total Ocean**	**Pacific**	**East Tropical Pacific**
CH_3I	2.70	3.67	1.20	51784	23763	4028
$CHCl_3$	21.13	30.01	7.48	340581	185827	31496
CCl_4	-2.97	-3.78	-1.73	-61757	-26150	-4432
$CHBrCl_2$	3.13	9.84	1.53	69336	27567	4672
CH_2Br_2	1.14	0.74	1.77	26831	10053	1704
CH_2ICl	1.72	2.52	0.48	40881	15097	2559
$CHBr_2Cl$	3.13	4.48	1.07	88149	27567	4672
$CHBr_3$	7.01	7.55	6.17	239108	61624	10445
CH_2I_2	1.11	1.40	0.65	40070	9744	1652

- Open ocean fluxes of tens of thousands of tonnes VSLH into MBL
- This study - CH_3I global flux estimate of 51,784 tonnes $year^{-1}$
- Liss and Slater 1974 – CH_3I global flux estimate of 270,000 tonnes $year^{-1}$
- Flux estimates consistent with difference between coastal and open ocean measurements
- Virtually zero open ocean flux data available especially for iodocarbons!

VSLH fluxes – contribution to reactive halogen

Bromocarbons	nmol m^{-2} day^{-1}					Bromine Tonnes $year^{-1}$		
per bromine atom	$CHBrCl_2$	CH_2Br_2	$CHBr_2Cl$	$CHBr_3$	Bromine	Total ocean	Pacific	East tropical Pacific
All	3.13	2.29	6.27	21.02	32.72	777513	356792	60473
NH	9.84	1.48	8.96	22.65	42.93	1019388	467786	79286
SH	1.53	3.53	2.14	18.52	25.71	597939	274388	46506
Iodocarbons								
per iodine atom	CH_3I	CH_2ICl	CH_2I_2		Iodine	Iodine Tonnes $year^{-1}$		
All	2.70	1.72	2.22		6.64	172806	79299	13440
NH	3.67	2.52	2.81		9.00	231990	106457	18044
SH	1.20	0.48	1.31		2.98	81631	37460	6349

- 777,513 tonnes of bromine and 172,806 tonnes of Iodine released into MBL per year when extrapolated to the global ocean

Species	Flux (Yokouchi Scw) A&WSL	Flux (Johnson Scw) WSL	Flux (Johnson Scw) A&WSL	%reduction (Johnson WSL Vs A&WSL)	%reduction (Yokouchi Vs Johnson)
CH_3I	3.18	2.74	2.70	1	15
$CHCl_3$	25.97	21.63	21.13	2	18
CCl_4	-3.43	-2.98	-2.97	0	13
$CHBrCl_2$	7.45	6.84	6.56	3	11
CH_2Br_2	1.26	1.24	1.14	7	10
CH_2ICl	1.90	1.87	1.72	7	9
$CHBr_2Cl$	3.35	3.37	3.13	6	6
$CHBr_3$	7.11	8.14	7.01	13	1
CH_2I_2	1.11	1.36	1.11	17	0

VSLH intercalibration – Aircraft Vs Ship

Compound	vs. NCAR Lab	vs. NOAA Air spike	vs. NOAA gravimetric	vs. NCAR in-flight cals	Actual*
CH_3I	3.50	2.75		3.71	**3.80**
CH_2Br_2	2.25	2.04	2.39	2.13	**2.60**
$CHBr_3$		5.14	5.89	4.60	**5.40**
CH_2I_2	0.83	1.12	0.50	0.72	**0.80**
CH_2BrCl	7.43	5.87		6.71	**5.80**
$CHBr_2Cl$		3.53		1.64	**3.70**
CH_2IBr	1.79	1.49	2.03	1.72	**1.40**

* This is only based upon the quoted values by NOAA and will change very slightly due to bottle losses upon filling

- 3L SilcoSteel canister was filled using SX-3570 NOAA spiked air at the end of the campaign
- Sampled analysed after filling using VSLH instrument on KA
- Preliminary intercalibration results look very promising
- Will need adjustment to take into account losses between filling, analysing and arriving in Boulder for the intercalibration