CAST: VOC observations from WAS using GC-FID and GC-MS

Stephen Andrews, Jimmy Hopkins, Richard Lidster, Shalini Punjabi, Jamie Minaeian, Dene Bowdalo, Tomas Sherwen, James Lee, Mat Evans, Lucy Carpenter, Neil Harris and the CAST team. Elliot Atlas, Eric Apel, Rebecca Hornbrook, Dan Riemer and the ATTREX/CONTRAST teams

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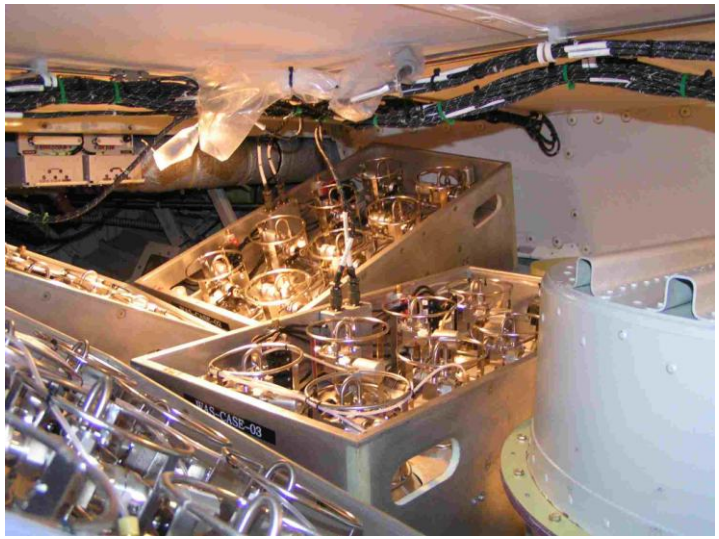
CAST VOC observations- sampling and calibration

•Whole air samples (WAS) taken from BAE-146

• 3 L SilcoSteel canisters evacuated and filled to ~30-40psi

• 620 samples analysed by GC-DCFID for NMHC and DMS

• 667 samples analysed by GC-MS for DMS and halogenated VSLS



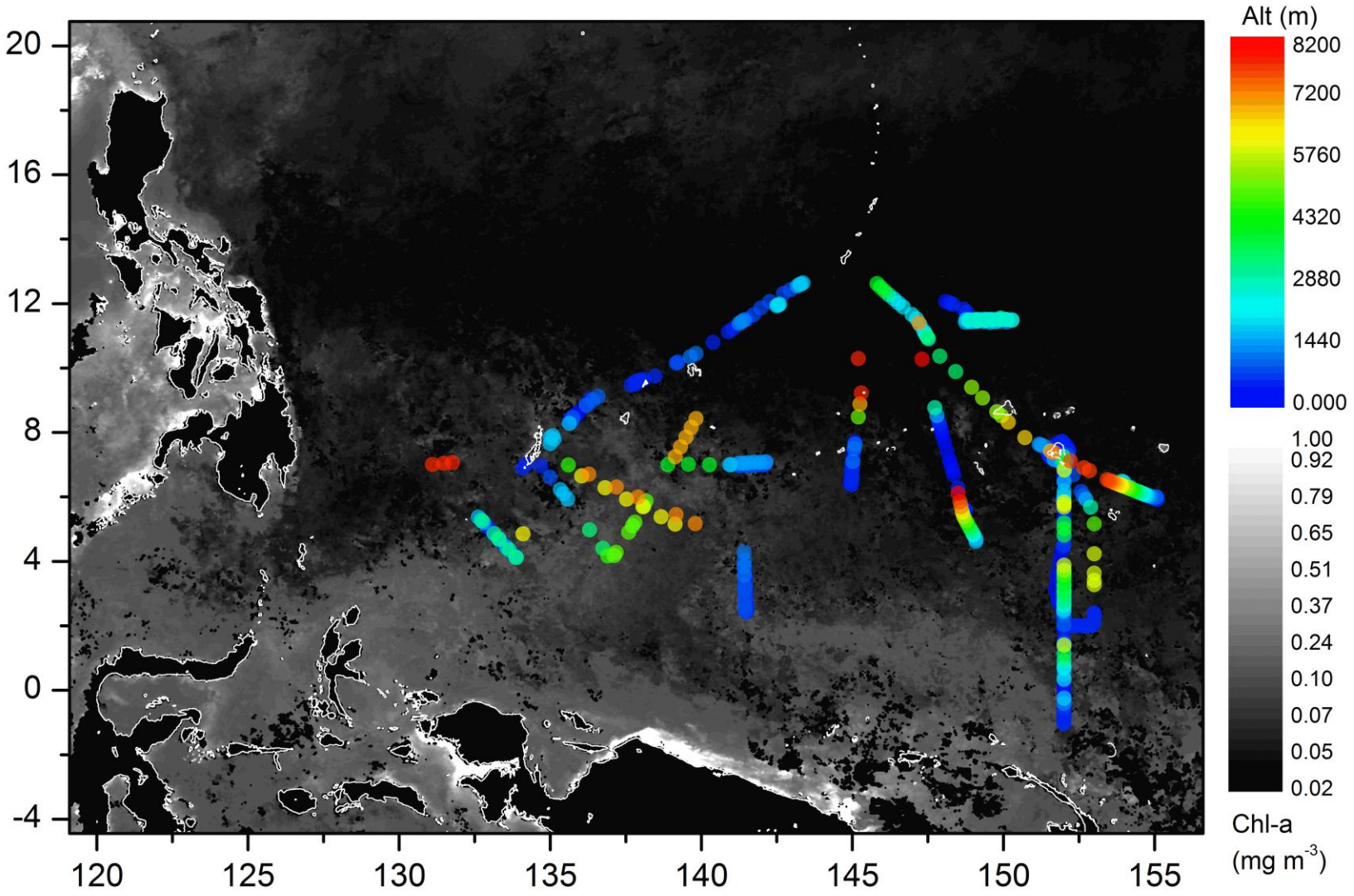
Calibration scales:

NMHC on NPL/GAW scale
DMS from primary KRISS standard
Halocarbons on NOAA scale

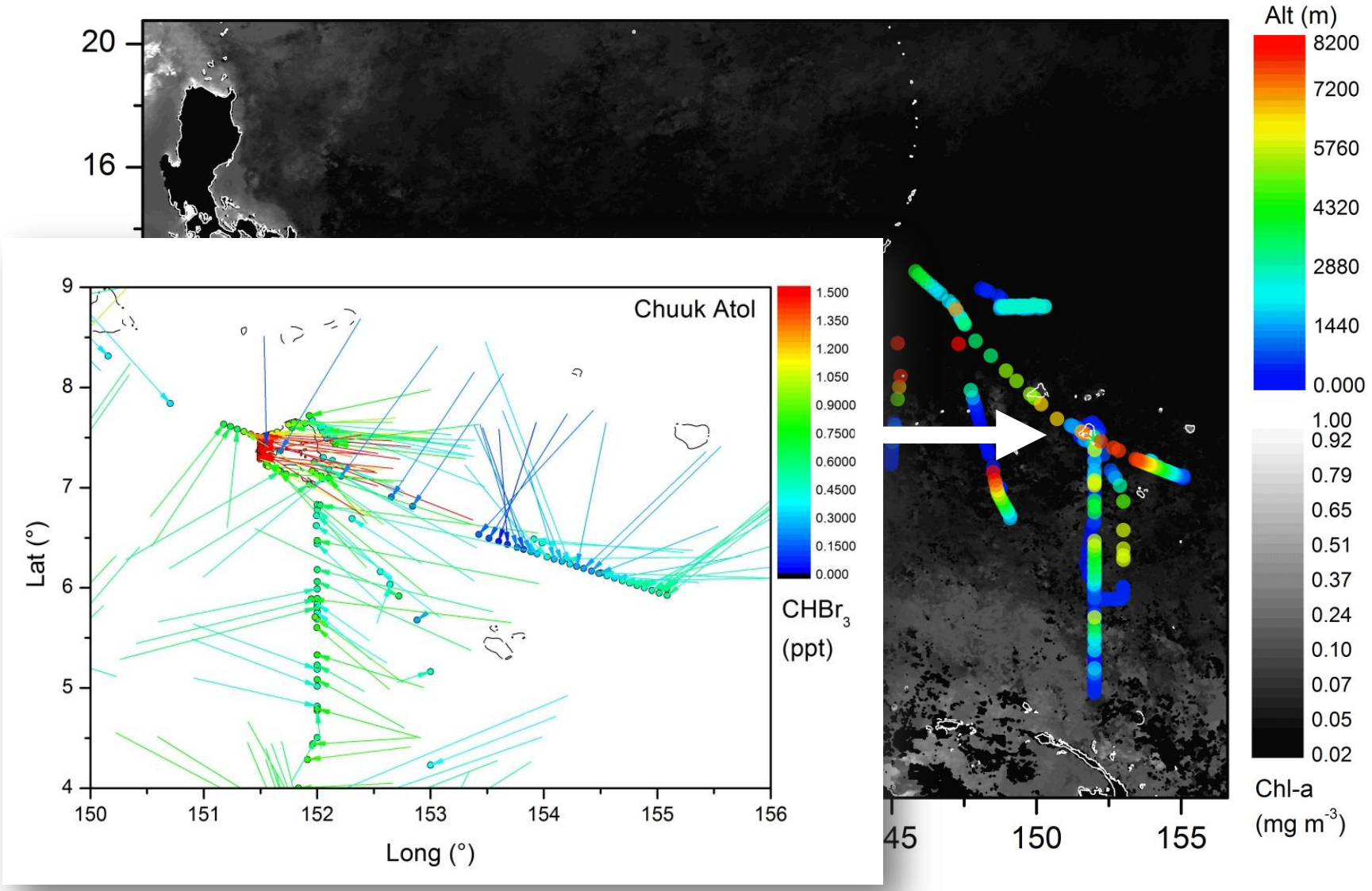
Intercalibration:

WAS (BAE-146), AWAS (GV/GH) and TOGA (GV) inter-calibrated using NOAA standard cylinder and a Miami Essex cylinder standard

CAST VOC observations- WAS sampling region

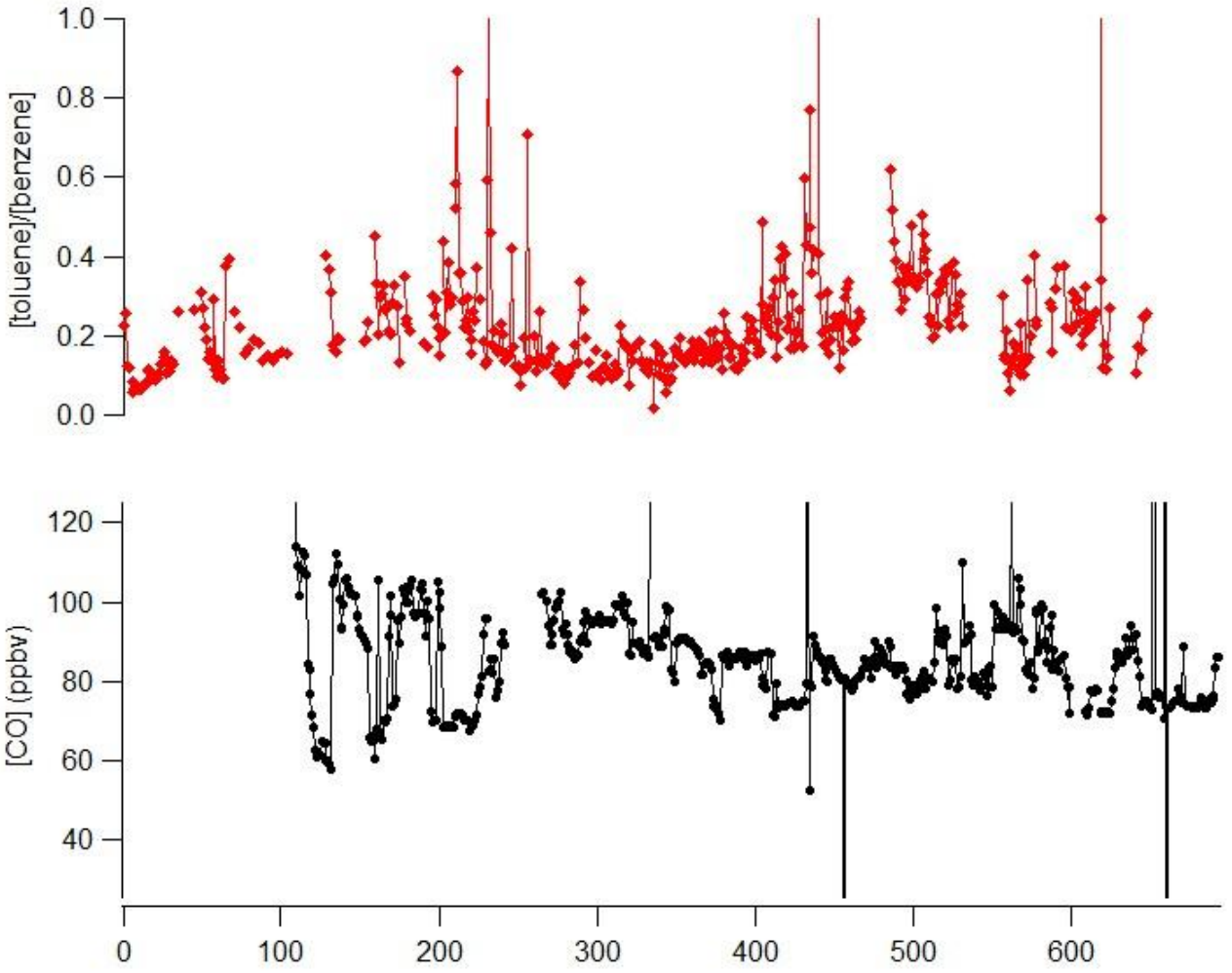


CAST VOC observations- WAS sampling region

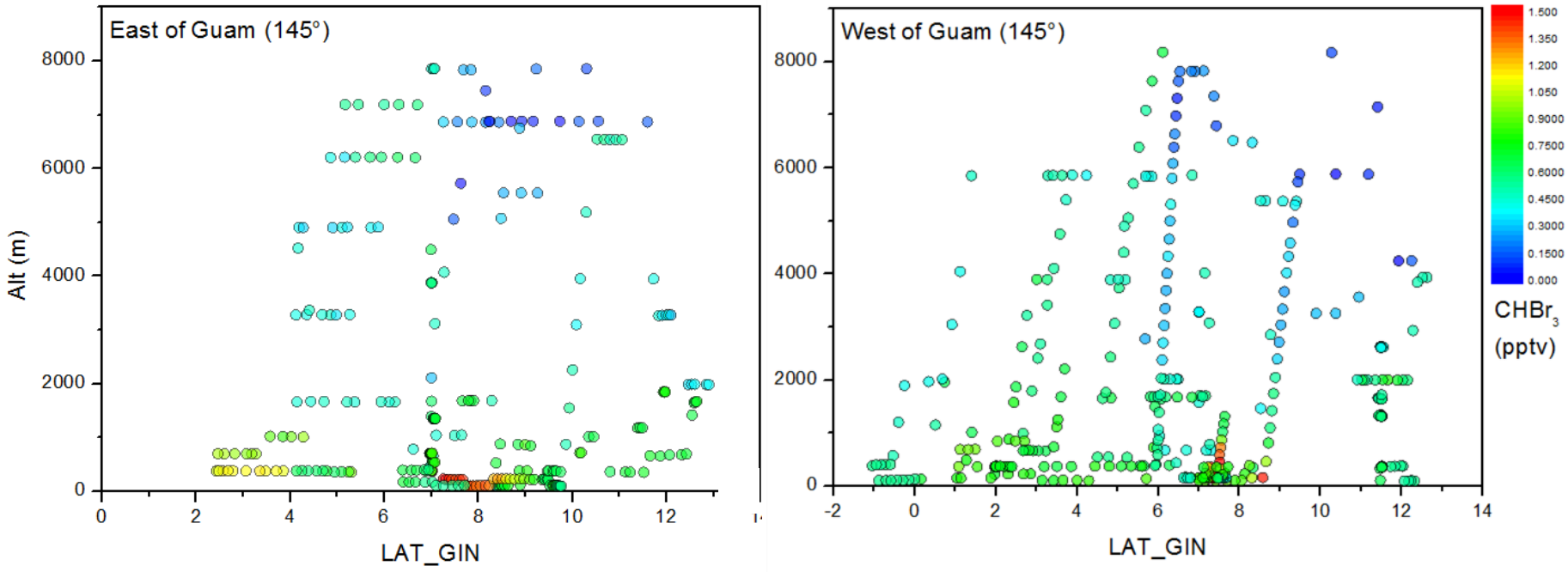


CAST VOC observations – air mass characteristics

- In general, air masses appeared well-processed and representative of background. At source the ratio of toluene/benzene would be approximately 4.0



CAST VOC observations – CAST WAS sample spatial distribution



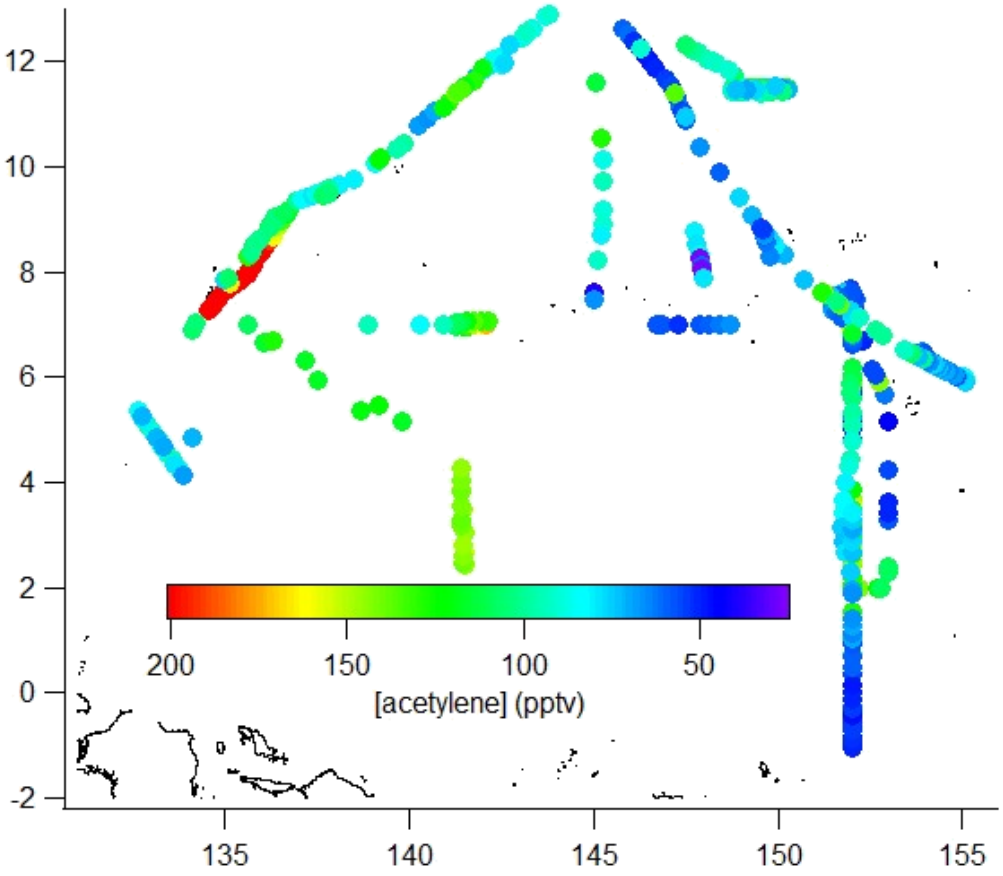
- No unusual concentrations in dataset

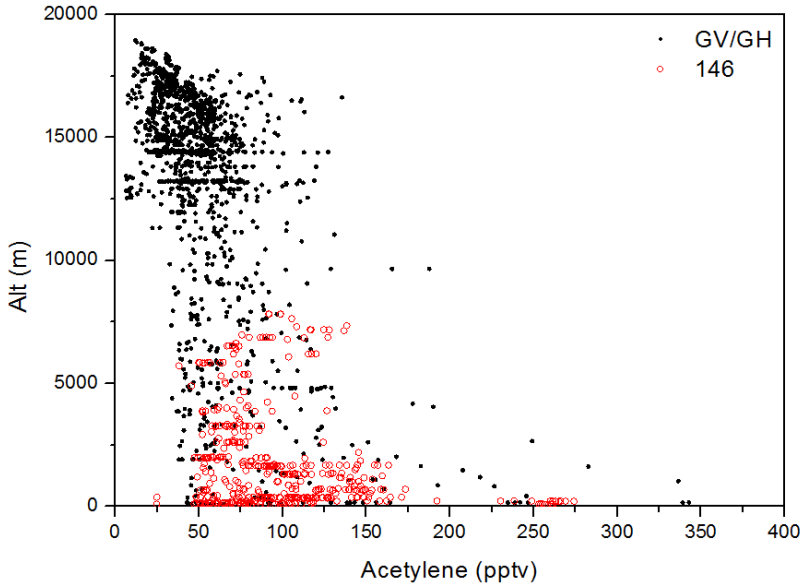
- Aimed to capture variation in surface concentration at maximum range

- Sample full vertical profile up to operational ceiling (~8 km)

CAST VOC observations

- acetylene (marker for anthropogenic pollution): fairly even distribution with perhaps decreased levels to the south and east and enhancements around Palau

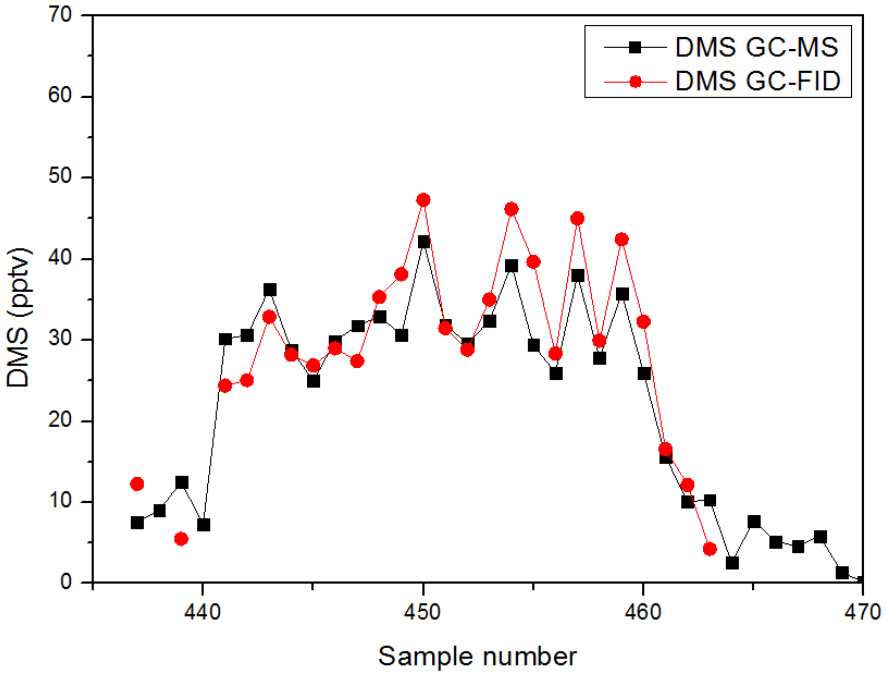


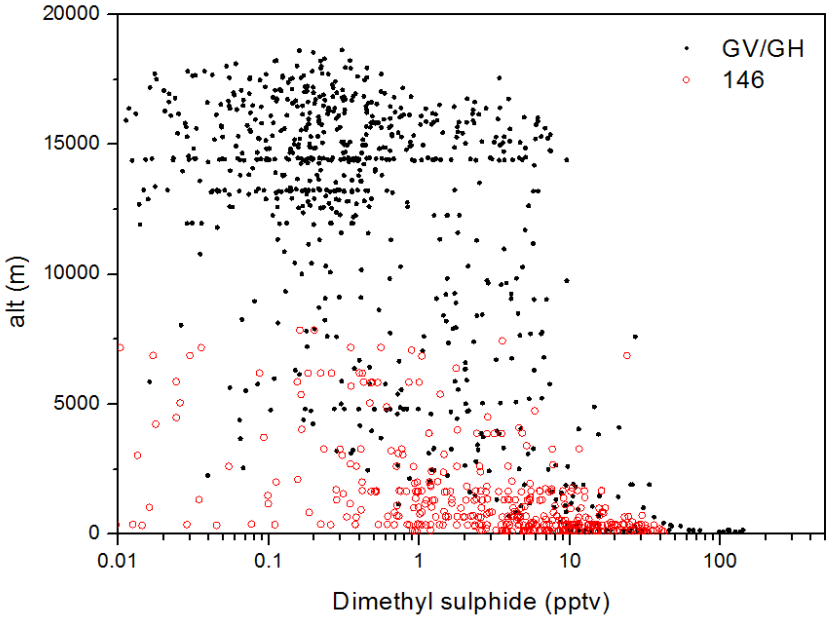


- Concentrations compare well between platforms

CAST VOC observations – dimethyl sulphide (DMS)

- DMS highly variable due to short lifetime (~1day) and production mechanism



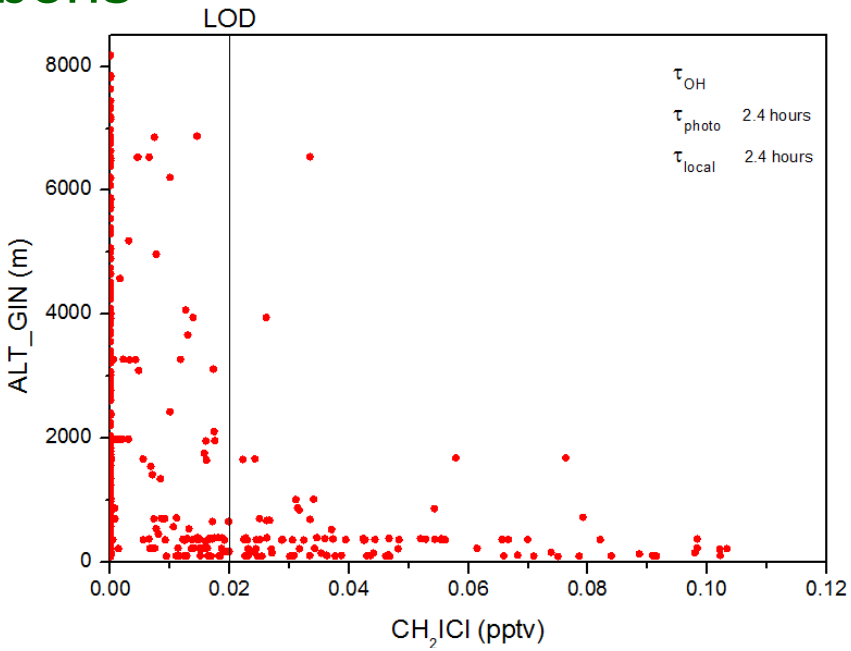


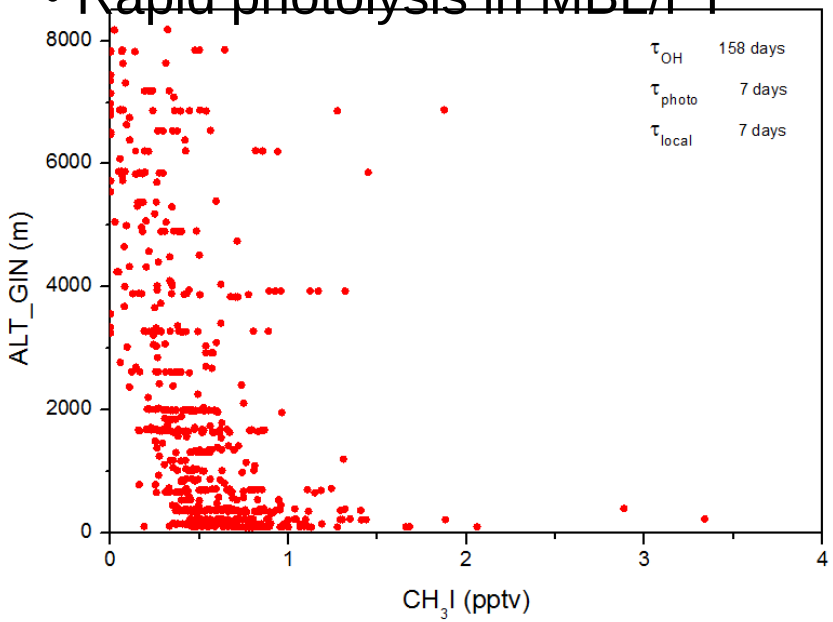
- DMS well characterised between CAST WAS instruments

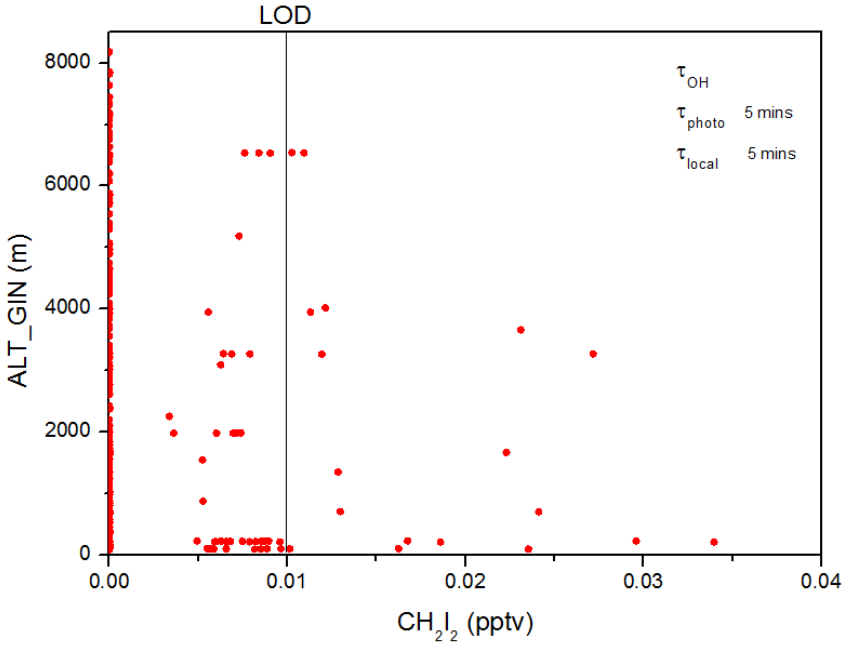
- Compares well in vertical profile to AWAS (GV/GH)

CAST VOC observations - iodocarbons

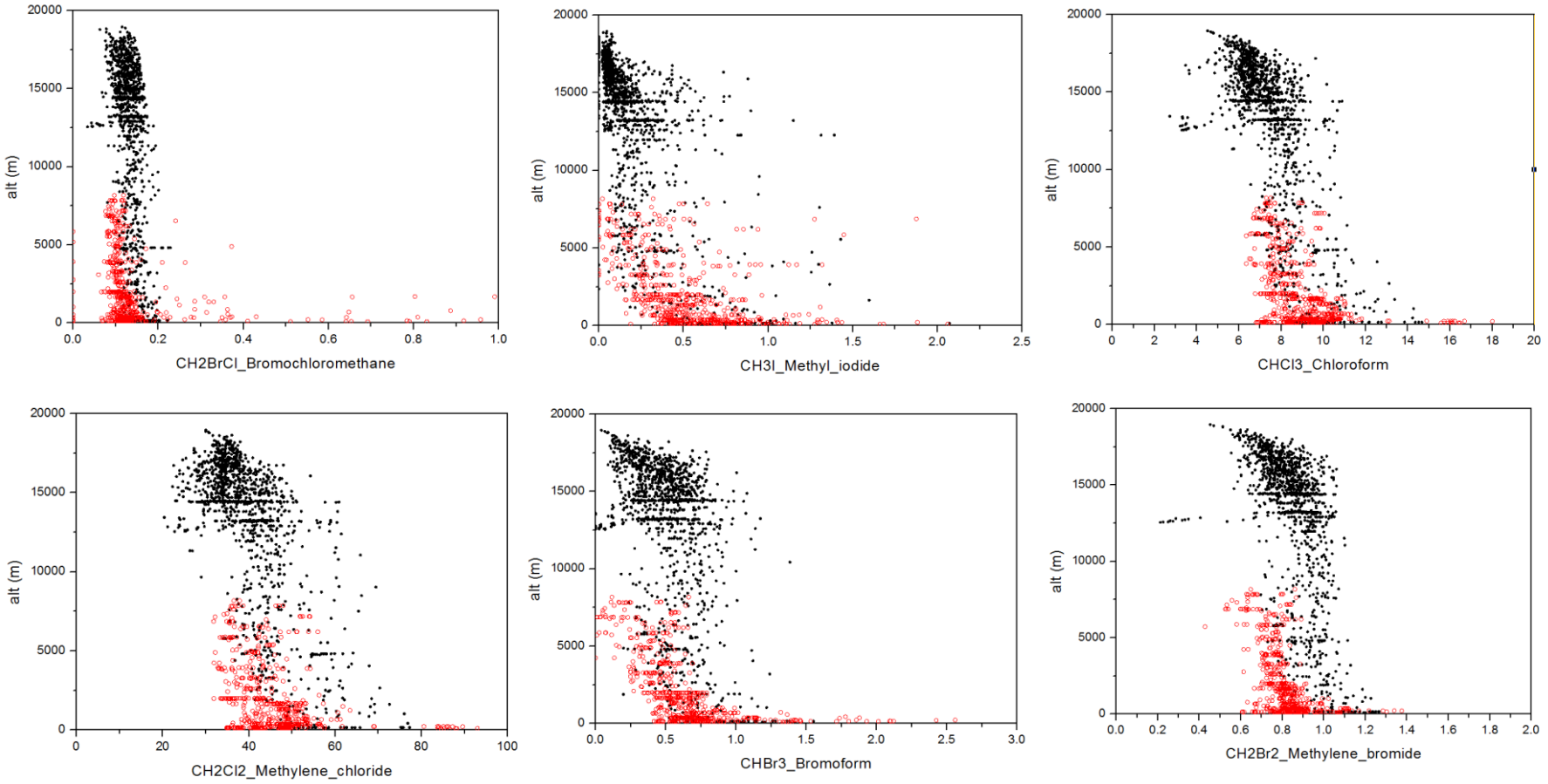
- Iodocarbons quantified including CH_3I, CH_2ICl and CH_2I_2
- CH_2I_2 mostly below limit of detection (LOD)
- CH_2ICl mainly below 2 km
- Rapid photolysis in MBL/FT





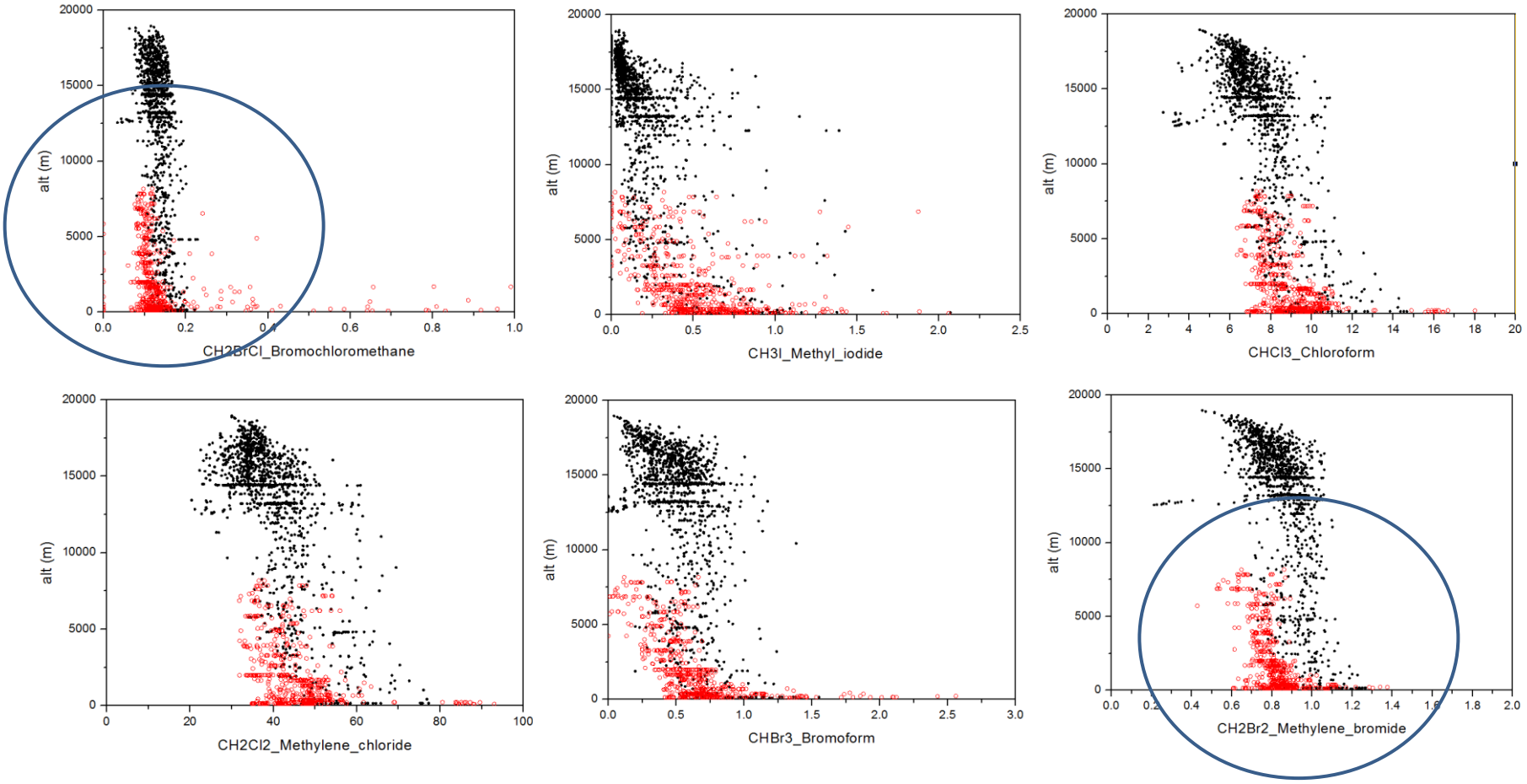


CAST VOC observations – combined vertical profiles



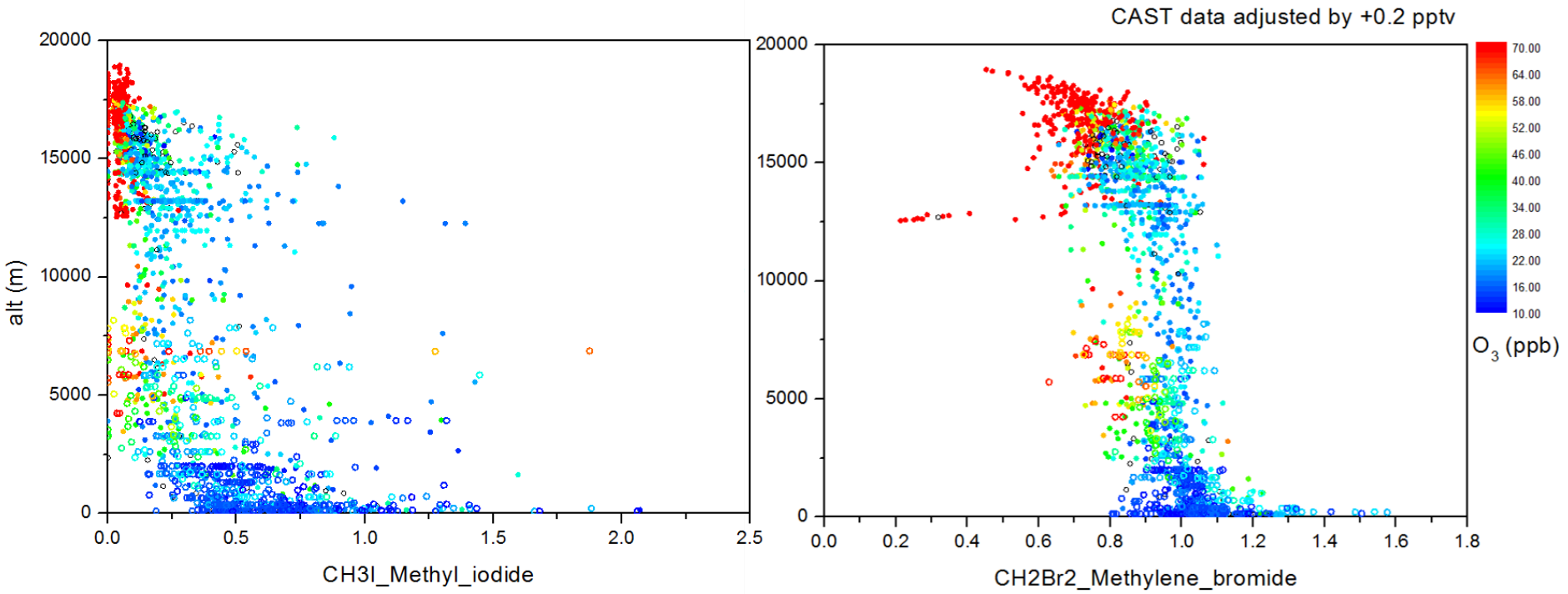
- Combined WAS/AWAS dataset provides a balanced distribution of data throughout the vertical profile

CAST VOC observations - combined vertical profiles



- Some species show slight concentration offset which may get resolved using inter-calibration work

CAST VOC observations

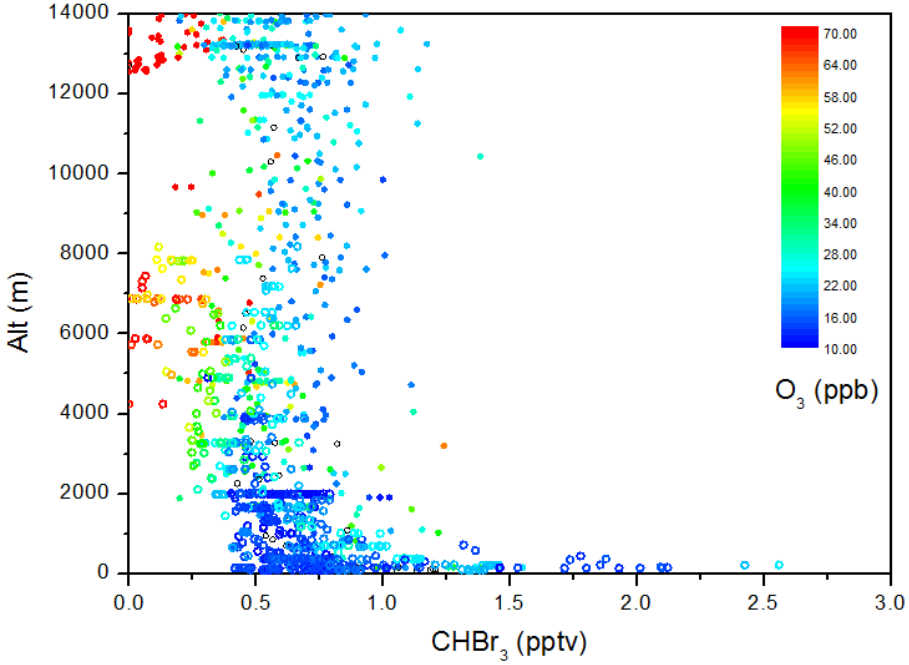


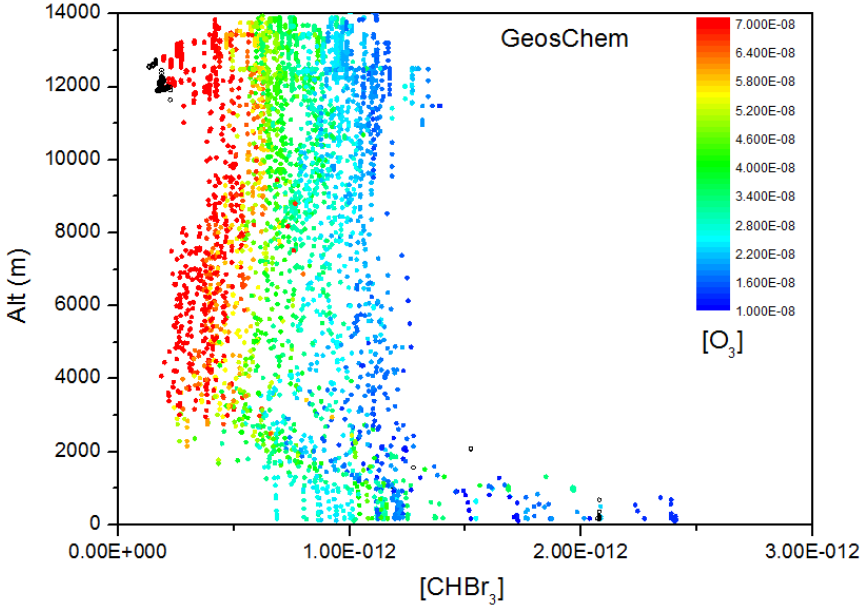
- Combined datasets provide a comprehensive vertical profile

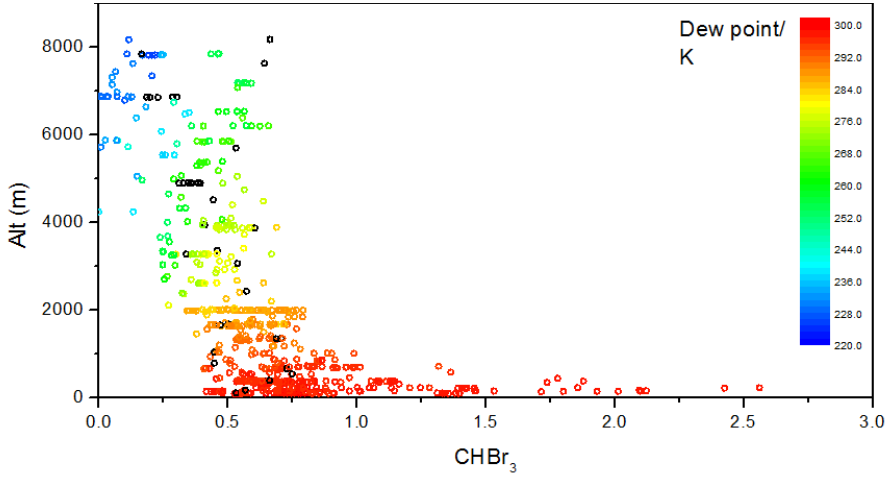
- Parameters such as O_3, H_2O and CO can be used to estimate the emission age/history

- Interception of aged, possibly entrained UTTL air at ~5-7 km

CAST VOC observations – bromoform vertical profile

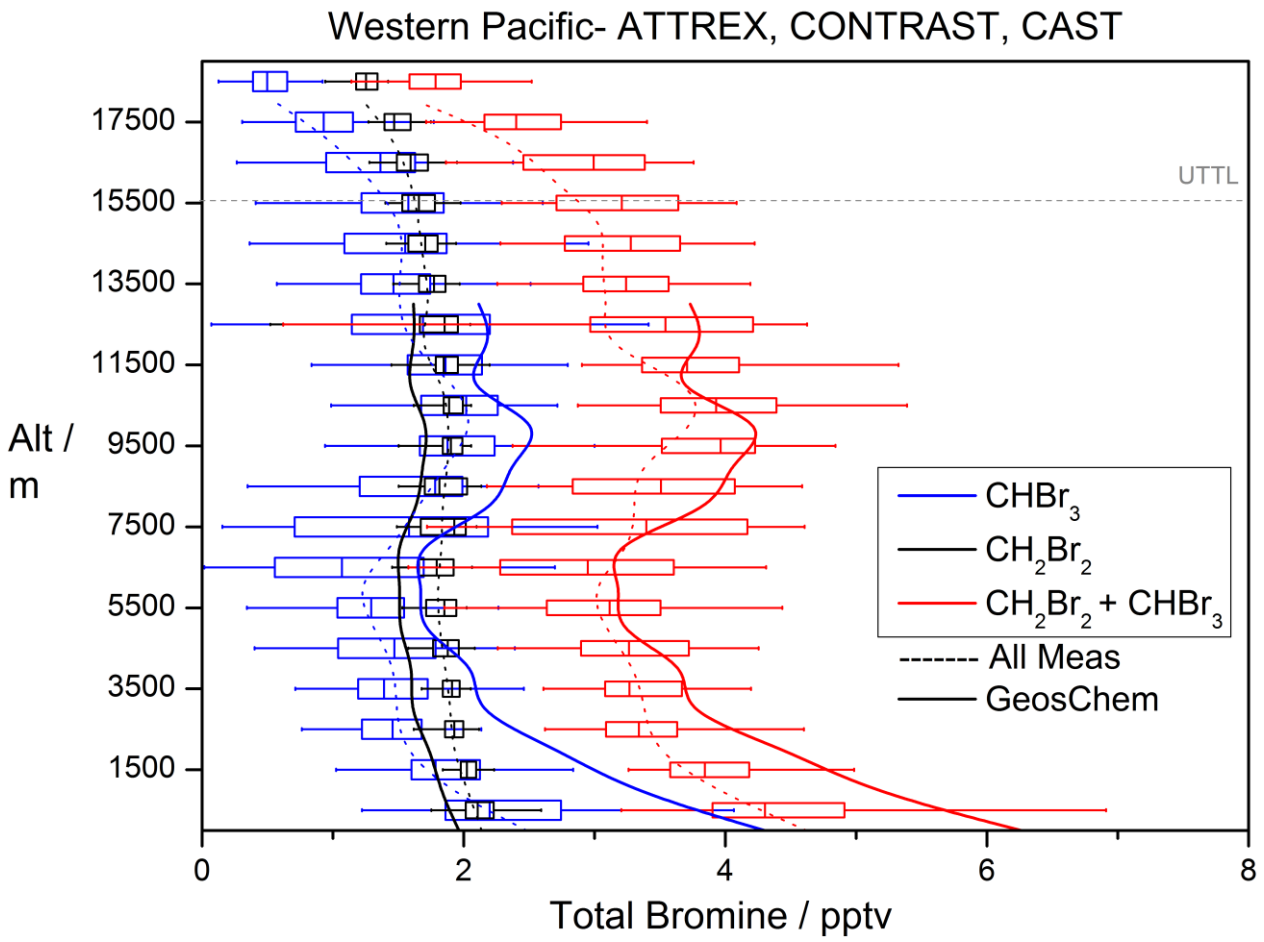






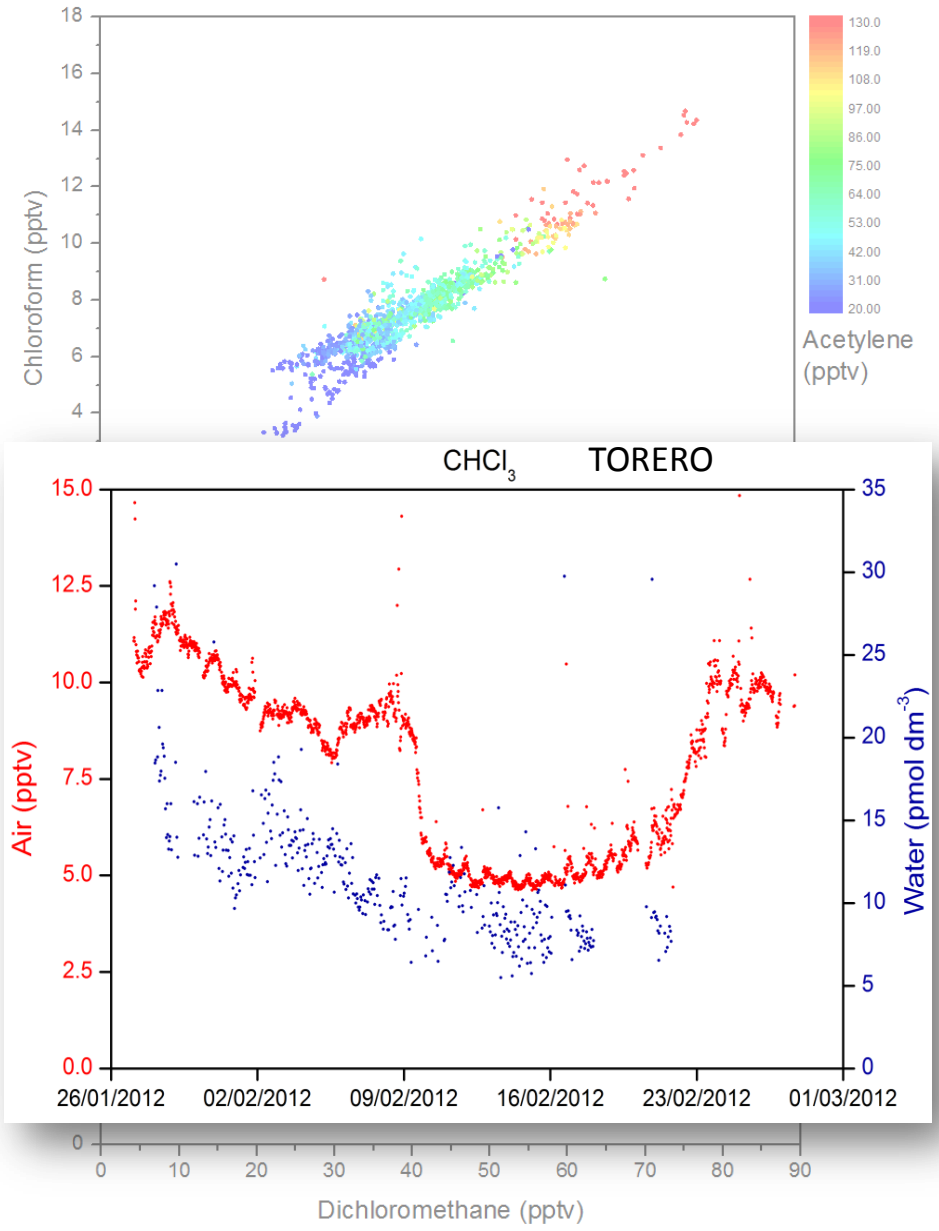
- GeosChem output along GV and 146 flight track
- Over-estimates at the surface
- possibly vertical transport too

CAST VOC observations – Stratospheric bromine contribution



- GeosChem modelled profile reproduces vertical structure fairly well
- CH_2Br_2 and $CHBr_3$ contribute around 2-4 ppt to upper TTL as SG

CAST VOC observations – Anthropogenic influences?



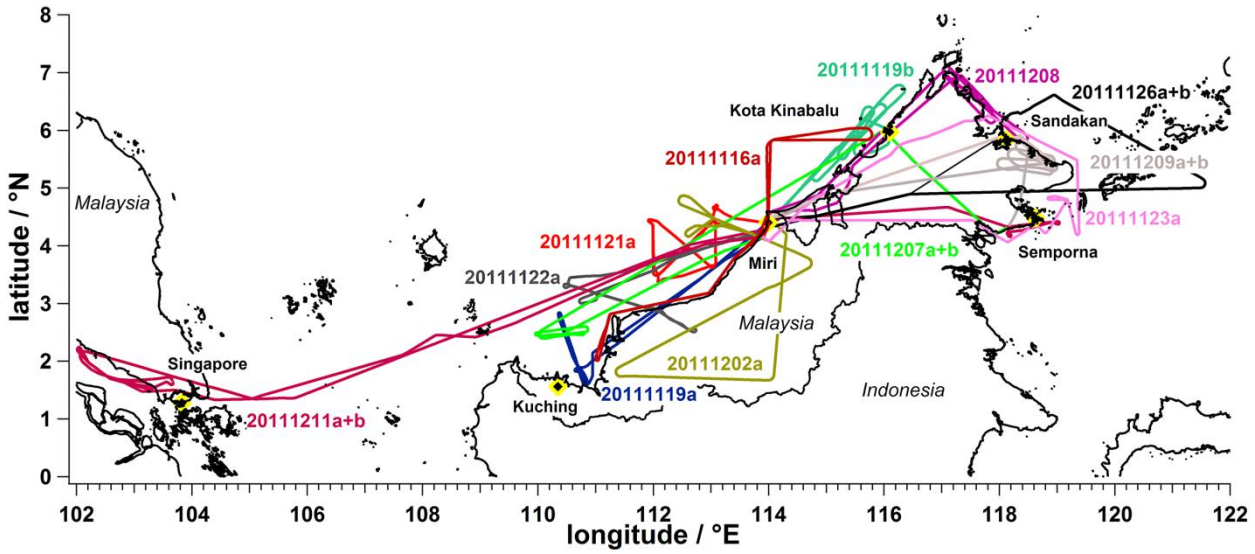
- CH_2Cl_2 concentrations are increasing globally

- Very clear correlation between $CHCl_3$ and CH_2Cl_2 and correlation with anthropogenic tracers

- CH_2Cl_2 ~70% industrial source
  ~20% oceanic

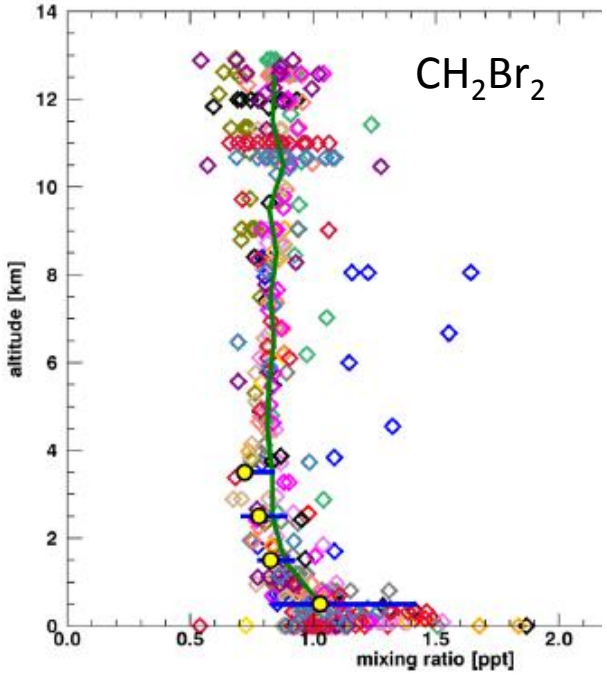
- $CHCl_3$ ~15% industrial source
  ~50% oceanic
  ~35% soil

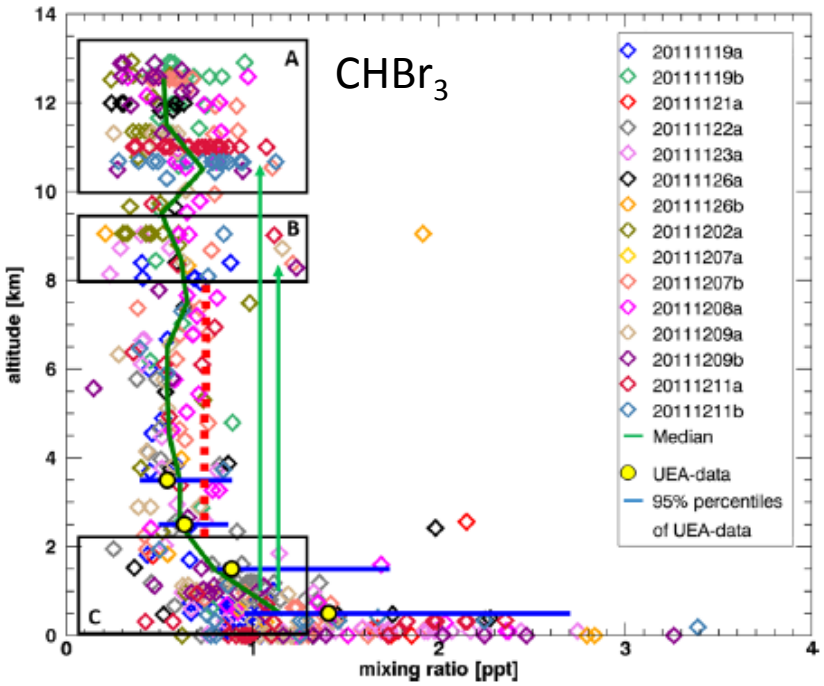
CAST VOC observations – SHIVA comparison



SHIVA
Stratospheric Ozone: Halogen Impacts in a Varying Atmosphere
Nov-Dec 2011

Sala, S. et al. 2014 Deriving an atmospheric budget of total organic bromine using airborne in situ measurements from the western Pacific area during SHIVA, ACP

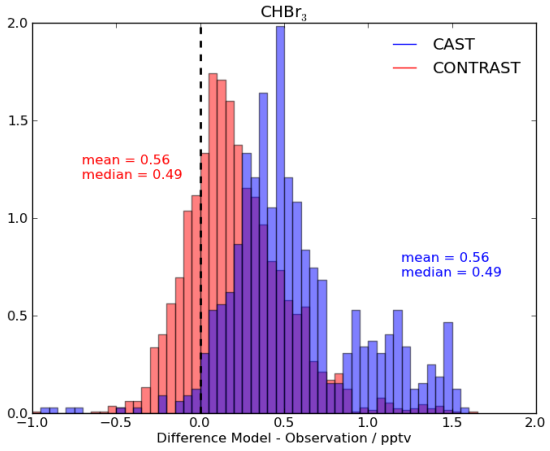




Model Developments for VSLS During CAST

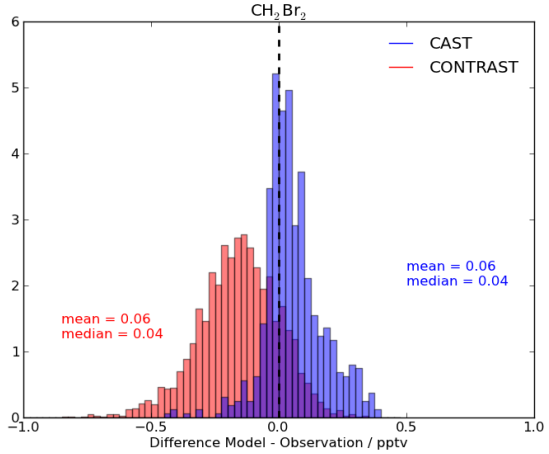
Robyn Butler (r.butler-2@sms.ed.ac.uk), Paul Palmer and Liang Feng

- Principal modelling tool - GEOS-Chem
  - CAST & CONTRAST measurements used to evaluate VSLS chemistry and transport
  - Potential problem with oceanic fluxes of VSLS – positive model bias
  - Tracer:tracer ratio plots will be used to understand chemistry & transport over the region



- Tagged-VSLS Model Simulation to understand the role of different geographical emissions of VSLS
  - To be used in conjunction with inversion modelling to better estimate emission fluxes
  - Air-sea flux formulation will be used to better represent seasonal & daily flux variations of VSLS emissions

= Method to calculate the physical age of recent emissions over the region



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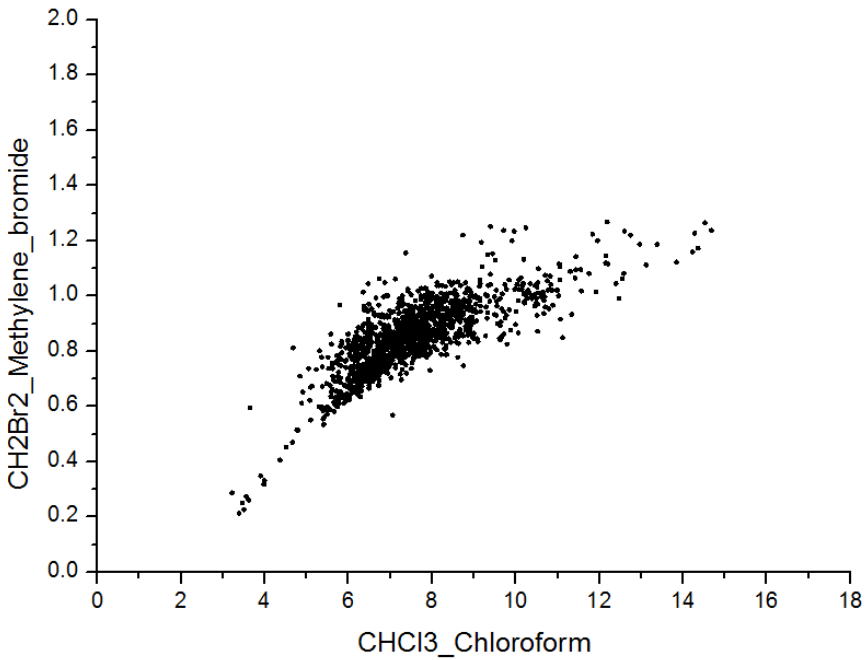
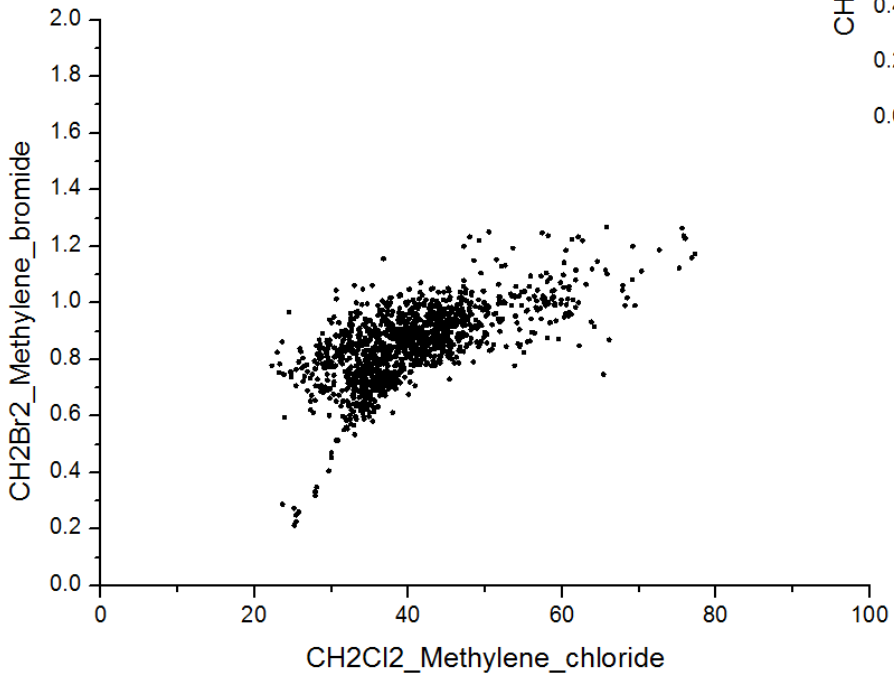

CH2Br2_Methylene_bromide
CHCl3_Chloroform
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
0
2
4
6
8
10
12
14
16
18


CH2Br2_Methylene_bromide
CH2Cl2_Methylene_chloride
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
0
20
40
60
80
100