Contributions to tropical VSLS emissions from the equatorial Atlantic upwelling region

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Introduction

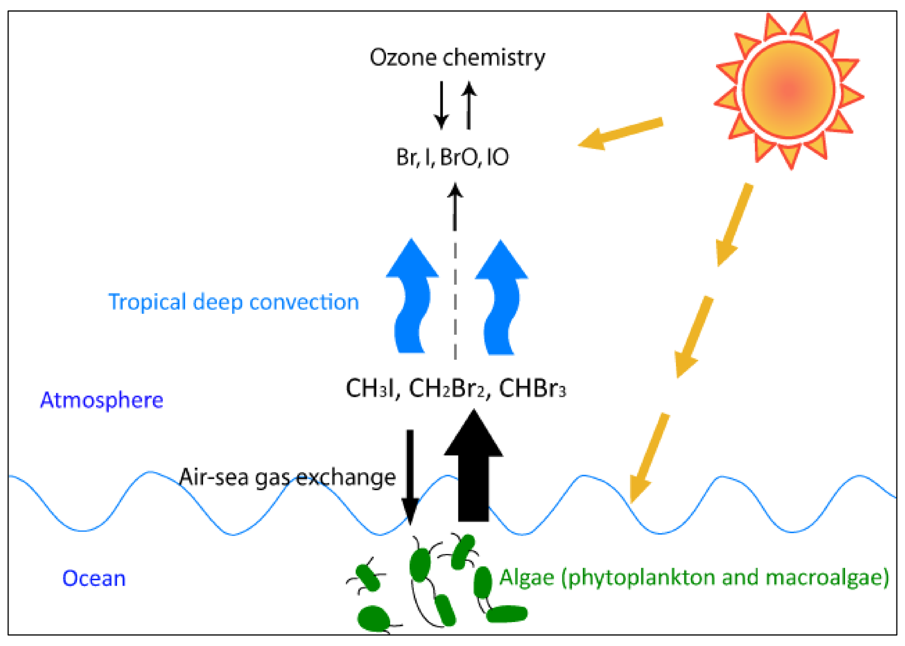

Figure 1: Halogenated VSLS in the tropical ocean. Transport into the tropical tropopause layer via tropical deep convection is crucial with regard to global transport of halogens to the stratosphere.

Very short lived halogenated substances (VSLS) such as bromoform ($CHBr_3$), dibromomethane (CH_2Br_2) and methyl iodide (CH_3I) are of biological or photochemical origin in the oceans and take part in ozone chemistry both in the troposphere and the stratosphere. Tropical oceanic upwelling areas have been identified as source regions for these compounds but their global significance is still uncertain. Deep tropical convection can lift considerable amounts of VSLS into the stratosphere, underlining the importance of the tropical ocean.

VSLS emissions

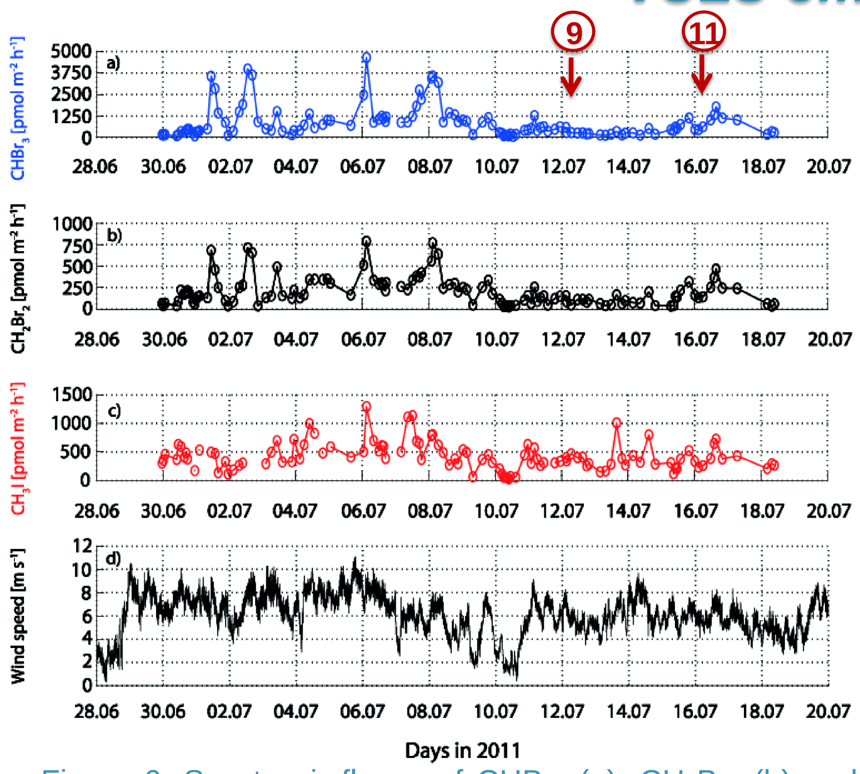

Figure 6: Sea to air fluxes of $CHBr_3$ (a), CH_2Br_2 (b) and CH_3I (c) using background atmospheric mixing ratios of 0.6 ($CHBr_3$), 1.0 (CH_2Br_2) and 0.7 ppt (CH_3I) for calculations. Wind speed is depicted in (d)...

Sea to air fluxes of $CHBr_3$, CH_2Br_2 and CH_3I were on average 847.3 (61.9 – 4654.3) pmol m^{-2} h^{-1}, 202.8 (-1.4 – 789.6) pmol m^{-2} h^{-1} and 422.7 (33.4 – 1295.0) pmol m^{-2} h^{-1}. Fluxes of brominated VSLS were generally lower than from the Mauritanian upwelling due to low wind speeds during MSM18/3. In contrast, fluxes of CH_3I were twice as high as a consequence of much higher oceanic CH_3I during MSM18/3 (Hepach et al. 2013). Potential losses at stations 9 and 11 from the surface due to flux into the atmosphere were for all three VSLS much higher than potential contributions from diapycnal fluxes from below the mixed layer into the surface.

SOPRAN cruise MSM18/3

During the SOPRAN cruise MSM 18/3 (Mindelo – Libreville, June 22 to July 21 2011) onboard the RV Maria S. Merian, VSLS were measured every 1 – 3 h in the surface and from CTD profiles with a purge and trap system and GC-MS. Parallel to this, phytoplankton pigment samples were taken.

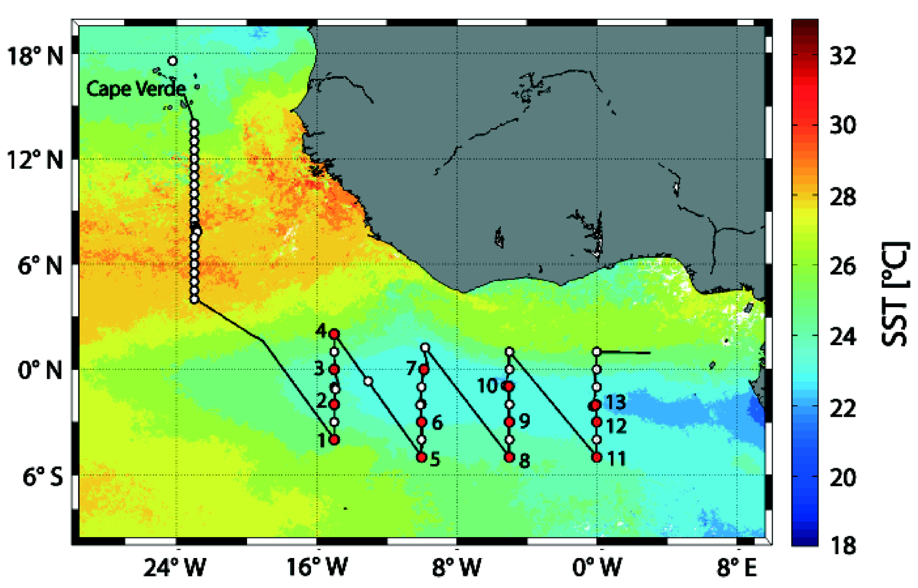

Figure 2: White dots stand for CTD stations on monthly averaged MODIS Aqua sea surface temperature (SST) data from July 2011. Red dots indicate stations where halogenated VSLS in the water column were measured.

Summary and conclusions

- Brominated VSLS in and close to the equatorial cold tongue were found to be in similar ranges as other tropical upwelling regions. Although only low correlations were found, $CHBr_3$ seemed to be associated to *Chrysophytes* both in the sea surface and the deeper water column. This applies to surface CH_2Br_2 as well, but deeper CH_2Br_2 coincided with low light adapted *Prochlorococcus*. Despite high concentrations, low wind speeds led to comparably low emissions.
- CH_3I was found to be high, leading to high emissions in comparison to other upwelling systems. It appeared to be connected to both *Synechoccus* (surface and water column) and *Diatoms* (water column), as well as to global radiation, or daylight, respectively hinting towards photochemistry as additional factor.
- At the exemplary stations 9 and 11, diapycnal fluxes were low in comparison to losses to the atmosphere. Hence, other advection and production processes need to be taken into account as well to determine the mixed layer budget of VSLS.

Transport in the water column

For two exemplary stations (9 and 11) diapycnal fluxes F_{dp} into the mixed layer were calculated according to Kock et al. (2012) using microstructure data to determine the diapycnal diffusivity K_p, and VSLS data over a defined depth:

$$F_{dp} = K_\rho \cdot \frac{d[VSLS]}{dz}$$

Station	Compound	Flux [pmol m^{-2} h^{-1}]
9	CH_3I	15.5 - 19.1
	CH_2Br_2	4.3 - 4.7
	$CHBr_3$	32.8 - 43.2
11	CH_3I	2.2 - 2.9
	CH_2Br_2	1.1 - 2.2
	$CHBr_3$	9.0 - 18.4

Table 1: Preliminary results of diapycnal flux calculations exemplary for 2 stations

All in all, these are weak mixture rates. Of all three VSLS, diapycnal fluxes of $CHBr_3$ were due to its large concentration gradient the highest.

VSLS in sea surface water

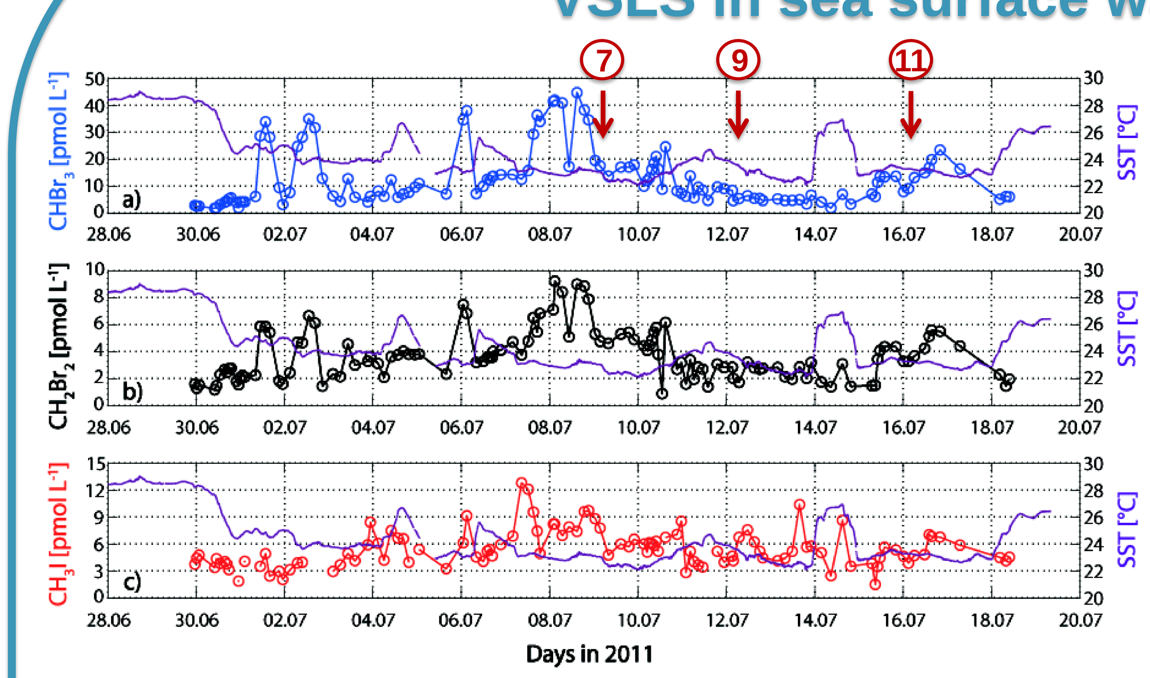

Figure 3: $CHBr_3$ (a), CH_2Br_2 (b), and CH_3I (c) in sea srufce water on the left side. SST is depicted on the right side. Red numbers indicate stations.

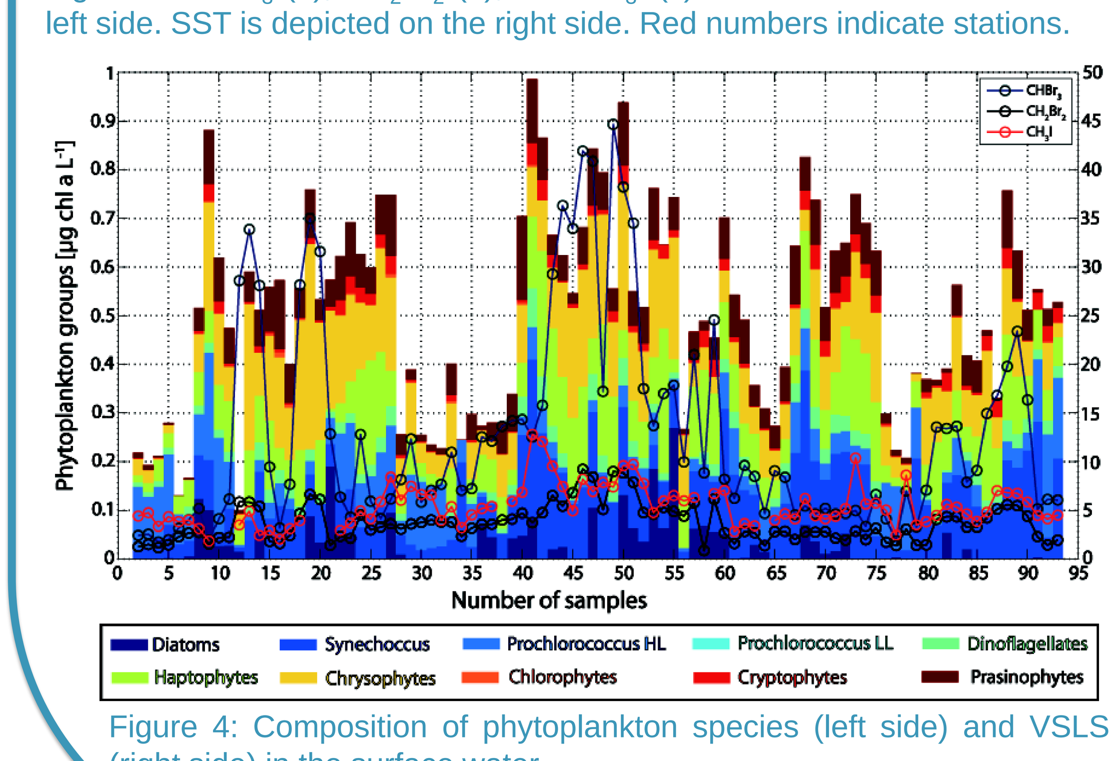

Figure 4: Composition of phytoplankton species (left side) and VSLS (right side) in the surface water.

While $CHBr_3$ with 12.9 (1.8 – 44.7) pmol L^{-1} and CH_2Br_2 with 3.7 (0.9 – 9.2) pmol L^{-1} show similar distributions to each other and compare well in their range to measurements from the Mauritanian upwelling, CH_3I was nearly twice as high with 5.5 (1.5 – 12.8) pmol L^{-1} (Hepach et al., 2013). In the second part of the cruise, CH_3I was also consistent with global radiation (not shown).

In combination with VSLS, no particular species stands out. The two phytoplankton groups that showed the highest abundances throughout the cruise included *Synechococcus* and *Chrysophytes*. Although only low correlations were found, $CHBr_3$ and CH_2Br_2 followed generally a similar pattern as *Chrysophytes* (R^2=0.29 and 0.23). CH_3I showed a more comparable distribution to *Synechococcus* (R^2=0.13).

Production in the water column

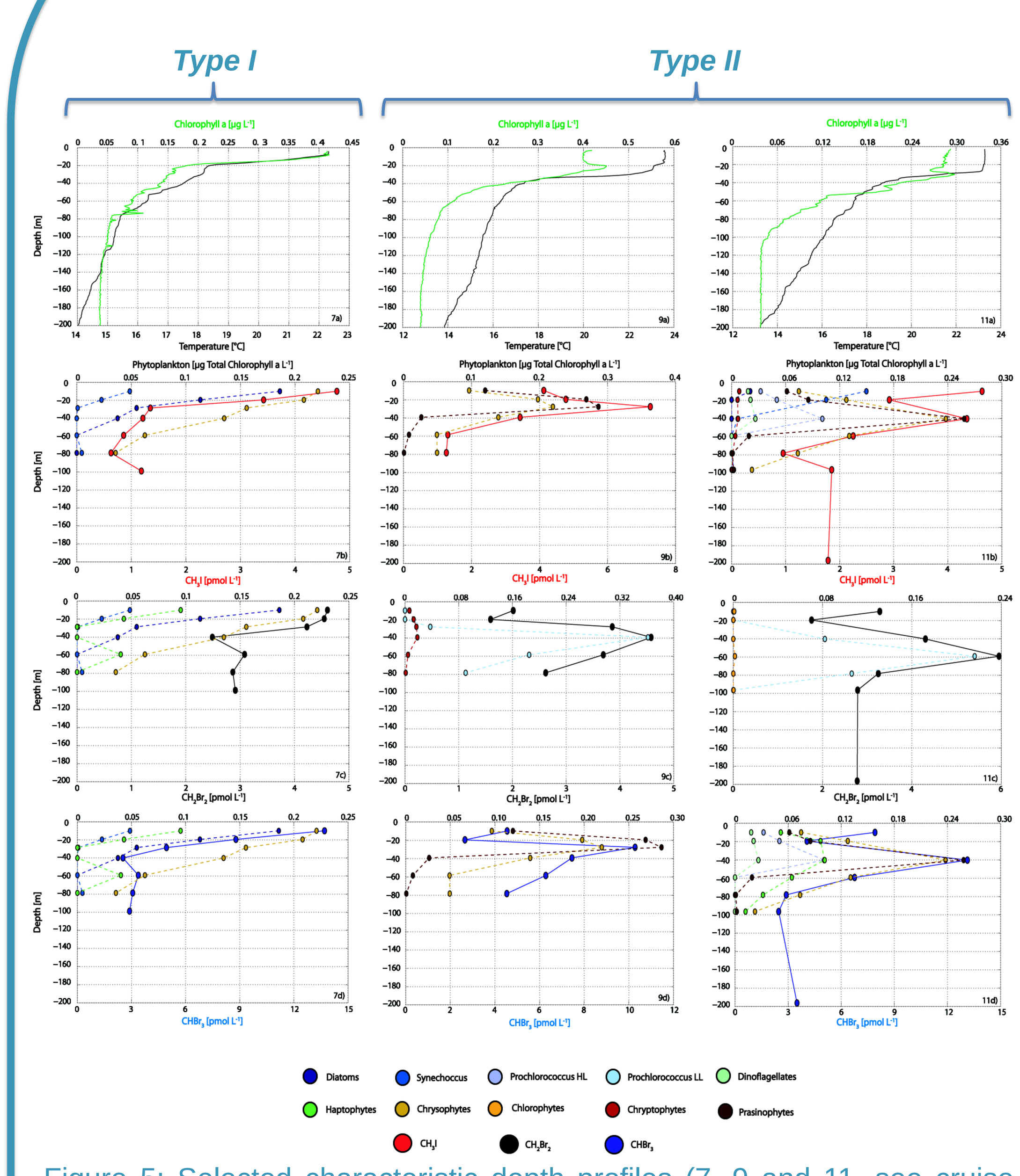

Figure 5: Selected characteristic depth profiles (7, 9 and 11, see cruise map for information on the location of these profiles) of total Chl a and temperature, as well as VSLS along with phyotplankton species with similar distributions in the water column.

Two general types of VSLS profiles were identified:

Type I showes Chl *a* maxima close to the surface along with a shallow mixed layer and maximum VSLS concentrations at the surface. High VSLS concentrations there could be a result of both phytoplankton activity and/or photochemistry.

Type II is characterized by deeper VSLS maxima below or at the bottom of the mixed layer. They are partly consistent with Chl *a* maxima but, especially in the case of CH_2Br_2, lay from time to time below.

There is no species standing out as possible producer. However, while CH_3I is often consistent with the distribution of *Diatoms* and *Synechococcus*, $CHBr_3$ is frequently associated to *Chrysophytes*. This is both consistent with surface distributions. Deep CH_2Br_2 maxima often coincide with high *Prochlorococcus LL*.

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