1. Executive Summary (max 1 page)

It is well known that halogens (e.g., chlorine, bromine and iodine) contributed to the past decline of ozone in the global stratosphere. More than 25 years after the first discovery of the Antarctic Ozone Hole and the ratification of the Montreal Protocol in 1987 and its amendments, reductions in ozone destroying halogens are now becoming obvious in the stratosphere. It has been realized however that not only man-made but also naturally emitted, so-called organic Very Short Lived Species (VSLS) are also contributing to the stratospheric halogen load. This is most noticeable for stratospheric bromine and iodine where the contribution by VSLS has been estimated to be 20% and 100%, respectively. The world's largest sources of VSLS are various types of marine biota (mostly micro- and macro algae) as well as abiotic processes in near surface oceanic waters, though details of their emissions, the atmospheric transport, transformation and delivery to the stratosphere were not well characterized before. The SHIVA project addressed all these issues by experimental and theoretical studies. Further, the relevance of VSLS for past present and future stratospheric ozone was investigated using global chemical transport models (CTM) and prognostic chemistry climate models (CCM). The main outcomes of SHIVA are:

1. Globally the most important emitters of brominated VSLS (primarily $CHBr_3$, and CH_2Br_2) are phytoplankton of various types (i.e. hapto-, chryso-, and chlorophytes), but VSLS emissions by natural or cultivated macro-algae are potentially regionally also important. Emissions from the latter are likely to increase in the future given the current projected rise in seaweed cultivation, particularly in tropical regions.
2. Cyanobacteria - besides photochemical production - seem to be potent CH_3I emitters, but the largest oceanic source of iodine to the atmosphere are emissions of I_2 and HOI, produced by inorganic reactions involving ozone, and in certain oceanic regions other iodinated VSLS such as CH_2I_2 and CH_2ClI.
3. For the major halogenated VSLS ($CHBr_3$, CH_2Br_2, and CH_3I) of stratospheric relevance, best estimates of global sea-air fluxes (source/sink) are +2.96/-0.56, 1.09/-0.12, and 1.45/-0.0001 Gmol atoms/year, including oceanic sources and sinks for the first time.
4. Theoretical and as well as experimental studies indicate that less than 0.3ppt of organic and inorganic iodine are transported into the stratosphere.
5. For different longitudes of the tropics, typical upper tropospheric mixing ratios of brominated VSLS range between 3.5 (WMO-2011) and 4.2 ppt, and in particular for the western Pacific VSLS mixing ratios of 4.1±0.6ppt (SHIVA 2011) and 4.2±0.6 ppt (CARBIC) are found.
6. This may correspond to a stratospheric injection of 1.5-2 ppt bromine due to organic source gas (SG), while the inorganic method suggests a total source and product gas (PG) injection of 4 – 5ppt VSLS. Further since modeling suggests that 75% of the injection is due to organic SG and 25% due to inorganic PG injection, together with the combined uncertainties of both methods, progress towards a consistent picture of VSLS bromine in the stratosphere has been made during SHIVA.
7. From its maximum (20-21ppt) reached in the stratosphere around 2000, total stratospheric bromine is presently decreasing at a rate of (0.8-0.9 ± 0.2)% per year and reached a level 19-20 ppt in 2011.
8. Theoretical studies indicate that VSLS-derived bromine presently reduces O_3 by about al percent at low-latitudes to several percent at high-latitudes, and up to 20% O_3 in polar regions during winter. Radiative forcing due to reduced ozone by VSLS released halogens also leads to modified stratospheric temperatures and transport.
9. Since stratospheric chlorine is likely to decrease in future, the influence of VSLS released bromine on stratospheric ozone will also diminish due to its effect in the combined ClO_x/BrO_x ozone loss cycles.
10. In a future warmer world, VSLS emissions and their contribution to stratospheric bromine loading may increase by 15-60% from present, assuming only physical forcings.

Finally, all data collected during SHIVA can be found here (ftp server: shiva.iup.uni-heidelberg.de) and are available for use by the wider community.

2. Project context and the main objectives (max 4 pages)

The year 2012 marked the 25th anniversary of the Montreal Protocol on ozone depleting substances (ODS). After two and half decades of signing the protocol and its subsequent amendments involving global participation, the future trend in the atmospheric ODS (mostly of halogenated origin) from anthropogenic activities is thought to be understood well (assuming universal compliance with international agreements). Likewise the science behind the Montreal Protocol has matured over three decades, to the point where model agreement on the impact on stratospheric ozone of predicted ODS trends is tight for scenarios where climate and climate gases do not vary. Hence stratospheric levels of ozone destroying halogens (e.g., chlorine, bromine and iodine) have been reported to decline now (e.g., for chlorine, and bromine see WMO, 2011; Dorf et al., 2006; Hendrick et al.,2008) or to be irrelevant (e.g., for iodine see WMO,2011; Bösch et al., 2003; Butz et al., 2009) for the destruction of stratospheric ozone.

Increasing scientific evidence, however, suggested that there are additional contributions to the stratospheric halogens (e.g. mostly bromine and iodine) from mostly biogenically–derived, halogen-containing “Very Short-Lived Substances” (VSLS) and Medium Short-Lived Substances (MSLS) (e.g., for details see chapter 2 in WMO, 2007, or in chapter 1 of WMO, 2011) (Figure 1). One particularly problematic aspect of the uncertain contribution of VSLS, MSLS, and their inorganic product gases (PGs) to stratospheric halogen loading was that it may be very sensitive to changes in climate and therefore cause significant surprises in the future, unless the system is better understood.

Most of the VSLS have sources in the ocean, the terrestrial ecosystem, or are produced by biomass burning (the first two would be a natural contribution, the latter mostly an anthropogenic) (Redeker et al., 2004; Chuck et al., 2005; Yang et al., 2005; WMO, 2007 and WMO, 2011). The relative importance of these sources and the biological contribution to VSLS emissions was largely unknown but the biogenic production was thought to be dominant. Moreover, while it was clear that by enzyme-mediated synthesis (e.g., bromo-peroxidase) marine bacteria, fungi, and especially micro- and macro-algae (seaweeds) are potent producers of halogenated VSLS, their specification according to their relevance for stratospheric ozone was yet largely unclear.

Evidences obtained from prior field observations as well as theoretical studies suggested that for the contributions of VSLS to stratospheric bromine mostly marine emission of $CHBr_3$ and $CH2Br_2$ - but not exclusively - are relevant, while for stratospheric iodine marine emissions of CH_3I and CH_2I_2 are potentially crucial (WM-2011). Further inorganic sources for atmospheric iodine were also suspected to be relevant in this context.

Within the SHIVA project, the stratospheric budget of bromine could be tightened, and its declining stratospheric trend now can firmly be confirmed. For iodine, further evidence was found that its concentrations in the tropical tropopause layer (TTL) and lowermost stratosphere are too low to be significant for stratospheric ozone loss (Butz et al., 2009, and Tegtmeier et al., 2013).

At project beginning the atmospheric transformation and transport through the troposphere to the upper troposphere of these crucial species was far from being well understood, but one major pathway was thought to lead from the western Pacific source region into the upper tropical troposphere, and finally into the stratosphere (e.g., Fueglistaler et al., 2004 and 2009; Ashfold et al., 2012). Alternatively, ODS emitted from surface sources, in particular those located on the continents, e.g., plant emissions or biomass, may also become rapidly transported into the upper troposphere or lower stratosphere by deep convection (e.g., Danielson, 1982).

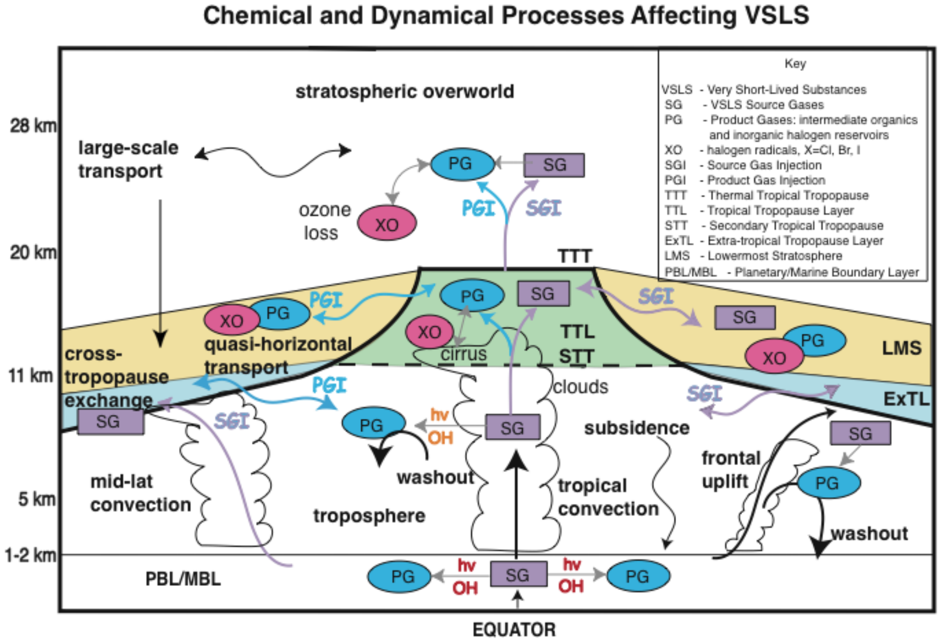

Figure 1: Schematic showing principal chemical and dynamical pathways for halogenated VSL source gases (SGs) and organic/inorganic product gases (PG) between the boundary layer and the stratosphere (WMO, 2007).

Since direct oceanic and atmospheric measurements of these critical species in the western Pacific were largely lacking at project beginning, their source strengths could be estimated only from inverse modeling using different atmospheric transport models (Warwick et al., 2006; Kerkweg et al., 2008; Liang et al., 2010; Ordonez et al., 2012). Therefore, more field observations from critical regions (e.g., in upwelling and tropical waters) appeared necessary, in on order to improve previously existing global emission inventories of halogenated VSLS relevant for stratospheric ozone (e.g., Ziska et al., 2013).

Another uncertainty arose from the divergent estimates of the contribution of VSLS to the stratospheric halogens being in particular large for bromine 1–8ppt, or about 5 to 30% of the total stratospheric bromine content. In part, this uncertainty arose from systematic lower estimates based on the organic method as compared to the inorganic method, and largely diverging estimates among those, most experimental studies addressing the inorganic bromine method. Here a common uncertainty of the inorganic method came into play since photochemical corrections to estimate total bromine from measured BrO were all affected by uncertainties in thermo-chemical and kinetic data, which were in particular large for the formation and destruction of $BrONO_2$ at stratospheric temperature. Within SHIVA, new field data on the formation and destruction of $BrONO_2$ became available which tend to resolve largely the existing gap in VSLS derived bromine among the organic and inorganic method (Kreycy et al., 2013).

More uncertainties arose from the poor understanding of various aspects of radiative and dynamical troposphere/stratosphere coupling that can significantly change the dynamical and chemical structure of the stratosphere. This lack of understanding was partly caused by the fact that global models that are used for climate predictions (atmosphere/ocean general circulation models: AOGCMs) did not resolve stratospheric chemistry, while global models of atmospheric circulation and detailed stratospheric chemistry (chemical climate models: CCMs) typically did not include an interactive ocean. Efforts to close the gap between AOGCMs and CCMs were underway from both sides by including detailed stratospheric chemistry in AOGCMs or by coupling CCMs to ocean models; but these required further development.

In summary, model predictions of future ozone loss due to halogenated VSLS were based on a constant input of natural ODS into the stratosphere, but the entire classification of halogenated VSLS and MSLS, partly of natural origin, have been excluded from most predictions, despite strong evidence that they contribute to the stratospheric halogen budget (WMO, 2007, and WMO, 2011). In all cases the impact of natural ODS will be highly sensitive to climate change in terms of their emissions to the atmosphere, their transport, and their chemical processing.

Since the future changes in the mechanisms that regulate these processes were largely unknown, the VSLS and MSLS have the potential to cause significant surprises in the future evolution of the ozone layer in the changing climate, unless they are better understood. These uncertainties were partly solved within the SHIVA project (e.g., Dessens et al., 2009, Schofield et al., 2011, Ordóñez et al., 2012, Hossaini et al., 2012b, Aschmann et al, 2013, Ziska et al., 2013, and studies under way).

SHIVA aimed at improving our understanding of the role halogenated VSLS and MSLS play for present and future stratospheric ozone, expressed in 4 overall themes:

Main SHIVA objectives

At the beginning of the SHIVA project in 2009, lacking understanding in the role halogenated VSLS may play in past, present and future global ozone came with all relevant processes related to the atmospheric fate of VSLS. These included their marine sources and emissions, their atmospheric transport and transformation, uncertainties in their contribution to the stratospheric halogen budget and finally how they may modify stratospheric ozone and transport in a climate change affected world. Therefore, at the beginning of the project the following major objectives had been identified:

1. The oceanic emission strengths of a suite of halogenated gases in two prominent source regions, i.e. the western Pacific and the tropical Atlantic, needed to be further characterized. These studies aimed at investigations of the source strengths of the targeted substances as a function of season, climate-sensitive factors (such as sea surface temperature (SST), nutrient supply and biological activity) and meteorological parameters in the near surface air (e.g. temperature and wind speed). Intentionally these studies comprised station and ship-based measurements, as well as a literature review and the construction of an ocean–lower atmosphere database of all available halogenated VSLS and MSLS measurements, including those of SHIVA. The collected data would be used for the development of interpretable air–sea gas flux products, for the modelling component of SHIVA and for the investigation of parameterisations and sensitivity studies in order to predict possible climate feedbacks on oceanic emissions of the target gases.
2. The atmospheric transport and transformation of the halogenated SGs and PGs within the tropical troposphere, the tropical tropopause layer (TTL) and the tropical lower stratosphere (LS) would be investigated by systematic field and modelling studies. The field studies performed within SHIVA (e.g., in the western Pacific were suspected to be to key region for VSLS emissions relevant to stratospheric) should combine ship and aircraft measurements, both using sophisticated instrumentation. The data gained during these field studies would further be corroborated by ground-, aircraft- and balloon-borne and satellite observations, which would be undertaken by the partners within nationally funded projects. The transport and transformation modelling should include process-oriented studies to assist interpretation of the field observations and studies that should include air mass trajectory and meso-scale convective modelling. Major emphasis would be put on the fate of brominated and iodinated substances.
3. The past, present and likely future trend of the total halogen burden, and measures of it such as effective equivalent chlorine (EECl) and effective equivalent stratospheric chlorine (EESC), would be established for the global stratosphere. Analysis of past and present trends of the targeted halogens (chlorine, bromine and iodine) would be continued using available and future data from the respective measurements taken by the project partners. Future trends of stratospheric halogens would be established by including surface data of the longer-lived halogenated species (LLS) and their atmospheric lifetimes, as well as the likely contribution of VSLS and MSLS to the individual halogen burdens.
4. The impact of long- and short-lived halogenated trace gases and their inorganic product gases would be investigated for past, present and future ozone within the upper troposphere, TTL and global stratosphere.

> These studies would include global chemical transport model (CTM) simulations driven by past and present decadal long assimilated meteorological fields and those calculated with general circulation models (GCMs) for the future climate of Intergovernmental Panel of Climate Change (IPCC) standard simulations.

Besides investigating all the relevant processes leading from the mostly marine emissions of halogenated VSLS, their atmospheric transport, transformation into product gases, to the entry of source and product gases into the stratosphere by experimental and theoretical models, central aims of SHIVA would address the role halogenated VSLS played in past, present and future global ozone. Worth noting was that, while the recent influence of VSLS on global ozone and transport could be diagnosed from experimental data and further assessed from theoretical studies, their impact on future ozone has been much harder to be assessed. Here major uncertainties were coming into play when assessing the role of VSLS in the future climate change affected world. These range from uncertainties in predicting the future oceanic fertility, sea surface temperatures, the mostly wind velocity driven efficiencies of water atmosphere boundary layer transport, and vertical transport in the atmosphere in relevant regions, as well as uncertainties related in predicting the future oxidation capacity of the lower atmosphere, as well as the composition and dynamics of the overlaying stratosphere. Accordingly, any prediction the role halogenated VSLS may play for future stratospheric ozone would remain highly uncertain.

3. Main Science & Technology results/foregrounds

WP-2: Field observations

1. Long-term trends of halons

The UEA long-term record of halon concentrations at Cape Grim, Tasmania has been updated to the year 2012 (Newland et al., 2013). Halons are long-lived bromine-containing chemicals used primarily as fire suppressants. The atmospheric concentration of 3 halons (H1211, H2402, H1202) are in decline as a result of falling emissions, whilst that of a fourth (H1301) continues to increase, albeit at a slower rate than previously reported.

2. Atmospheric measurements of VSLS

During the 4 years of the SHIVA project over 1200 samples have been analysed for halocarbons (including VSLS). Around half of these were samples collected in the upper troposphere and lower stratosphere (UTLS) by the European CARIBIC aircraft during regular flights between Germany and destinations including India, South Africa, Central America and SE Asia (Figure 2). Other sampling has focused on tropical and extra-tropical regions including the western Pacific (South China, Sulu and Sulawesi Seas) e.g. during TransBrom (Krüger and Quack, 2012; Brinckmann et al., 2012), the eastern Atlantic (Cape Verde and Mauritanian upwelling region; Fuhlbrügge et al 2013; Hepach et al., 2013), the Galapagos Islands (eastern Pacific), Amsterdam Island (Indian Ocean) and Brazil (biomass burning). Establishment of a longer-term sampling station at Bachok (NE Malaysia) has proved difficult (see previous reports), but will be commencing in Jan 2014.

Table 1: Canister sampling locations for VSLS

Location	Latitude	Longitude	Platform	No. of samples
Amsterdam Island	37°S	77°E	coast	46
Cape Verde	16°N - 28°N	15°E – 31°E	aircraft	132
South China Sea - 2009	2°N – 7°N	102°E – 119°E	ship	27
Galapagos Islands	1°S	90°W	coast	23
SHIVA: aircraft	2°N – 8°N	102°E – 120°E	aircraft	216
SHIVA: local boats	2°N – 7°N	111°E – 119°E	ship	46
CARIBIC	77°N – 30°S	120°W – 100°E	aircraft	~800
TransBrom	42°N – 19°S	120°W – 100°E	ship	23
Brazil (Amazonia)	2°S – 12°S	46°W - 68°W	aircraft	120

With respect to bromoform ($CHBr_3$), the highest concentrations tend to be found at the island sites (Galapagos, Amsterdam Island) and also in the region of the Mauritanian upwelling. Concentrations of VSLS in the western Pacific tend to be at the lower end of the observed range. Biomass burning appears not to be a source of brominated VSLS.

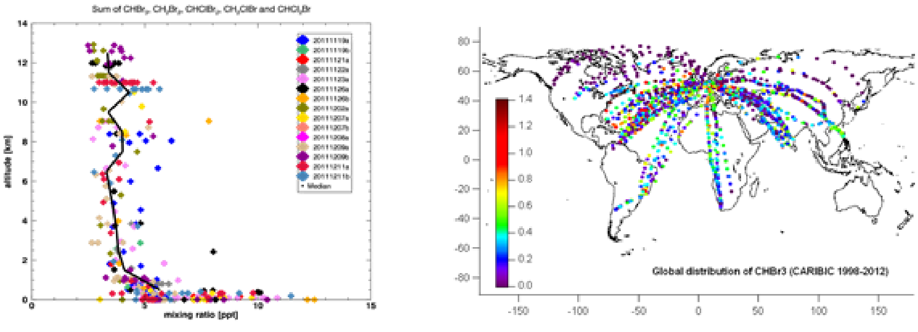

Figure 2: (a) Vertical distribution of total VSLS bromine from SHIVA-Falcon flights in the western Pacific (GHOST data); (b) Global distribution of $CHBr_3$ in the UTLS (10-12 km) from CARIBIC.

In addition to the canister sampling described above, GUF has developed an airborne in situ GC-MS instrument (GHOST) which was flown for the first time during the SHIVA field campaign and, more recently, during the TACTS and ESMVal mission with the new German research aircraft HALO. During SHIVA 2011 there was generally very good agreement between the in situ and canister samples for brominated VSLS. Total VSLS bromine was in the range 4-15 pptv in the marine boundary layer and around 4 ppt in the mid-upper troposphere (Figure 2), which is also in close agreement with recent CARIBIC observations in this region. Total organic bromine in the tropical mid-upper troposphere, which includes contributions from the longer-lived halons and CH_3Br, was 20.0 ± 1.6 ppt.

3. VSLS production by tropical macro-algae

In the first comprehensive study of its type, 15 different species of tropical seaweeds have been studied to determine emission rates of various VSLS (Keng et al., 2013; Leedham et al., 2013). A broad range of production rates were measured (<5 to >1000 $pmolg^{-1}FWhr^{-1}$), a similar range to that found in temperate species. Red seaweeds, which are commonly farmed in tropical regions, were the strongest emitters of bromocarbons. Rapidly increasing aquaculture in the tropics is likely to result in larger VSLS emissions in the future.

4. Ship measurements

A substantial amount of oceanic fieldwork has been conducted during the SHIVA project period. Halocarbon data from two cruises in the tropical Atlantic, one cruise in the Eastern Pacific and two cruises in the western Pacific are available for scientific investigations within SHIVA. Cruise details are provided in Table 2. The cruises were additionally supported by national funding from Germany (TransBrom Sonne (BMBF 03G0731A), SHIVA-SONNE (BMBF 03G0218A), SOPRAN I (BMBF 03F0462A), SOPRAN II (BMBF 03F0611A).

Table 2: Halocarbon data from GEOMAR cruises

Ship/ Cruise	Date	Region	Atmospheric halocarbons	Oceanic halocarbons	Air-sea fluxes
RV Sonne/ TransBrom	October 2009	western Pacific	78 samples	104 surface samples	104 fluxes
RV Poseidon/ DRIVE	June 2010	Mauritanian upwelling	235 samples	116 surface samples 8 depth profiles	116 fluxes
RV Maria S. Merian/ MSM18/3	June 2011	Equatorial Atlantic	50 samples	114 surface samples 12 depth profiles	110 fluxes
RV Sonne/ SO218-SHIVA	November 2011	South China and Sulu Seas	193 samples	80 surface samples 12 depth profiles	80 fluxes
RV Meteor/ M91	December 2012	Peruvian Upwelling	198 samples	97 surface 20 depth profiles	not yet available

During the cruises, a wide variety of measurements were performed. These included atmospheric and seawater concentrations of trace gases; the physical, chemical and biological properties of seawater; and meteorological analysis, including the launches of sondes. For SHIVA one of the most important outputs is the calculation of halocarbon sea-air fluxes, which are subsequently available for WPs 3, 4 and 6. An additional aim of SHIVA was to investigate the links between in situ phytoplankton populations and satellite ocean colour products (see section 5).
The atmospheric halocarbon measurements normally included many VSLS (CH_3I, CH_2Br_2, $CHClBr_2$, $CHBr_3$, CH_2Cl_2, $CHCl_3$, CH_2ClCH_2Cl, C_2HCl_3, C_2Cl_4), as well as a number of longer-lived species including CH_3Br, CH_3Cl, CH_3CCl_3 and CCl_4.

These measurements were made by University of Miami and are separate to those listed in Table 1. Halocarbons measured in seawater included; CH_3I, CH_2Cl_2, $CHCl_3$, CCl_4, CH_3CCl_3, CH_2Br_2, CH_2ClI, $CHBr_2Cl$, CH_2BrI, $CHBr_3$ and CH_2I_2. Flux calculations have been performed for; CH_3I, $CHCl_3$, CCl_4, $C_2H_3Cl_3$, CH_2Br_2, $CHBr_2Cl$, $CHBr_{3.}$ CH_2ClI and CH_2I_2.

The cruises have investigated a number of different tropical and sub-tropical regions, some for the first time, which contain a diverse range of biological regimes, influenced by differing seawater properties, currents, productivity and atmospheric dynamics. Some highlights include:

a. **TransBrom Sonne: Western Pacific, Japan (42°N/141°E) to Australia (19°S/147°E), October 2009**

The first reported seawater measurements of VSLS in the tropical western Pacific (Krüger and Quack, 2012). Substantial sea to air fluxes of VSLS in areas of high wind speed, especially south of the equator in the vicinity of coastlines (Tegtmeier et al., 2012/ 2013).

b. **DRIVE: eastern Atlantic (inc Mauritanian upwelling), June 2010**

Focus on regional and diurnal variation of fluxes in coastal areas, influenced by local emissions and land-sea breezes. A good correlation between oceanic and atmospheric brominated VSLS has been found, which was due to a combination of varying oceanic emissions and changes in boundary layer height (Fuhlbrügge et al., 2013 and Hepach et al., 2013).

c. **M91: eastern Pacific (Peruvian upwelling), December 2012**

This is an integrated biogeochemical study in an oceanic upwelling region, in order to assess its importance for emissions of various climate-relevant atmospheric trace gases and tropospheric chemistry. First results show that the region comprises strong source regions of iodinated halocarbons to the atmosphere.

d. **SHIVA-Sonne SO218, western Pacific, November 2011**

The joint aircraft/ship campaign of SHIVA took place in the region of the South China and Sulu Seas in Nov 2011. The RV Sonne (cruise SO218) sailed from Singapore to the Philippines (15-29 Nov), following a track along the coast of Borneo and through the Sulu Sea (Figure 3). The route incorporated two diurnal stations off the western coast of Borneo, two contacts with local boats from the universities in Kuching and Kota Kinabalu, and was overflown by the Falcon on three occasions. During SO218, the first halocarbon measurements in waters of the coastal western Pacific were performed. Halocarbon concentrations where determined in water and air, and sea-to-air fluxes calculated. Many other atmospheric trace gases, transport processes and various oceanic chemical, physical and biological parameters were also determined.

Atmospheric $CHBr_3$ measured during the SHIVA-Sonne campaign generally ranged between 2 and 3 ppt in coastal regions and decreased above the more open ocean waters (Figure 3b). Similar levels and patterns were observed by the Falcon aircraft and during the PESC-09 cruise. Oceanic $CHBr_3$ was elevated in coastal waters as well (Figure 3c), but was more pronounced at the southern coast. Concentrations there ranged between 12 and 57 pmol L^{-1}. Possible reasons for elevated $CHBr_3$ close to Singapore and Borneo include nutrient rich river runoff supporting biological productivity: $CHBr_3$ maxima in deeper waters often coincided with chlorophyll a maxima suggesting a biological source.

Compared to other tropical regions such as the Atlantic, coastal oceanic concentrations measured in the South China Sea were slightly higher. Close to the Mauritanian coast, between 8 and 42 pmol L^{-1} $CHBr_3$ was measured. In contrast, atmospheric $CHBr_3$ above the Mauritanian upwelling was generally higher (4–9 ppt), due to the stable stratification of the marine atmospheric boundary layer (Fuhlbrügge et al., 2013 and Hepach et al., 2013). Tropical deep convection in the atmosphere above the western Pacific is more intensive than above the tropical Atlantic upwelling systems, leading to enhanced vertical transport and, in combination with the prevailing NE Monsoon and low background concentrations from the open western Pacific, leads to lower atmospheric mixing ratios above the South China and Sulu Seas (Fuhlbrügge et al. in prep.). Elevated water concentrations and high oceanic emissions (Figure 3d) underline the potential importance of this region for stratospheric ozone depletion.

Together the 5 cruises show that all tropical oceans can be a significant source of short-lived halocarbons, especially $CHBr_3$, to the stratosphere (Tegtmeier et al., 2012/ 2013) and that the oceanic regions comprise different sources, such as coastal biota, river input, and open ocean phytoplankton for the various compounds. The data are available from the GEOMAR data server: https://portal.geomar.de/ and from the SHIVA ftp server: ftp://shiva.iup.uni-heidelberg.de and from Birgit Quack (bquack@geomar.de).

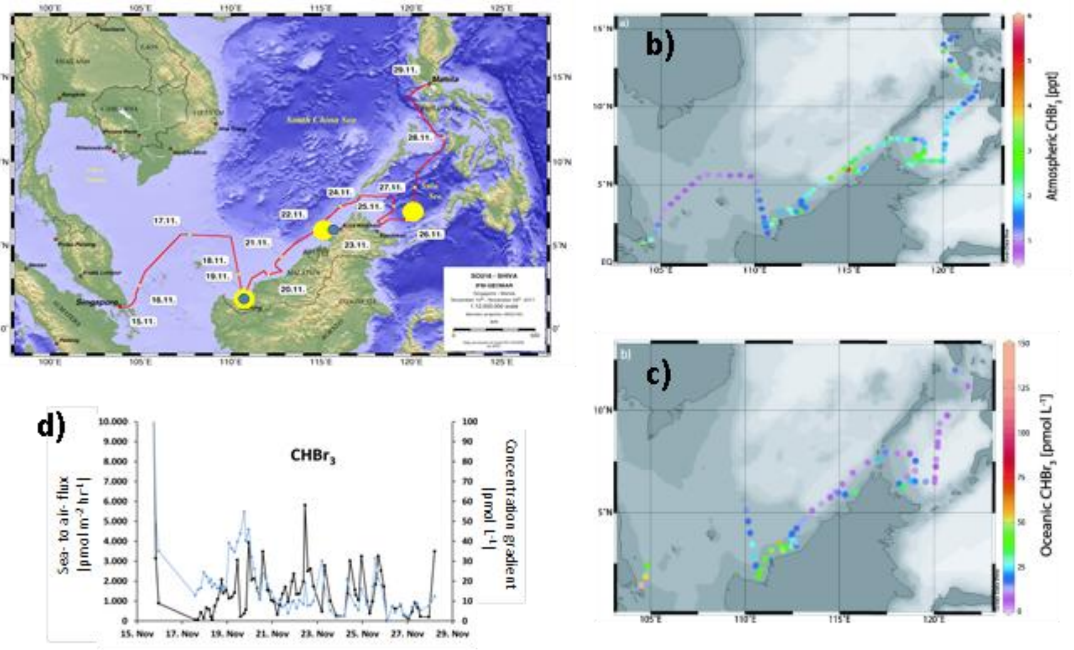

Figure 3: (a) Cruise track of RV Sonne, Singapore-Manila, with local boat contacts and coastal sample exchange (blue circle) and overflights of the DLR-Falcon (yellow circle); (b) atmospheric $CHBr_3$; (c) oceanic $CHBr_3$; (d) concentration gradient (blue) and oceanic emissions of $CHBr_3$.

5. Phytoplankton: Satellite and in-situ observations and the link to VSLS emissions

Prior to SHIVA, phytoplankton had been recognized as a major source of VSLS emissions in the open ocean. In order to prove the hypothesis, during all ship campaigns shown in Table 2, concurrent water sampling and analyses for identifying phytoplankton, its bio-optical characteristics and seawater VSLS conc. were performed. The bio-optical measurements were made in order to improve satellite retrievals of phytoplankton composition which can be later used within WP3 of SHIVA to infer VSLS conc. in seawater. In order to sample regions of high phytoplankton biomass, the campaign planning was supported by high spatially and temporally resolved total phytoplankton biomass maps supplied from the merged SeaWiFS-MERIS_MODIS ESA-GlobColour product (http:www.globcolour.info) for TransBrom and from the MERIS HYGEOS-Polymer products (Steinmetz et al., 2011) for the SHIVA-Sonne cruise. The latter satellite products were unfortunately only available for the later cruise, but were chosen for SHVIA-Sonne because of the improved spatial resolution (1km) and coverage (5-days) as opposed to the ESA-GlobColour products (4.9 km resolution, biweekly coverage). This turned out to be a big advantage as during SHIVA-Sonne many more areas of high phytoplankton biomass were sampled by the in-situ measurements.

Details of the phytoplankton characteristics for the TransBrom cruise have been published (Zindler et al., 2013) and papers have recently been submitted for SHIVA-Sonne (Cheah et al., 2013) and DRIVE (Hepach et al., 2013). The main results from the concurrent sampling of phytoplankton and VSLS (Hepach et al., 2013 and Raimund et al., in prep.) reveal that when phytoplankton concentrations were high, VSLS (mainly $CHBr_3$) concentrations were also high. The relationships between dissolved VSLS and individual phytoplankton species varied during the 3 cruises, but significant relationships were found with certain dominating groups. While for $CHBr_3$ these were haptophytes and chlorophytes for DRIVE and SHIVA-SO218 and chrysophytes for MSM18-3. During MSM18-3 and SHIVA-SO18, CH_3I was significantly linked to cyanobacteria, as well as to solar radiation, suggesting that photochemical production is an additional important factor. Phytoplankton group in-situ data from the various cruises were used to validate the satellite biomass products of diatoms, dinoflagellates, coccolithophores (a large group within haptophytes) and cyanobacteria from the satellite sensor SCIAMACHY on ENVISAT analyzed with PhytoDOAS (more in WP-3). Results show that the PhytoDOAS products agree well with the in-situ phytoplankton group data. Validation of the HYGEOS-POLYMER MERIS satellite chl-a data showed good correlations (r^2 of 0.77 for 24 collocations) for collocations between in-situ and satellite chl-a, but there was a general underestimation (~50%) by the satellite. These improved satellite algorithms for deriving phytoplankton characteristics will be used in the future for inferring seawater VSLS concentrations on global scale with high temporal and spatial coverage, which is a future outlook for WP-3.

6. New measurements of inorganic halogen gases

With the enforced change of aircraft prior to the campaign, it was not possible to install the Leeds LIF IO instrument on the DLR Falcon. Instead, it was operated from the RV Sonne and IO was detected in the marine boundary layer throughout the cruise, although often at levels close to the detection limit (~0.5 pptv). The mean concentration of 1.2 pptv is similar to the levels seen during the TransBrom cruise (Großmann et al., 2013). The highest levels (max = 2.4 pptv) were seen to the north of Borneo in agreement to simultaneous observations of the iup Bremen MAX-DOAS instrument. The reason for the geographical distribution is unclear as there were no significant correlations of reactive iodine with parameters such as chlorophyll or SST. Higher levels of IO (~2 pptv) were also detected close to seaweed fields at Bohey Dulang Island by co-workers from the University of Bremen. Ground-based profile measurements showed evidence of uplifted layers of IO, which were also seen during 2 Falcon flights in the Semporna region. I_2 (0-12 pptv) and the sum of HOI+ICl (0-7 pptv) were also measured on the Sonne (Uni. Mainz). I_2 was much lower than has been seen at a number of coastal locations, but was broadly in agreement with previous open ocean measurements. It is apparent that I_2 and HOI are more important for IO production than the various organic iodine source gases (e.g. Carpenter et al. 2013, Großmann et al., 2013).

Various measurements of inorganic bromine species were attempted during the SHIVA campaign. Novel CIMS measurements of HBr (Falcon) and HBr and [Br_2 + HOBr] (Sonne) were attempted but with limited success. The instruments installed on the Sonne were originally designed to measure trace gas concentrations at low mixing ratios under dry, upper tropospheric conditions. Extensive laboratory tests yielded high sensitivities and relatively low detection limits (3-10 ppt) for both HBr and Br_2. However, as discovered during the cruise, in order to measure under marine conditions, with high sea salt deposition on the inlet walls and high humidity, further development will be required. Ambient levels during the cruise were always below the detection limit. The instruments did, however, measure SO_2 and HNO_3. Similarly, optical (DOAS) measurements of BrO on the Falcon, on the RV Sonne and on Bohey Dulang island were always below the detection limit (~0.8 ppt / 3 ppt for the Falcon instrument).

7. Satellite observations: Global maps of tropospheric BrO and IO from GOME-2 and SCIAMACHY

During SHIVA, the BIRA group has developed a BrO product from METOP-A/GOME-2 satellite nadir observations. BrO total and tropospheric column densities have been derived and compared to correlative data for verification. A good agreement is obtained with SCIAMACHY BrO total column and with ground-based UV-vis observations at 60°N and 45°S (tropospheric and stratospheric columns). It is also found that satellite and ground-based UV-vis observations are both consistent with a mean tropospheric BrO column of 1.5 x 10^{13} molec/cm². Although the BIRA tropospheric BrO columns retrieval algorithm has been primarily developed to study BrO plumes in polar spring, the possibility to use it to retrieve tropospheric BrO over tropical regions has been investigated. It has been found that current BrO data from the GOME-2 satellite instrument do not reach the required sensitivity and accuracy/precision to allow reliable mapping of tropical BrO emissions. The main reasons are the too small BrO signal, low sensitivity to BrO in the MBL due to low albedo, uncertainties in spectroscopy data.

Maps of IO columns derived from SCIAMACHY nadir measurements have been provided by the IUP-Bremen group in support to the SHIVA campaign. As for BrO, the main focus for the IO satellite analysis was the Polar Regions, as ozone depletion events (ODE) in Polar Spring time had drawn a lot of attention. The Bremen IO retrieval algorithm

(Schönhardt et al., 2008) has been applied to SCIAMACHY measurements over tropical regions. Due to the better measurement sensitivity in the marine boundary layer for IO than for BrO, evidences have been found for IO spots in the Tropics in contrast to BrO. For several regions the spatial pattern of IO was found to be similar than for indicators of biological activity like Chl-a. However, there is no one-to-one relationship and the spots are found to be sensitive to both cloud cover and surface reflectance, so they need to be interpreted with caution and further validation studies are necessary.

8. Satellite observations (b) Vertical profiles of stratospheric BrO from SCIAMACHY

During SHIVA, a retrieval method has been developed to deduce vertical profiles of BrO in the stratosphere between 16 and 30 km altitude based on limb-scatter measurements from the SCIAMACHY/Envisat instrument. It further extends the previously developed global climatology of stratospheric partial BrO columns from SCIAMACHY limb (Hendrick et al., 2009). Version 3.2 and 3.3 data were provided to the SHIVA data base and are available for scientific use. The actual version is now taken a pointing-misalignment correction into account that, in particular, improves tropical measurements. The data set was evaluated against synthetic spectra as well as profile-wise to retrieval methods from other institutions and ground-based observations (Hendrick et al., 2009 and Rosanov et al., 2011). Within SHIVA, consistency of the vertically resolved BrO climatology was demonstrated with respect to total columns measured in nadir mode and total columns from GOME-2 retrieved at BIRA.

Within WPs 4 and 5 of SHIVA, the height-resolved SCIAMACHY limb BrO climatology has been applied to assess the annual and inter-annual variability of BrO in the tropical lower stratosphere in relation to the tropospheric abundances of brominated substances measured during SHVA, and to infer the long-term trend in BrO and the associated total inorganic bromine abundance of the stratosphere.

9. Additional Outcomes

A number of activities, not directly related to the central theme of SHIVA, were undertaken with the DLR Falcon aircraft. Firstly several new instruments (GHOST, SPIRIT, CIMS) were successfully installed and operated for the first time. As discussed in section 2, GHOST provided essential data on the total organic bromine budget (including VSLS) from the surface to 14 km. SPIRIT was used to measure CO and CH_4 and has provided a valuable dataset in a region where few previous measurements have been reported. CO in particular has also been a useful tracer for anthropogenic pollution (and convective uplift) during the flights. Although CIMS was not successful in detecting inorganic bromine species, it has generated a unique dataset of SO_2 measurements. In addition to measurements of IO, a fourth instrument (DOAS) was able to measure HCHO, NO2 which provide useful insights into the composition and chemistry of the western Pacific region. Finally, we were able to carry out two successful tracer release experiments to further evaluate this novel technique and to provide a useful test of the various transport models used during flight planning.

As additional outcome, the BIRA group has provided satellite maps of NO_2, formaldehyde (HCHO), and glyoxal (CHOCHO) vertical column densities (VCDs) above South-East Asia for the November-December 2011 period in support to the SHIVA campaign. These satellite data were retrieved from the OMI and GOME-2 instruments. Preliminary comparison results with SHIVA airborne mini-DOAS measurements of HCHO and NO_2 performed by UHEI show that HCHO and NO_2 spots are present in both satellite and aircraft data along the coast of Borneo around Bintulu on November 16, 2011. Large CHOCHO columns are also detected by the GOME-2 satellite instrument in this region. These high HCHO, NO_2, CHOCHO spots could be related to the presence of natural gas production facilities close to Bintulu (off-shore and in the port area). Aircraft profiles have been also used to validate model profiles used for the calculation of airmass factors (AMFs) in the BIRA HCHO satellite retrievals.

WP-3: Emission inventories, present and future scenarios

1. Background

While global emissions of brominated volatile organic compounds with short atmospheric lifetimes (VSLS) have a significant influence on the bromine and ozone loading in the stratosphere, the magnitude and nature of their sources and oceanic emissions are poorly understood. The impact of shorter-lived gases on ozone depletion is highly dependent on the magnitude, location, and timing of their emission (Tegtmeier et al., 2012; Hossaini et al., 2013). Prior to SHIVA, global 'maps' of such emissions had only been informed from top-down modeling studies (Liang et al., 2010; Warwick et al., 2006; Pyle et al., 2011; Ordonez et al., 2012) and they displayed significant disagreements. Further, their intra-annual cycles, and long-term trends were all unknown before the SHIVA-project started. The main objective of this work package was the exploration of the global oceanic emission strengths of a suite of prominent halogenated gases, comprising the major marine contributors to stratospheric bromine dibromomethane (CH_2Br_2) and $CHBr_3$. The work included the initialisation of a global database and compilation of existing air-and sea water measurements, the calculation of VSLS emissions based on these existing data with emphasis on tropical oceanic regions, and an assessment of potential future changes in VSLS emissions. In order to investigate proxies and parameterisations for VSLS concentrations and emissions, satellite products of phytoplankton composition and concentration have been developed.

1. Global data base and global emission scenarios

The main objective of the global data compilation was the production of best estimates of air-sea fluxes of VSLS compounds from a bottom-up approach, which was not available in this form at the start of the project. Ziska et al. (2013) published the first comprehensive global sea-to-air flux climatology of three important short-lived halocarbons $CHBr_3$, CH_2Br_2 and methyl iodide (CH_3I) in SHIVA.

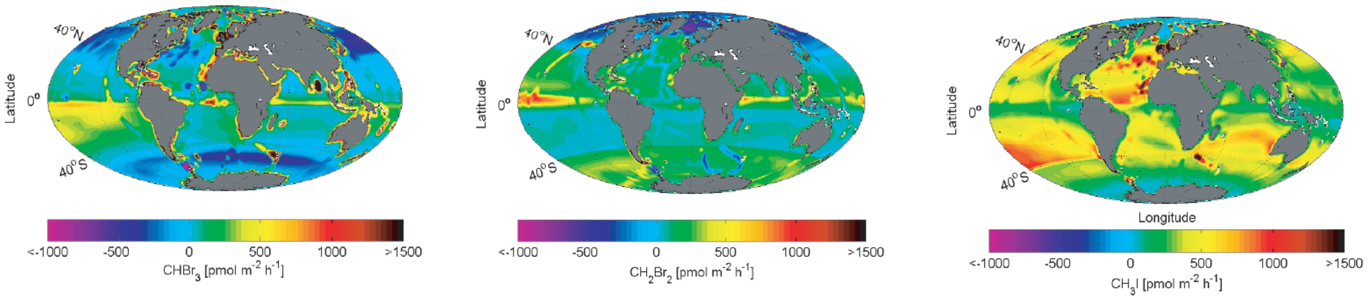

Figure 4: Global sea-to-air fluxes (pmol m^{-2} h^{-1}) for $CHBr_3$ (left), CH_2Br_2 (middle) and CH_3I (right) in pmol m^{-2} h^{-1} based on the robust fit regression technique (Ziska et al., 2013).

The surface oceanic and atmospheric measurements from the HalOcAt database, considering the period from 1989 to 2011, were divided between coastal, shelf and open ocean regions and interpolated onto a global 1°x1° grid, while missing values were interpolated with latitudinal and longitudinal dependent regression techniques. Resulting from this, global sea-to-air fluxes were calculated using physical forcing fields with a high temporal resolution of 6 hours (Figure 5). Based on these calculations a total global flux of 1.5/ 2.5 Gmol Br yr^{-1} for $CHBr_3$ 0.78/ 0.98 Gmol Br yr^{-1} for CH_2Br_2 and 1.24/ 1.45 Gmol I yr^{-1} for CH_3I (Robust Fit/ Ordinary Least Square regression techniques) was derived. Contrary to recent studies, negative fluxes occur in each sea-to-air flux climatology, mainly in the Arctic and in the Antarctic. 'Hot spots' for global polybromomethane emissions are located in the equatorial belt, whereas methyl iodide emissions are enhanced in the subtropical gyre regions. The seasonal variation of the global climatological flux (9-21 %) of the three VSLS compounds is larger than the inter-annual variability, which is generally less than 5 %. Compared to earlier studies, our global fluxes are at the lower end of estimates, especially for $CHBr_3$. We interpret this as an underrepresentation of coastal emissions and of extreme events, which cannot be resolved in the 1°x1° estimate. The data are available to the scientific community as supplements to the final publication by Ziska et al. (2013).

Different VSLS emission climatologies were used by different SHIVA-partners in sensitivity studies which led to the publications by Tegtmeier et al. (2013), and Hossaini et al. (2013). The global sea-to-air flux bottom-up estimates improves the quantification of the impact of brominated and iodinated VSLS on global (future) climate and ozone budget. Hossaini et al. (2013) evaluated different top-down and bottom-up emission scenarios. The Ziska-climatology (Ziska et al., 2013) is at the lower end of published halocarbon scenarios and shows the best agreement with the compilation of $CHBr_3$ surface observations in the tropics. Hossaini et al. (2013) created an optimized estimate of bromine contribution of 4 ppt from with the Ziska–emissions for $CHBr_3$ and the dibromomethane (CH_2Br_2) emissions from Liang et al. (2010) to the stratospheric loading (see also WP4 final report).

Tegtmeier et al. (in preparation) preliminary estimates upper air concentrations of $CHBr_3$ and CH_2Br_2 in the West Pacific of 0.26 ppt and 0.89 ppt, respectively from simulations with the Lagrangian transport model FLEXPART initialized with the Ziska climatology. The two major VSLS contribute about 2.6 ppt bromine to the stratosphere through source gas injection which is in close agreement with estimates calculated based on measurements during the SHIVA aircraft campaign (2.7 ppt, Sala et al., in preparation). The overall contribution in form of source and product gases is found to be about 4.3 ppt bromine (preliminary results) based on the FLEXPART simulations.

2. Future oceanic emissions

The objective of WP3 to estimate halogenated emissions in a future changing environment has also been addressed. As first approach, future emission scenarios were achieved by assuming current oceanic and atmospheric climatological concentration estimates (Ziska et al., 2013) driven by projected oceanic hydrological and meteorological parameters (wind speed, sea surface temperature, salinity, sea level pressure) from the MPI-ESM-LR (a complex earth–system model, developed at the Max Planck Institute for Meteorology, Hamburg, Germany) using CMIP5 model scenarios. The model runs were delivered to the CMIP5 (Coupled Model Inter-comparison Project Phase 5) data-base (http://ipcc-ar5.dkrz.de/home.htm) for the 5th assessment report of IPCC (Intergovernmental Panel on Climate Change). We used the future climate scenario RCP 8.5 corresponding to an enhancement in radiative forcing exceeding 8.5 W/m^2 in 2100 (approx. equal to 1370 ppm CO_2) in order to estimate an extreme of projected VSLS flux changes. In addition, input parameters from the coupled Chemistry Climate Model CMAM (Canadian Middle Atmospheric Model, including ozone chemistry and coupled ocean) REF-B2 scenario were used as well, taking Chlorofluorocarbons and Greenhouse gas changes in the future into account.

Both model projections reveal a future increase in global VSLS emissions based only on a change of the physical forcing parameters, in particular an enhancement of sea surface temperature and wind speed and a decrease of sea level pressure and sea surface salinity. CMAM yields lower future values especially for $CHBr_3$ compared to MPI-ESM-LR (Table 3, Figure 5), which is mainly due to a lower increase in sea surface temperature and sea surface wind speed

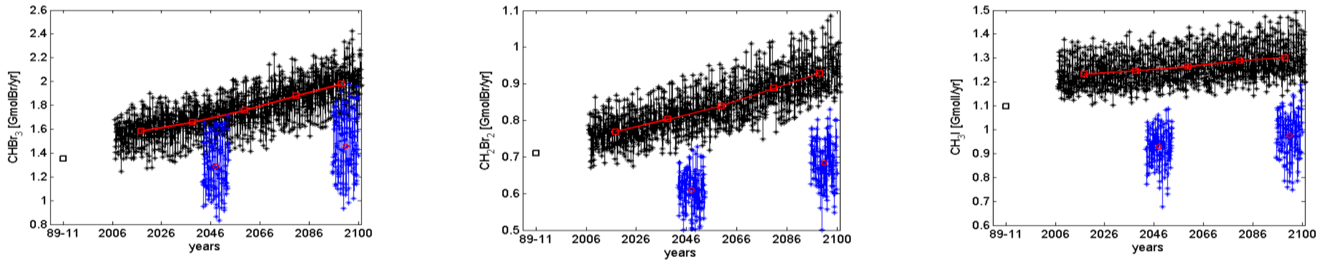

Figure 5: 20 year averages (red) of projected global sea to air fluxes of $CHBr_3$ (left), CH_2Br_2 (middle) in GmolBr/yr and methyl iodide (right) in Gmol I/yr, calculated with the future physical forcings from MPI-ESM (black) and CMAM (blue). Open circles: Emission climatologies are from 1989-2011 (Ziska et al., 2013).

data, projected by this model. $CHBr_3$ emissions exhibit the largest increase with ca. 25% (MPI-ESM-LR) to the year 2100, compared to other related VSLS (Table 3). In contrast, the total global sea to air fluxes of methyl iodide show the same low increase of ca. 5% for both models, likely due to the already large super saturation of this compound and possibly on the basis of minor changes in future wind speed projection.

Table 3: Changes of future global VSLS emission in % relative to 2006 using CMAM (decadal mean between 2040-2049 and 2090-2099) and MPI-ESM LR (20 year means between 2006-2100) data.

$CHBr_3$	CH_2Br_2	CH_3I	Model
13.4	11.9	~5	CMAM
~25	13.4	5	MPI-ESM LR

The current results give an idea of the projected change of halogenated fluxes in the future based on physical parameters using one CCM and one CMIP5 model. These future emissions estimates were also used in WP4.

3. Phytoplankton functional types as VSLS proxies

The evolution of halocarbon air and seawater concentrations in a future climate is obscure, since the present underlying biogeochemical controls on the environmental concentrations and their development are hardly known. In order to assess possible production rate changes of VSLS in the future and changes in possible underlying biogeochemical controls, different proxies and parameterizations for environmental VSLS distributions were tested. Before SHIVA started, only relationships between total biomass (chl a) and VSLS have been studied in specific locations. Within SHIVA we were able to elucidate the relationships of main phytoplankton groups to VSLS emissions (see results of WP2). Within WP3, in order to get proxies and parameterisations for VSLS concentrations and emissions on global scale, satellite products for four different phytoplankton groups have been developed. The composition and concentrations of dominant PFTs (Phytoplankton Functional Types) were derived from measurements of the satellite sensor SCIAMACHY on ENVISAT analysed with PhytoDOAS, a version of Differential Optical Absorption Spectroscopy (DOAS) formerly specialised for the detection diatoms and cyanobacteria (Bracher et al., 2009). This method has been improved within SHIVA for detecting four different types of PFTs (Figure 6) by using simultaneously fitting of the differential specific absorption spectra of each species to the satellite measurement (Sadeghi et al., 2012a). These PFTs are diatoms, cyanobacteria, dinoflagellates and coccolithophores. Also within SHIVA the whole SCIAMACHY (SCanning Imaging absorption spectrometer for Atmospheric CharographY) data set (Aug 2002 until April 2012 - end of ENVISAT mission) has been analysed with PhytoDOAS for all four PFT. These data are reasonable for use at monthly mean and 0.5° grid resolution, reflecting the coverage and pixel size of the SCIAMACHY sensor. For the entire mission these gridded data have been calculated, which are also available as global maps.

PhytoDOAS is a novel and completely different ocean colour retrieval of phytoplankton groups, which does not retrieve different phytoplankton groups from multi-spectral satellite observations. The use of multi-spectral data limits the ability to differentiate among the optical imprints of different water constituents and empirically derived relationships as well as assumptions had to be developed. This results in systematic errors, which occur from the knowledge of the regional (not global) distribution of the in-situ dataset. PhytoDOAS allows the determination of the biomass of the four above mentioned different phytoplankton groups (Figure 6) analytically and independent from a priori information using high spectrally resolved satellite data from SCIAMACHY.

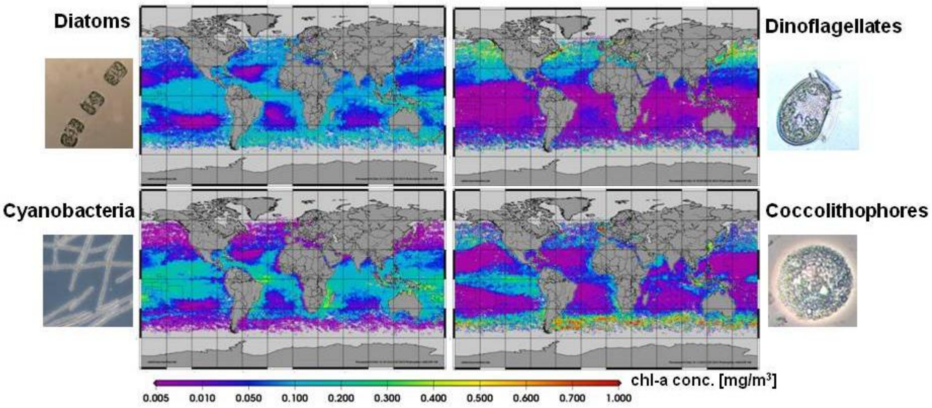

Figure 6: Mean chl-a conc. in March 2007 of different phytoplankton groups derived with PhytoDOAS (Bracher et al., 2009; Sadeghi et al., 2012a) from SCIAMACHY data. Representative photographs for each group from S. Kranz and S. Wiegmann (AWI).

The method is an extension of the DOAS, commonly used in satellite retrievals of atmospheric trace gas concentration; PhytoDOAS accounts in addition to atmospheric compounds also for the differential absorption of water itself and its constituents. One drawback of the hyper-spectral SCIAMACHY data is the coarser spatial resolution of the ground scene (30 km by 60 km) which is nonetheless acceptable for open ocean conditions. PhytoDOAS data products were evaluated by comparisons to similar satellite products and in-situ data (Sadeghi et al., 2012b; Altenburg Soppa et al., 2012), but also used to study phytoplankton variability in lower latitude regions (Sadeghi et al., 2012b) and for evaluating parameterizations in a biogeochemical model (Ye et al., 2012).

Global data sets of phytoplankton groups from PhytoDOAS cover so far 10 years until 2012. The future perspective is to adapt the retrieval to all available hyper-spectral ocean color data and merge the information with the high spatially resolved multi-spectral ocean colour information on total phytoplankton group distributions. These long-term ocean colour data (starting in 2002 until present with a perspective to the late 2020s and longer) will be used for evaluation and improving parameterizations in coupled ecosystem-ocean circulation modelling. The final model dataset, which covers areas and times invisible to remote sensing, will contribute significantly to a better understanding for the attribution of anthropogenic and natural sources of climate change to the marine ecosystem and biogeochemical cycles.

The direct relationship between phytoplankton group abundances and bromocarbon concentrations was analysed in WP-2 of SHIVA, revealing varying dependencies during the TransBrom, Poseidon, M. S. Merian and SHIVA-SONNE campaigns. Although for the later cruises correlations with chl-a have been observed for $CHBr_3$ as well as CH_2Br_2 sea surface concentrations, which are elevated at coast lines and in productive upwelling areas of the Atlantic ocean, there is no robust relationship between chl-a concentrations in the ocean and the observed concentrations. Also, direct correlations of $CHBr_3$ with different phytoplankton groups have been variable for different cruises (see WP-2).

The high variability of VSLS (especially for $CHBr_3$) in both ocean and atmosphere is not explicable with a simple correlation. Common parameterization applying multiple linear regressions and polynomial fits with biological and physical parameters (e.g. chlorophyll *a*, SST, SSS, SLP, mixed layer depth) did not provide straightforward results (Figure 6). Major reasons are the complexity of biogeochemical processes (sources and sinks) for the different phytoplankton species. Further other marine organisms existing in coral reefs, and macro-algae are also known to be VSLS efficient producers. Finally, abiotic oxidation processes can also produce halogenated VSLS. Therefore in future work more environmental variables and the PFT’s shall be explored for the use in parameterizations of oceanic VSLS production and concentrations.

4. Future oceanic VSLS concentrations

It is likely that oceanic VSLS concentrations and emissions increase in the future due to anthropogenic and environmental physical forcings. Intensifying coastal upwelling systems might play a crucial role in a changing climate. Primary production could increase with enhanced entrainment of nutrient rich deep water into the surface ocean leading to amplified biological production and production of brominated VSLS (Hepach et al., 2013). Enhanced land-sea pressure gradients due to increasing SST and surface air temperature, could lead to increasing wind speeds which would also directly influence the sea-to-air fluxes of all trace gases via a faster gas transfer. Increasing SST might also influence the oceanic production of halocarbons, through intensification of the microbial loop in surface waters with unknown consequences for VSLS production and increase the oceanic emissions via reduced solubility. Hence, the relevance of the tropical ocean with respect to halocarbon emissions will likely increase. In addition to the anthropogenic induced physical and biological forcings which likely lead to increased oceanic VSLS emissions, direct anthropogenic influences as increasing water disinfection processes and macro algae farming, both producing large amounts of bromocarbons, likely lead to further increases. The projected increased stratification of the surface ocean entailing lower primary productivity and suboxic subsurface waters, created by the enhanced upwelling intensities of eastern boundary systems, may counteract the concentration increases. Over fishing, having significant impacts on the structure of food webs, possibly affecting primary production and shifting coral reefs to a more algal dominated regime, may also impact the production of halocarbons. In order to understand the future development and roles of marine halocarbon emissions on global ozone changes and atmospheric chemistry, it is important to continue to better quantify the relative roles and interactions of the oceanic biological and abiotic production. For obtaining more realistic VSLS emission scenario than presently available, such study would also need to include factors such as the variation of wind speed with space and time, height of the marine atmospheric boundary layer, sea surface temperature as well as anthropogenic and other relevant forcings to the global ocean (e.g. Fuhlbrügge et al., 2013; Hepach et al., 2013).

5. Emission scenarios for the South-China Sea region

During the SHIVA-project various present day emission scenarios have been developed for the South China Sea. First Ooi et al., (2013) studied the spatial and temporal variations primary productivity (phytoplankton growth) as a function of meteorological conditions in the South China Sea. Leedham et al. (2013) extrapolated results from tropical macro-algal incubation studies to the coastal South – East Asian region, while Ashfold et al. (2013) applied inverse trajectory modeling to identify source regions for atmospheric concentrations measured at both coastal and inland sites in eastern Borneo. Pyle et al., (2011) reproduced an early sample of the same coastal atmospheric concentrations from eastern Borneo with a top-down emission scenario with the p-Tomcat model. All emission scenarios appear to derive different emission rates per unit time and space. Considering their different spatial resolutions and their definition of the coast line, which is especially critical for $CHBr_3$, as it reveals highest emissions at the coast globally, the different emission scenarios show comparable rates. Most chemistry transport models, which apply emissions scenarios to project their halogen burden to the stratosphere, do not need to resolve high spatial and temporal variations of VSLS emissions to match the observed upper air abundances. However, they may get the right answer for the wrong reason due to low horizontal resolution and model parameterization biases. Thus, the temporal and spatial resolution of the applied emission scenario needs to be critically assessed. For the dynamic situation of highly variable VSLS emissions and highly variable transport, trajectory modeling driven by observed fluxes appears to be the most realistic scenario (Tegtmeier et al., 2012 and 2013; Marandino et al., 2013).

WP-4: Process studies: Transport and pathways

1. Background

In this work package, key processes of the chemistry, transport and microphysics of very short-lived substances (VSLS) were examined in a number of modeling studies. The results were used to improve the understanding of the processes and their representation in large scale models and to assess uncertainties in the parameterization of the processes. Several models of transport and chemistry of VSLS and their product gases (PG) were developed and applied, covering a wide range of different modeling approaches. In particular, the following models were developed further to include VSLS and PG chemistry and employed in case studies:

- The Eulerian model SLIMCAT/TOMCAT (UNIVLEEDS) was used for end-to-end studies of the transport and chemistry of VSLS from the surface to the stratosphere.
- The Eulerian model Bremen CTM (UNIHB) was also used for end-to-end studies of transport and chemistry of VSLS.
- The mesoscale model C-CATT-BRAMS (CNRS) was used for case studies on a smaller and more detailed scale, including deep convection.
- The Lagrangian model ATLAS (AWI) was used for studies of transport and chemistry of VSLS with a focus on different OH conditions. AWI also employed a simplified conceptual model.
- As basis for the studies, a comprehensive chemistry scheme for VSLS and their organic and inorganic product gases was developed by UNIVLEEDS, CNRS and UNIHB, including heterogenous chemistry and microphysics.

Additionally, the work package included the flight planning for the campaign with the FLEXPART model (NILU), model studies of UCAM, which are in WP6, and derivation of Br_y and I_y from satellite observations (UNIHB). Model calculations in this work package were based on the surface emission inventories from WP3.

1. Major results

- A comprehensive chemistry and microphysics scheme of the chemistry of VSLS and their product gases was successfully developed, including heterogeneous chemistry, solubility and washout.
- The amount of Br_y originating from VSLS transported to the stratosphere crucially depends on the amount of soluble species and their washout (all non-soluble species in the form of VSLS or PG reach the stratosphere and contribute to Br_y).
- The most abundant inorganic product gas is HBr, which is very soluble and efficiently washed out on convective clouds. The heterogeneous reactions of HBr in clouds reduce the efficiency of washout under certain conditions.
- Uptake of HBr on cirrus ice and irreversible removal are likely to be of minor importance.
- Short-lived organic product gases of VSLS can be neglected in VSLS chemistry schemes and inorganic product gases can be formed directly from the source gases. Inorganic Br_y should be speciated to represent its washout.
- The overall contribution of VSLS and PG to the stratospheric Br_y budget is about 5 ppt, in good agreement with stratospheric DOAS measurements of Br_y. Sensitivity runs show budgets ranging from 4 to 8 ppt.
- About 75% of the stratospheric Br_y originating from VSLS reaches the stratosphere in the form of source gases.
- For $CHBr_3$, the emission inventory of Ziska et al. (2013) shows best agreement with observations. For CH_2Br_2, the emission inventory of Liang et al. (2010) gives good results.
- A tropospheric OH minimum was discovered over the Pacific warm pool, which is the main source region for stratospheric air, and can potentially have a large impact on the composition of the stratosphere.

2. Detailed scientific results

The University of Leeds developed a detailed chemistry scheme for the VSLS, including the degradation of the source gases into short-lived organic product gases and further into inorganic product gases (Hossaini et al., 2010). The model contains a detailed degradation scheme for the species $CHBr_3$ and CH_2Br_2 and reactions for several other minor VSLS like $CHBR_2Cl$ or $CHBrCl_2$. Figure 7 shows the scheme for $CHBr_3$. A main result of Hossaini et al. (2010) is that organic product gases can be neglected in VSLS chemistry schemes due to low mixing ratios and fast reaction rates and that inorganic product gases can be formed directly from the source gases.

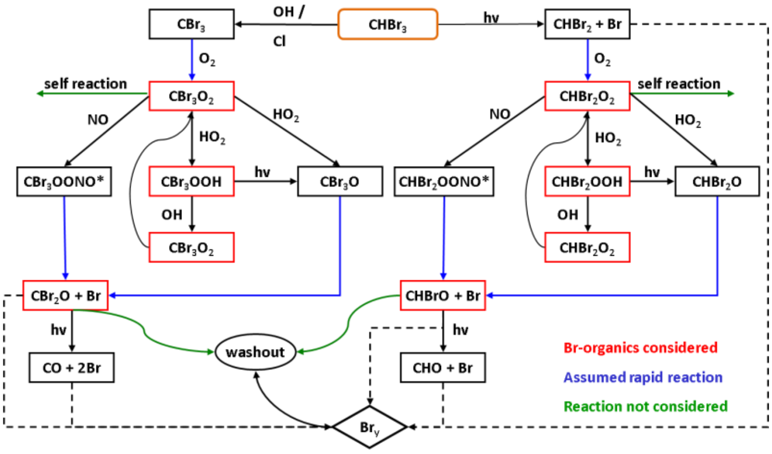

Figure 7: Degradation scheme for $CHBr_3$ used in the SLIMCAT/TOMCAT model.

Model runs of the TOMCAT model were used to compile a detailed budget for the Br_y originating from VSLS and to determine the ratio of source gases to product gases (Hossaini et al., 2012, Table 4). The modeled Br_y from VSLS reaching the stratosphere is about 5 ppt, in good agreement with estimates from the difference of stratospheric DOAS measurements and the sum of long-lived gases (Dorf et al., 2006).

UNIVLEEDS performed global simulations to evaluate a range of different emission inventories (Hossaini et al., 2013). Within the tropics, a better agreement between simulated and observed profiles of $CHBr_3$ are obtained with a lower (bottom-up) derived emission inventory (Figure 8 and 9). However, no single inventory gives the best agreement in all locations for $CHBr_3$. For CH_2Br_2, the inventory of Liang et al. (2010) provides good agreement in all locations.

Table 4: Source and product injection into the stratosphere according to Hossaini et al., (2012).

	SGI (pptv)	**PGI (pptv)**	**Total**
Long-Lived			
CH_3Br	6.90	0.29	7.19
H1211	3.98	0.19	4.17
H1301	3.09	0.04	3.13
H2402	0.87	0.04	0.91
VSLS			
$CHBr_3$	1.41	0.91	2.32
CH_2Br_2	1.58	0.16	1.74
Other	0.97	0.21	1.18
∑ VSLS	**3.96**	**1.28**	**5.24**
∑ ALL	**18.80**	**1.84**	**20.64**

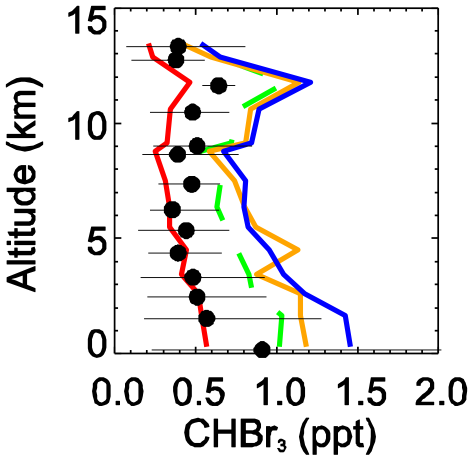

Figure 8: Observations of $CHBr_3$ during the 2009 NSF HIPPO-1 campaign (filled circles). Error bars on the observations show the min-max range for a given level. Also shown are simulated profiles from the TOMCAT model. Blue, orange and green profiles: $CHBr_3$ emissions from the top-down inventories of Ordonez et al. (2012), Pyle et al. (2011) and Liang et al. (2010). The red profile, which seems to give the best agreement with the observed data, is obtained when using the bottom-up derived emissions from Ziska et al. (2013) (Hossaini et al., 2012).

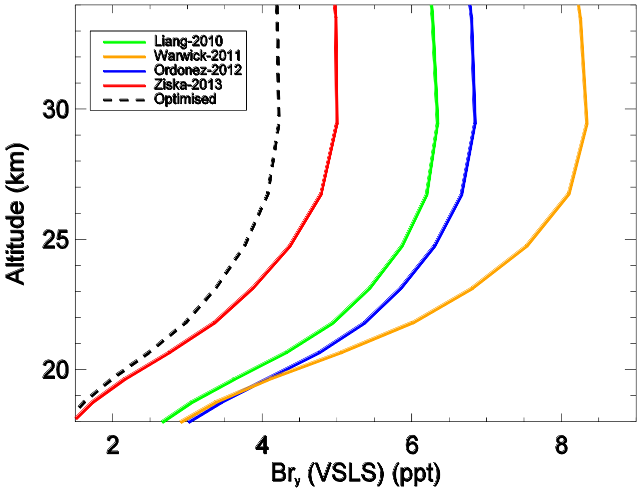

Figure 9: Modelled profiles of Br_y^{VSLS} from the TOMCAT CTM. The various colours indicate $CHBr_3$/CH_2Br_2 emission inventories. As no single inventory gave the simultaneous best agreement for both species with observations in the tropics, a optimized simulation was also performed ($CHBr_3$ field from Ziska et al. (2013) and CH_2Br_2 from Liang et al. (2010)). As both of these had the lowest total emissions, the optimised estimate of ~4 ppt is lower than when considering both source gases from the same inventory (Hossaini et al., 2012).

The C-CATT-BRAMS mesoscale model was used for studies on a more detailed and smaller scale. A chemistry model similar to the one used by UNIVLEEDS was implemented into the model, including heterogeneous chemistry, the solubility of species and washout. Krysztofiak et al. (2012) developed a detailed degradation scheme of $CHBr_3$ and CH_2Br_2 and performed detailed model runs to determine the major pathways in the degradation scheme and to study the effect of air pollution on the pathways (Figure 10). Marécal et al. (2012) and Hamer et al. (2013) examined the VSLS chemistry in deep convective events (Figure 11). The studies show that $CHBr_3$ dominates the vertical transport of bromine and that the most abundant inorganic product gas HBr is rapidly removed within clouds due to its solubility. Washout strongly depends on the solubilities in the model and on cloud and rain microphysics. In accordance with UNIVLEEDS, CNRS concludes that organic product gases can be ignored in modeling studies. Pollution shifts the balance between the soluble and non-soluble product gases and can change the amount of Br_y transported into the stratosphere (Figure 10). Increased pollution increases the production of the less soluble PGs.

The University of Bremen examined the transport and chemistry of VSLS and PG with the Bremen CTM (Aschmann et al., 2009, 2011, Aschmann and Sinnhuber, 2013). One of the main findings of the model runs is that uptake of bromine on cirrus ice and irreversible removal of bromine is likely to be of minor importance. This is caused by a combination of the low adsorption of HBr on ice and low mixing ratios of HBr in the TTL region, which are caused by heterogeneous chemistry, in accordance with the results of CNRS (Figures 12 to 13).

Low O_3 mixing ratios near the detection limit were measured during the TransBrom cruise with the RV Sonne in 2009 (Figure 14), implying low OH mixing ratios. Calculations with the GEOS-Chem model (UNIHB, Ridder et al., 2012) were able to reproduce the low O_3 values and showed very low OH values in the same area (Figure 15), which were confirmed by in situ-measurements in the tropopause region during the STRAT campaign. OH concentrations have a large effect on the composition of the troposphere and on the amount of species reaching the stratosphere. The main source area of stratospheric air and the low OH concentrations are geographically coincident, so that the OH

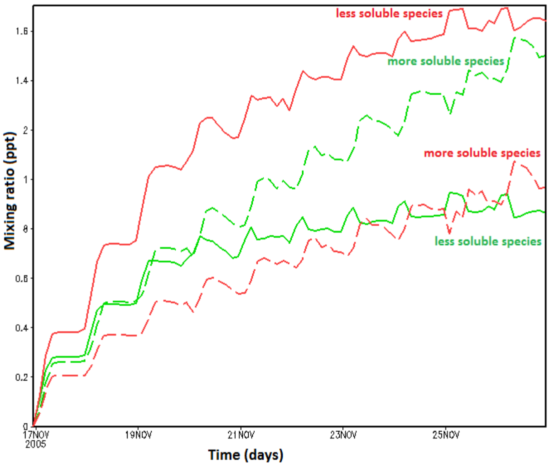

Figure 10: Product gases of CHBr3 degradation for polluted conditions (red) and unpolluted conditions (green) in C-CATT-BRAMS, shown as the sum of soluble species (dashed lines) and non-soluble species (solid lines) .

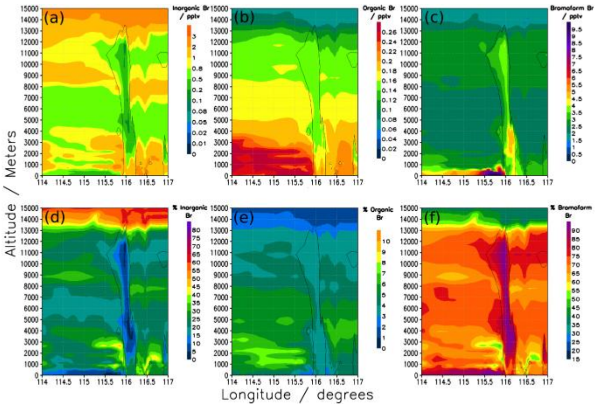

Figure 11: Mixing ratios of inorganic Br (a,d), organic Br (b,e) and CHBr3 (c,f) simulated by the C-CATT-BRAMS model for a convective case study of the SHIVA campaign (Hamer et al., 2013).

minimum potentially plays a large role in the determination of stratospheric composition. As examples, the amount of CH_2Br_2 and SO_2 reaching the stratosphere under different OH conditions were calculated with the ATLAS model. For CH_2Br_2, lifetime increased from 55 days (standard OH) to 188 days and for SO_2, lifetime increased from 5 days to 18 days. Stratospheric aerosol surface area was increased by 5% (Rex et al., 2ß12). SO_2 was further studied with a more detailed chemistry model including reactions of SO_2 with O_3 and H_2O_2 in cloud droplets (e.g. Kremser et al., 2012).

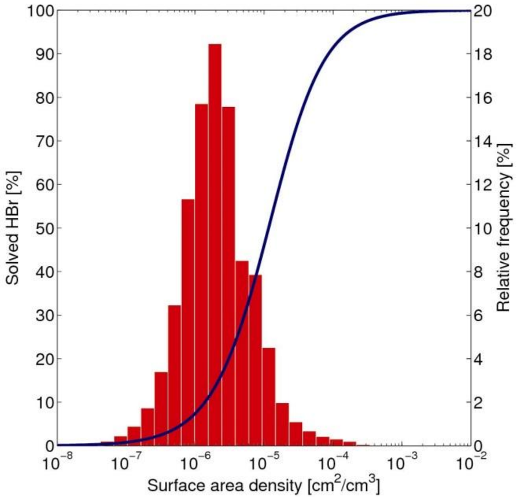

Figure 12: Absorption of HBr on cirrus ice as a function of the surface area density of the clouds (blue line) and the surface area densities actually observed in the Bremen CTM as a density function (red bars)

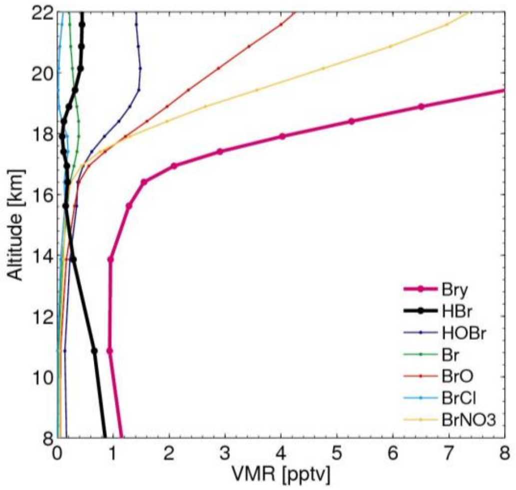

Figure 13: Partitioning of bromine species in the TTL in the Bremen CTM .

In addition, AWI performed calculations with a simplified conceptual model (Schofield et al., 2011), where the main processes were represented by simple equations governed by only one parameter. This approach allows an easy determination of approximate lower and upper bounds of stratospheric Br_y^{VSLS} by the uncertainties of the input parameters. The parameterized processes were the rate of conversion of organic source gases to inorganic product gases, the efficiency of washout of product gases, the efficiency of convection and the boundary layer emissions. Figure 16 shows that the resulting Br_y^{VSLS} for different sensitivity runs is in the range of 3-8 ppt.

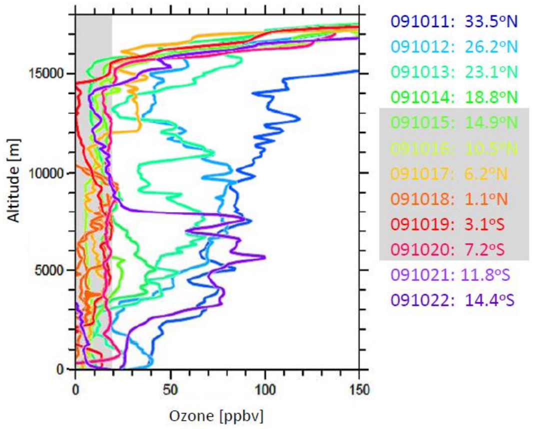

Figure 14: Ozone sonde measurements during the TransBrom Sonne cruise. Legend gives latitude and date. The measurements shaded in grey in the legend show ozone values near the detection limit throughout the troposphere (grey shaded area on the left) and have been taken in the West Pacific warm pool between 15 N and 10 S (Rex et al., 2012).

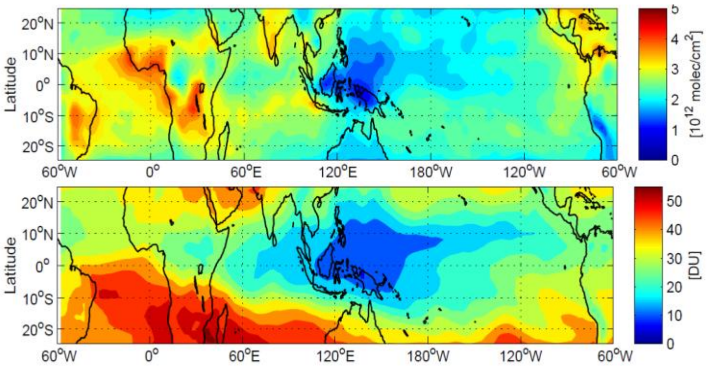

Figure 15: Mean tropospheric ozone column and OH number density in the GEOS-Chem model for Oct. 2009 (Rex et al., 2012).

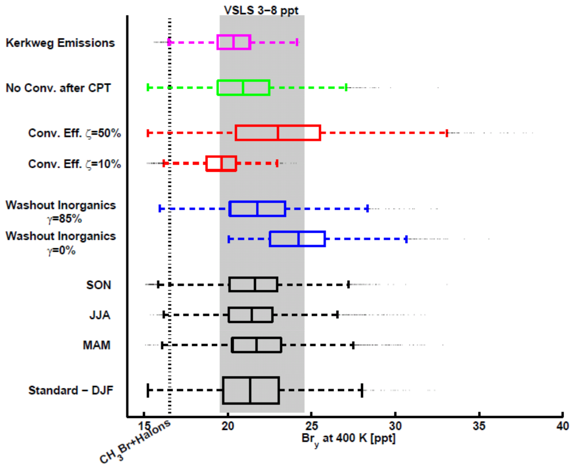

Figure 16: Mean Br_y^{VSLS} at the stratospheric 400 K level for a reference run (black, last row) and several sensitivity runs. The reference run (Dec-Mar) uses Yokouchi et al. (2005) emissions, a 30% boundary layer component to the convective outflow, and a wash-out efficiency at the cold point of 100%. The sensitivity runs are (top to bottom): a run using the emissions of Kerkweg et al. (magenta), a run allowing no convection after the cold point (green), runs with a convection efficiency of 50% and 10% (red), runs with a washout efficiency of product gases of 85% and 0% (blue), and runs for different seasons (black). Boxes indicate mean, 25th and 75th percentiles. Dashed line: Halon and CH_3Br contribution to Br_y from WMO (2006). Grey shaded region: WMO recommendation for an additional VSLS contribution of 3-8 ppt (Schofield et al., 2011).

3. Work related to the field campaign

AWI developed a forecast system used for the planning of the campaign flights. Based on ECMWF operational forecast data, a proxy for convection (integrated cloud ice) and several measures for the air mass origin (e.g.

pressures that air masses originated from 1, 2, … days before the forecast date) were calculated for forecast dates from the actual day up to 5 days into the future. A web interface was set up for easy access.
NILU calculated the horizontal and vertical distribution of a $CHBr_3$ tracer with the FLEXPART model. Two different lifetimes were assumed for the tracer (5 and 15 days). Emissions were based on an average chlorophyll inventory for the tropical Pacific Ocean. Based on meteorological forecasts the distribution of this tracer for the following 5 days was calculated. A 3D field of the tracer was provided. In a tracer experiment the uplift of $CHBr_3$ into the upper troposphere was investigated. While the RV Sonne crossed a region of high emissions an artificial tracer was released which was transported along with $CHBr_3$ emissions originating from the sea. With the Falcon aircraft this tracer was sampled. To find the best timing for releasing the tracer and predict the region where it is transported to, the FLEXPART model was used.

WP-5: Stratospheric halogens: Analysis of measured trends and projections

1. Background

The observed amount of bromine monoxide (BrO) in the stratosphere is larger than can be explained by the known contribution of long-lived source gases methyl bromide (CH_3Br) and the halons (e.g., WMO, 2011; Dorf et al., 2006). It has been suggested that this discrepancy is due to the contribution of VSLS, but prior to SHIVA there was no consensus as to whether the observed amount of VSLS could explain the missing bromine derived from stratospheric BrO observations. Combined analysis of balloon-borne, ground-based and satellite observations of BrO during SHIVA together with tropospheric source gas measurements during the SHIVA campaign provide now a much more consistent picture on the stratospheric bromine budget. In addition, source gas measurements from previous campaigns have been reanalysed to provide an update of fractional release factors for a range of brominated and chlorinated source gases.

2. An update of stratospheric bromine trends

During SHIVA, long-term balloon-borne, ground-based and satellite measurements of stratospheric BrO have been analysed. Figure 17 shows an update of the inferred total stratospheric bromine based on balloon-borne (University of Heidelberg) and ground-based (BIRA) DOAS BrO observations. Stratospheric bromine has been increasing until around the year 2000 and since shows a slow decrease of roughly 1%/year. These observed changes in total stratospheric bromine are basically consistent with the observed changes in bromine source gases. These comparison results provide therefore further evidences that the effects of the Montreal Protocol restrictions on brominated substances have now reached the stratosphere. Small differences between the inferred total stratospheric bromine based on the balloon-borne and ground-based DOAS measurements can be to a large extent attributed to different BrO absorption cross sections used for the retrievals of the balloon and ground-based observations. The exact absolute amount of the inferred stratospheric total bromine and thus the inferred VSLS contribution depends on the calculated BrO to Br_y-ratio in the stratosphere. Recently, Kreycy et al. (2013) have shown evidence from University of Heidelberg balloon measurements that the photolysis of bromine nitrate could be larger than previously assumed, which would result in a reduction of the inferred total stratospheric bromine from BrO measurements by about 1 ppt.
For validation purpose, a trend analysis has been performed of stratospheric BrO columns retrieved from SCIAMACHY limb and ground-based UV-visible observations. We focused on SCIAMACHY limb observations collocated with three stations belonging to the Network for the Detection of Atmospheric Composition Change (NDACC) and where long-term time-series of ground-based UV-visible measurements of stratospheric BrO are available for comparison: Harestua (60°N, 11°E), Observatoire de Haute Provence (OHP; 44°N, 5.5°E), and Lauder (45°S, 170°E). Since stratospheric BrO shows a marked seasonality with a maximum in winter and a minimum in summer (related to the NO_2 seasonal cycle), a statistical model with a linear trend and seasonal components is used to fit the SCIAMACHY limb and ground-based UV-visible columns. Results of this comparison are shown in Figure 18.

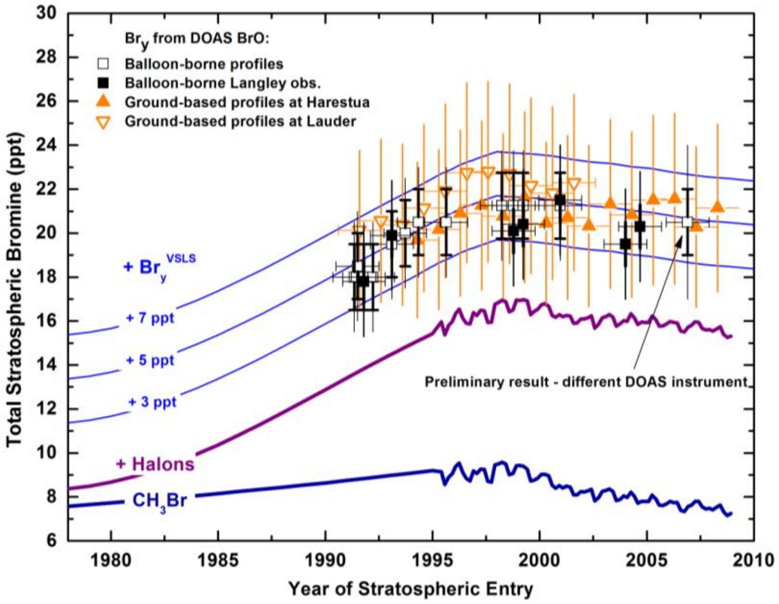

Figure 17: Trend of total stratospheric Bry derived from balloon-borne BrO observations (squares) (update of Dorf et al., 2006) and annual mean mixing ratios calculated from ground-based measurements of stratospheric BrO made at Harestua (60°N) and Lauder (45°S) (filled and open orange triangles, respectively, update of Hendrick et al., 2008), using a common BrO absorption cross section (Wahner et al., 1988). The stratospheric trends are compared to trends of global tropospheric bromine (CH3Br) plus halons) with varying amounts of Br_y VSLS added (+3, +5, and +7 ppt). For stratospheric data, the date corresponds to the time when the air was last in the troposphere, i.e., sampling date minus estimated mean age of stratospheric air parcel (updated from WMO, 2011).

Before 2001, a positive trend of about +2% per year is inferred over the three stations from ground-based observations while after 2001, a negative trend of about -1% per year is consistently found in SCIAMACHY and ground-based data sets. Given the mean age of air in the stratosphere, this decline is consistent with the decrease of long-lived bromine source gases (CH_3Br and halons) observed at the Earth's surface since 1998 (see Figure 17). To what extent the vertical and latitudinal distribution of BrO trends over the past decade derived from SCIAMACHY observations reflects changes in the stratospheric circulation over this period is currently under investigation.

3. Budget of stratospheric bromine

An important question regarding the current stratospheric bromine loading considers the consistency between the total bromine derived from source gas observations and the inferred total bromine from stratospheric BrO observations. The observations during the SHIVA campaign now provide a very consistent picture of the stratospheric bromine loading (Fig. 19). The source gas observations during SHIVA (University of Frankfurt and UEA) show a total bromine loading of about 20 ppt in the free troposphere, with locally higher values of between 20 and 30 ppt in the planetary boundary layer close to the surface. The measured VSLS ($CHBr_3$, CH_2Br_2, CH_2BrCl, $CHBrCl_2$, $CHBr_2Cl$) account for about 4ppt together in the free troposphere. Much higher values are observed locally in the boundary layer, but VSLS mixing ratios in the free troposphere show much less variability. The source gas observations during the SHIVA campaign are consistent with earlier source gas observations during the American TC4 campaign (E. Atlas), when accounting for the CH_3Br and halon trend between the time of the TC4 measurements (2007) and the SHIVA campaign (2011). The expected vertical decline of the source gases, as calculated by the Wamsley et al. (1998) relation constrained by the SHIVA observations in the free troposphere and CFC-11 from MIPAS/ENVISAT agrees well with the fall-off seen in the TC4 observations. More importantly the increase of inorganic bromine (Br_y) wth height calculated from the Wamsley relation constrained by the SHIVA source gas observations agrees well with Bry inferred from SCIAMACHY satellite BrO observations (University of Bremen) and the calculated BrO/Br_y ratio from the chemistry climate model EMAC. The Br_y inferred from SCIAMACHY BrO is consistent with a total bromine loading of 20ppt and thus consistent with the source gas observations of a VSLS contribution of 4ppt.

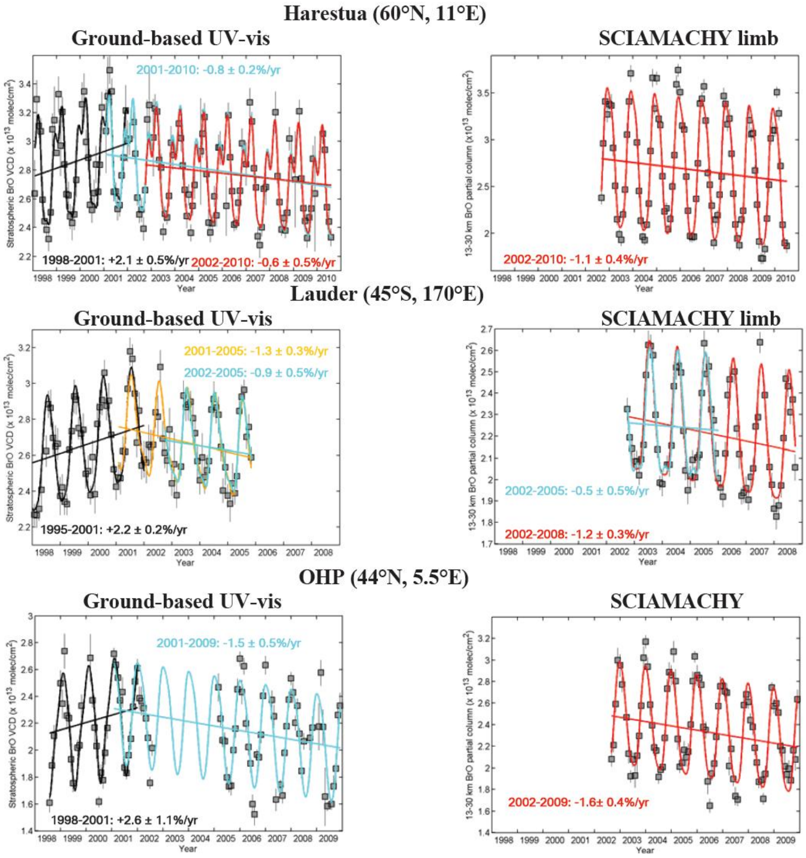

Figure 18: Trend analysis of stratospheric BrO using ground-based UV-vis (left) and SCIAMACHY limb BrO observations (right) over Harestua, Lauder, and OHP (from top to bottom, respectively). Note that the scale of the x-axis is not the same for all stations.

A VSLS contribution of about 4ppt to the stratospheric bromine loading is also consistent with the bottom up emission scenarios for $CHBr_3$ and CH_2Br_2 from GEOMAR (Ziska et al., 2013). Hossaini et al. (2013) (University of Leeds) performed calculations with a chemical transport model using a variety of different VSLS emission scenarios. They show that the Ziska et al. (2013) VSLS emissions that are based on calculated sea-to-air fluxes result in a VSLS contribution of about 4 ppt to the stratospheric bromine loading. This provides thus another independent but very consistent evidence for a VSLS contribution of about 4ppt during present day conditions.

4. Fractional release factors of halogenated source gases

Fractional release factors (FRF) describe the fraction of the halogen atoms in a specific halo-carbon that are released to the atmosphere. This is of specific relevance to the stratosphere, where the released halogen (in particular bromine or chlorine) can lead to ozone destruction. A high FRF implies that the halogen is readily released, whereas halocarbons which do not release their halogen atoms easily have low FRF values. E.g. a FRF of 0.5 means that half of the chlorine and/or bromine in a halocarbon is released.

FRF values were calculated by models or determined from observations. In the case of observations, the tropospheric trend of the halocarbon and the transport history must be taken into account. This was done based on the concept of age of air (see e.g. Engel et al., (2009), Laube et al. (2010)). By using this concept, both transport and mixing during the transport were taken into account. For this purpose the same parameterization of the age

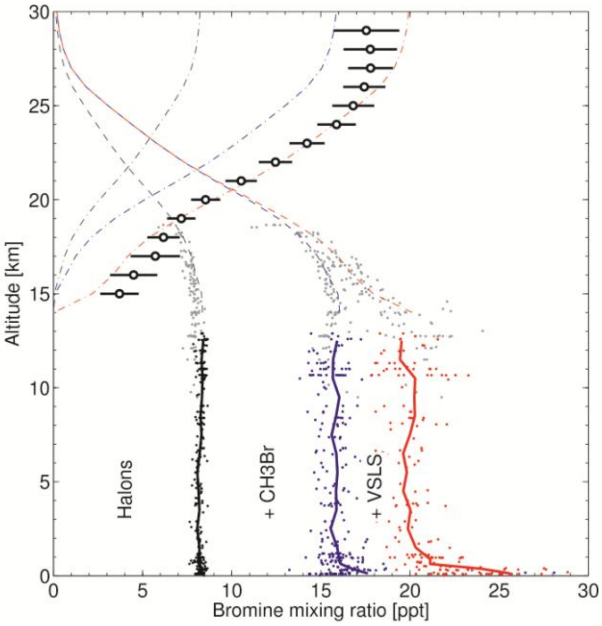

Figure 19: Budget of total bromine in the tropical troposphere and lower stratosphere based on observations of source gases from the Falcon aircraft performed during the SHIVA campaign (University of Frankfurt, blue, red, and black dots with corresponding coloured lines showing the mean over a 1km altitude bin), previous source gas measurements from the American TC4 campaign in the East Pacific (E. Atlas, gray dots) and inorganic bromine derived from SCIAMACHY BrO observations averaged over 20°S-20°N (University of Bremen, open symbols with error bars representing the standard deviation of the BrO measurements). TC4 data have been adjusted to account for changes in halons and CH_3Br between the time of the TC4 campaign (2007) and the SHIVA campaign (2011), based on global flask data from NOAA. The dashed and dashed-dotted lines show the expected vertical profiles of the source gases and inorganic bromine, respectively, based on the Wamsley et al (1998) relation constrained by the SHIVA observations relative to CFC-11 observations by MIPAS/ENVISAT.

Table 5: Fractional release factor (FRF) for mid-latitudes and tropics from whole air samples collected by balloons and aircraft. Here only data with mean ages between 2 and 4.8 years were included in the calculation. Relative FRF values are given with respect to CFC-11 FRF averaged over the same samples.

	Fractional Release factor							
compound	tropics				mid latitude			
	absolute	+/-	relative	+/-	absolute	+/-	relative	+/-
CF3Br(H1301)	0.66	0.35	0.84	0.44	0.29	0.20	0.68	0.29
CF2ClCF3(F115)	0.04	0.04	0.05	0.27	0.02	0.03	0.05	0.22
CF2Cl2(F12)	0.42	0.27	0.53	0.38	0.22	0.11	0.52	0.24
CHF2Cl(F22)	0.17	0.08	0.22	0.28	0.11	0.05	0.26	0.22
CF2ClBr(H1211)	0.93	0.22	1.18	0.35	0.55	0.28	1.32	0.35
CF2ClCF2Cl(F114)	0.10	0.05	0.13	0.27	0.07	0.05	0.17	0.22
CFCl2CF3(F114a)	0.52	0.29	0.66	0.40	0.24	0.11	0.56	0.24
CH3Cl	0.62	0.19	0.79	0.33	NA	NA	NA	NA
CH3CF2Cl(F142b)	0.09	0.05	0.11	0.27	NA	NA	NA	NA
CFCl3(F11)	0.79	0.27	1.00	0.38	0.42	0.22	1.00	0.31
CH3Br	0.80	0.22	1.02	0.35	NA	NA	NA	NA
CFCl2CF2Cl(F113)	0.53	0.22	0.67	0.35	0.28	0.13	0.66	0.25
CH3CFCl2(F141b)	0.56	0.24	0.71	0.36	NA	NA	NA	NA
CF2BrCF2Br(H2402)	1.00	0.00	1.27	0.27	NA	NA	NA	NA
CCl4	0.84	0.21	1.07	0.34	0.53	0.21	1.25	0.30
CH3CCl3(F140)	0.89	0.19	1.13	0.33	0.62	0.20	1.47	0.30
CHFClCF3(F124)	0.47	0.13	0.60	0.30	NA	NA	NA	NA

spectrum as in Engel et al. (2002) was used. The procedure for the calculation of FRFs has been described in Laube et al. (2010). FRFs can either be given as absolute values, e.g. for a given stratospheric sample, as averaged values over a range of mean age values or as relative values. In the case of relative values, the reference substance is generally

CFC-11. This means that the averaged FRF for a specific compound was divided by the respective value for CFC-11. FRF values were used in the calculation of ozone depleting potentials for individual compounds.
During SHIVA FRF values averaged over mean age values between 2.0 and 4.8 years of mean age have been reassessed. The data are extended from the ones used in Laube et al. (2010). They include samples collected in the tropics and mid latitudes from balloon borne whole air samplers and from an air sampler onboard the M55 Geophysica during the SCOUT-ozone campaigns. No FRF values were calculated for VSLS species and for species with unsecure calibration values. Therefore, only data for 15 species instead of 40 are available.

WP-6: Global modeling of VSLS, for the past, present and future

1. Background

Recent World Meteorological Organization (WMO) Scientific Assessments of Ozone Depletion have suggested that the contribution of very short-lived substances (VSLS) to the stratospheric halogen budget may be sensitive to climate change (e.g. WMO 2007, 2011). Specifically, oceanic emissions may change due to changes in SST, salinity, and surface wind speeds. Similarly, troposphere-to-stratosphere transport (TST) may change with implications for VSLS delivery to the stratosphere.

Within WP-6, the focus is on global modeling of VSLS for the past, present and future. Hence the objectives were (i) to improve modeling capabilities through inclusion of relevant chemical processes in global models and improvements in the dynamics and physical processes that affect the transport and physical (i.e. washout) of relevant chemical species; and (ii) to use the improved models to study the delivery of halogens from VSLS to the stratosphere for the past, present and future climate in more detail than done before the project start. Of particular interest here are also feedbacks from changes in VSLS delivery to the stratosphere on climate.

Two complementary modeling approaches were employed. First, transport pathways of TST were evaluated with trajectory calculations based on reanalysis data and model output from global climate models (GCMs). Second, model calculations with GCMs with detailed chemistry schemes were used. The results reported here are based on variants of the United Kingdom Chemistry and Aerosols (UKCA) CCM, which is based on the dynamical core of the Met Office Unified Model (UM) version 7.3. Variants include a version that contains a detailed description of stratospheric chemistry (so-called 'CheS' version) with a simplified tropospheric chemistry scheme; a tropospheric version (CheT), and a whole atmosphere version (CheST).

1. Main results

- The emission datasets of $CHBr_3$ and CH_2Br_2 for the UCAM model have been updated based on long-term observations in Borneo (Pyle et al., 2011), ditto for Halogen (mainly bromine) chemistry in UMUKCA. The corresponding model integrations (Yang et al., 2013a) indicate that (i) VSLS contribute about 5 pptv of inorganic bromine to the stratosphere for the present; (ii) VSLS bromocarbons cause more ozone loss (up to 20%) in the lowermost stratosphere of the southern than northern hemisphere, likely due to Br-triggered Cl reactions on PSCs.; and (iii) that the stratospheric ozone response to identical VSLS perturbations is different under different chlorine and bromine background, with larger ozone loss for a higher chlorine background.
- Top-down and bottom-up global emission inventories of $CHBr_3$ and CH_2Br_2 have been evaluated by UNIVLEEDS. UMUKCA simulations for 2100 show an increase, relative to 2000, in stratospheric source gas injection (SGI) of $CHBr_3$. The average $CHBr_3$ at 17 km increases from 0.1 ppt (2000) to 0.2 ppt and 0.36 ppt for 2100 under RCPs 4.5 and 8.5, respectively. Locally, increases are largest over the tropical West Pacific. The increase in $CHBr_3$ SGI is attributed mainly to convective transport changes in the tropical mid and upper troposphere. The primary tropospheric oxidant of VSLS, OH, differs significantly between RCP 4.5 and RCP 8.5 for 2100 due to changes in projected levels of CH_4. For RCP 8.5, a very large CH_4 increase reduces OH

significantly below ~12 km in the tropics, extending the lifetime of CH_2Br_2. Overall, we may expect an increase in source gas injection of VSLS in response to climate change, due to enhanced convection for shorter-live species (e.g. CH3Br), and due to changes in tropospheric oxidation from changes in OH.

- Trajectory calculations have been performed with ECMWF data (GEOMAR, UCAM, AWI) and with CCM and CMIP5 output (GEOMAR). GEOMAR finds a significant widening of the upper TTL between 1979 and 2011 that is not captured in results based on climate models. However, future simulations indicate a continuing widening, and an increase in importance of the TTL above the tropical western Pacific.
- Large uncertainties in the diabatic budget of reanalyses in the TTL reported by UCAM affect reliability of model calculations for the past and present, with an unclear role of parameterized mixing in GCMs in general. UCAM and AWI report that error calculation suggests range of 3-8ppt Br_y from VSLS, which implies limitations of model calculations to constrain stratospheric Br_y from VSLS.

2. Summary statement

Simulations with chemistry-climate models have revealed that the impact of bromine-containing VSLS on stratospheric ozone is significant at both mid-latitudes and polar regions. The perturbations to ozone due to VSLS can result in significant dynamical feedbacks in the stratosphere impacting temperature and circulation. Further investigation of these VSLS-chemistry-climate interactions is warranted to assess how the impact of VSLS (on ozone) may respond due to climate change and due to changes in stratospheric composition (e.g. chlorine loading). Furthermore, the absolute loading of VSLS into the stratosphere may increase due to climate-driven changes to tropospheric transport and oxidizing capacity. This would further be enhanced if emissions of VSLS were to increase in the future (see other work package reports). These results have therefore identified potentially important climate feedbacks that could significantly influence the future evolution of stratospheric ozone – feedbacks that were poorly understood, and not quantified prior to the SHIVA project.

Results from trajectory calculations indicate an increase of the Lagrangian Cold Point (LCP) occurrence over the tropical West Pacific additionally with a decrease of LCPs over other geographic regions. Together with a widening TTL, this highlights the importance of the tropical West Pacific in terms of transport of trace gases into the stratosphere in a changing climate. Analysis of troposphere-to-stratosphere transport based on reanalysis data (which provides the best available reconstruction of the atmospheric state over the past few decades) shows that observations of tracer fields like ozone and water vapor can be reproduced with quite some accuracy, though uncertainties remain in particular with respect to the TTL's diabatic heat budget, mixing, and very deep convection.

3. Specific results for UCAM

We improved UMUKCA halogen chemistry scheme in its three sub-versions: CheT (tropospheric version), CheS (stratospheric version) and CheST (whole atmospheric version). Five VSLS halocarbons ($CHBr_3$, CH_2Br_2, CH_2BrCl, $CHBr_2Cl$, and $CHBrCl_2$) were explicitly included, and emissions (originally based on Warwick et al. (2006)) were updated with long-term observations from Borneo (Pyle et al., 2011). Inorganic bromine sources from sea salt bromine depletion (including both open oceanic and sea ice sea salt) is also included. In the CheST model, a detailed tropospheric bromine chemistry scheme (same as in CheT) has been integrated, together with updated heterogeneous reactions on polar stratospheric clouds (PSCs) and sulfate aerosols. This implementation supports inactive halogens (e.g. HBr, HCl) to be reactivated via inter-halogen reactions on aerosol surfaces. This updated CheST version is used to investigate VSLS impacts on stratospheric ozone and feedback to the climate system.

We find that VSLS could contribute about 5 pptv of inorganic bromine (Bry) to the stratospheric Br burden, close to the earlier balloon-borne estimates of 5.2(±2.5) pptv (Dorf et al., 2008) and a similar recent model estimates (Hossaini et al., 2012). Model runs with and without VSLS emissions suggest that VSLS may cause stratospheric ozone loss by up to 20% in the lowermost stratosphere of the southern hemisphere (SH) (Figure 20), with less loss in the Northern Hemisphere due to less PSCs. In this scenario, the ozone reduction is accompanied by a temperature drop of ~2K (Figure 20), and a change in tropopause height.

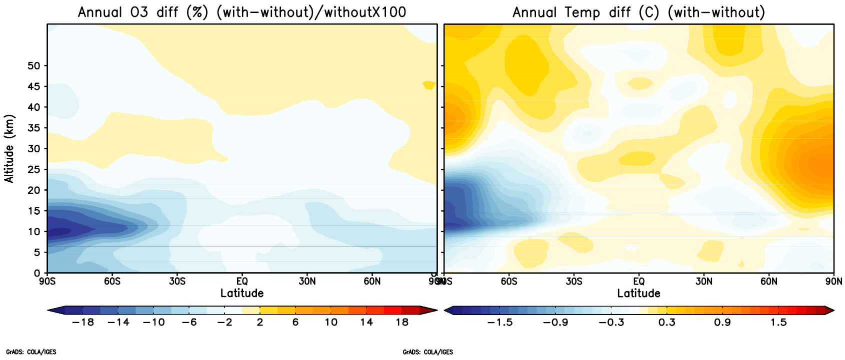

Figure 20: *Left: annually zonal mean ozone loss (in percentage) due to VSLS; right: annually zonal mean temperature difference due to VSLS. The differences are calculated based on two integrations one with and another without VSLS emissions.*

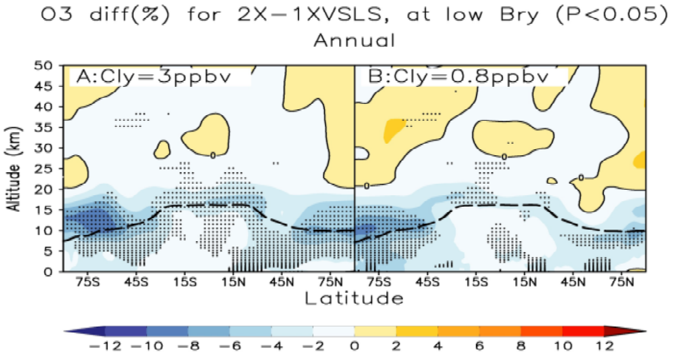

Figure 21: *Ozone differences (in percentage) due to doubled VSLS emissions. A (left) under a high stratospheric chlorine background; B(right) under a low Cl background. Note: in both A and B, bromine background is identical.*

The sensitivity of the climate to VSLS perturbations under different chlorine and bromine backgrounds is investigated with model calculations with stratospheric inorganic chlorine levels of 3/0.8 ppbv to represent present/preindustrial era, respectively. Similarly, two bromine levels (high/low) reflect anthropogenic Halons and CH3Br contributions to the stratospheric bromine. For each of the 4 scenarios, two perturbations were performed by doubling and halving the VSLS emissions. We found that the ozone change in response to the VSLS perturbations depends on chlorine and bromine backgrounds, with higher ozone loss under higher chlorine background (Figure 21). This is likely because of the inter-halogen (Br-Cl) reactions (higher background chlorine allows more chlorine to be reactivated by bromine). Also, near surface Ozone changes are seen at high latitudes, especially in the SH. This may reflect the changes in the southern annual mode (SAM) due to the perturbation of stratospheric ozone.

4. Specific results for UNIVLEEDS

UNIVLEEDS has investigated how stratospheric bromine loading due to the major bromine-containing VSLS $CHBr_3$ and CH_2Br_2 may respond to climate-driven changes of tropospheric transport and oxidizing capacity. For simulations representing the year 2000, UMUKCA was forced with prescribed monthly mean SST and sea ice fields (Rayner et al., 2003). For 2100, output of the HadGEM2-CCS climate model (Martin et al., 2011) was used for these fields. For 2000, greenhouse gas (GHG) loading and long-lived halocarbons (e.g. halons, CFCs), were prescribed according to the WMO A1 scenario (WMO, 2011). For 2100 experiments (S-RCP4.5 and S-RCP8.5) these gases were constrained by the Intergovernmental Panel on Climate Change (IPCC) *Representative Concentration Pathways* (RCPs) 4.5 and 8.5

(van Vuuren et al., 2011) (see Table 6). These scenarios span moderate to extreme climate change, with projected surface warming in the region of 2.0 K and 4.0 K by 2100, respectively.

Table 6: Surface volume mixing ratio for key GHGs and long-lived bromocarbons in UMUKCA simulations**.**

Experiment	**CO_2 (ppm)**	**CH_4 (ppb)**	**N_2O (ppb)**	**H-1211 (ppt)**	**H-1202 (ppt)**	**H-1301 (ppt)**	**H-2402 (ppt)**	**CH_3Br (ppt)**
S-2000	370	1765	316	4.04	0.05	2.73	0.41	8.66
S-RCP4.5	538	1577	372	0.05	< 0.01	0.98	< 0.01	6.40
S-RCP8.5	935	3750	435	0.04	< 0.01	0.78	< 0.01	5.70

In this study, five biogenic VSLS tracers were added to UMUKCA. For $CHBr_3$ and CH_2Br_2, the monthly-varying emission estimates of Ordóñez et al. (2012) were used for both 2000 and 2100 experiments. These species were the major focus of this work and their global source strengths are 533 Gg yr^{-1} and 67.3 Gg yr^{-1}. A comparison of modeled profiles in the TTL with recent aircraft observations shows good agreement (not shown).

Figure 22 shows the modeled change in $CHBr_3$ at 17 km for the two 2100 experiments. For 2000, the modeled average abundance of $CHBr_3$ at this level is ~0.1 ppt, in good agreement with available aircraft observations. For 2100, this estimate increases to 0.2 ppt under RCP 4.5, and significantly to 0.36 ppt, under RCP 8.5. The local increase is largest over the West Pacific during northern hemisphere winter, when transport through the TTL is most rapid (Fueglistaler et al., 2005). Here the modeled $CHBr_3$ increase peaks at 0.7 pptv (i.e. 2.1 pptv more of bromine).

For $CHBr_3$, whose primary tropospheric loss is by photolysis, it is expected that these increases are largely due to perturbations to tropospheric transport under the RCP scenarios. A comparison of the convective updraft mass flux (not shown) between the three experiments reveals a reduction in the annual mean updraft strength in the lower and mid tropical troposphere, but in the TTL the model shows a positive change, similar to the model results reported by Stevenson et al. (2005) and Dessens et al. (2009). We have also investigated how the primary tropospheric oxidant, the hydroxyl radical (OH), may respond to climate change. Figure 23 shows the modeled 2100 change in [OH] with respect to 2000. The warmer lower atmosphere leads to enhanced water vapour and thus enhanced OH production through the H_2O+O(1D) channel. Under RCP 4.5, [OH] increases throughout the troposphere, with a peak mean increase of 0.2×10^6 molecules cm^3 (15% increase w.r.t. 2000) at 15 km. Zeng et al. (2008) show a similar response for a 2100 CCM experiment with doubled [CO_2]. However, for RCP 8.5, despite enhanced water vapour, below 10 km the [OH] response is negative. Between RCPs there is large variation in [CH_4] (Table 6). Under RCP 4.5, a scenario where GHG emissions are mitigated until 2100, CH_4 is 10% lower w.r.t. 2000. Conversely, under RCP 8.5, a non-mitigation scenario, it increases by 112%. Enhanced CH_4 tends to decrease [OH] (e.g., Wuebbles et al., 1989) and has a positive feedback on its own lifetime. The rate of the CH_4 + OH reaction is strongly temperature-dependent and increases with the large warming under RCP 8.5 (>4.5 K at the surface). These changes are likely to have a relatively small impact on $CHBr_3$, but for CH_2Br_2 (loss dominated by OH oxidation), these changes will likely impact its tropospheric lifetime and thus the amount reaching a future stratosphere.

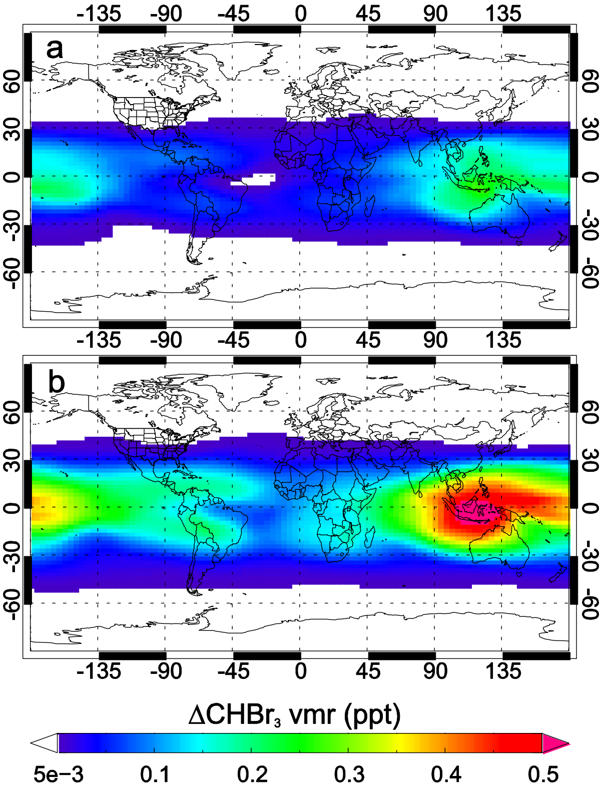

Figure 22: DJF mean modelled increase in $CHBr_3$ mixing ratio (ppt) at ~17 km for (a) S-RCP 4.5 and (b) S-RCP 8.5 2100 experiments.

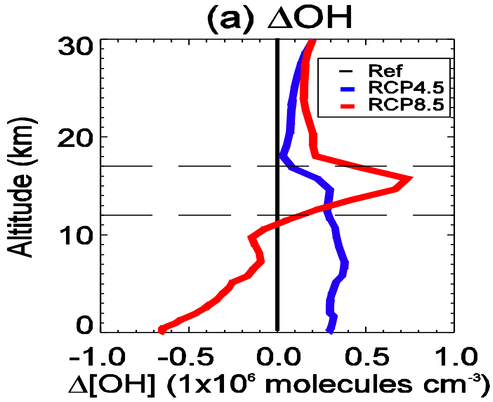

Figure 23: 2100 annual zonal mean change w.r.t. 2000 of [OH] for S-RCP 4.5 and S-RCP 8.5 experiments in the tropics (±20°).Upper and lower dashed lines denotes the cold point tropopause and the approximate base of the tropical tropopause layer, respectively.

5. Specific results for GEOMAR

Lagrangian calculations were carried out for ERA-Interim reanalysis from 1979-2011 and for future climate simulations from different climate models. Two coupled chemistry climate models (CCMs) within the CCMVal - 2 project (CMAM REF-B2 and NIWA-SOCOL REF-B2) and one coupled climate model from CMIP5 (MPI-ESM historical and RCP 8.5) were analyzed for three different decades 1990-1999, 2040-2049 and 2090-2099 (2089-2098 for NIWA-SOCOL REF-B2). CMAM REF-B2 and MPI-ESM are model simulations with a coupled ocean.

The resulting Lagrangian cold points (LCPs) were analyzed with respect to temperature and distribution. A broadening of the tropics in the upper troposphere has been reported (e.g. Seidel et al. 2008; Davis and Rosenlof, 2012), with implications for the LCP distribution (Figure 24). Figure 24 shows an increase in the LCP temperature of up to 2 K for the 2090s for MPI-ESM, similar to results from CMAM REF-B2 and NIWA-SOCOL REF-B2 (not shown), and similar to the cold point tropopause temperature increase of different CCMs reported by Gettelman et al. (2009) and SPARC CCMVal (2010). The models predict for the 2090s an increase of LCP occurrence over the West Pacific (green lines), and a decrease over West Africa and South America (red lines). For the future, a change of the total width of the upper TTL is projected with 1°-1.5° degrees latitude between the 1990s and 2090s by all three climate models. For the future, a change of the total width of the upper TTL is projected with 1°-1.5° degrees latitude between the 1990s and 2090s by all three climate models (Figure 25).

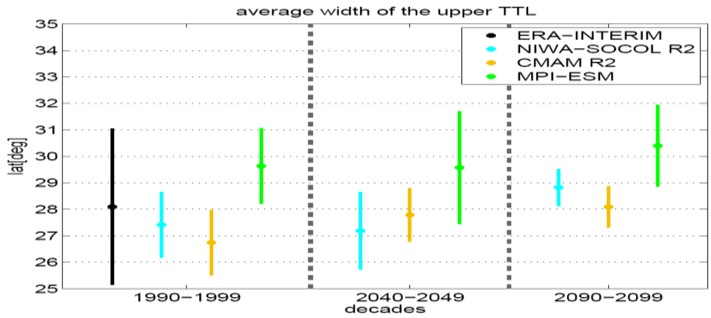

Figure 25: Average width of the upper TTL for ERA-Interim and climate models during the different decades. Vertical bars showing the variability of the poleward extent of the LCPs (V. Mohr, in preparation).

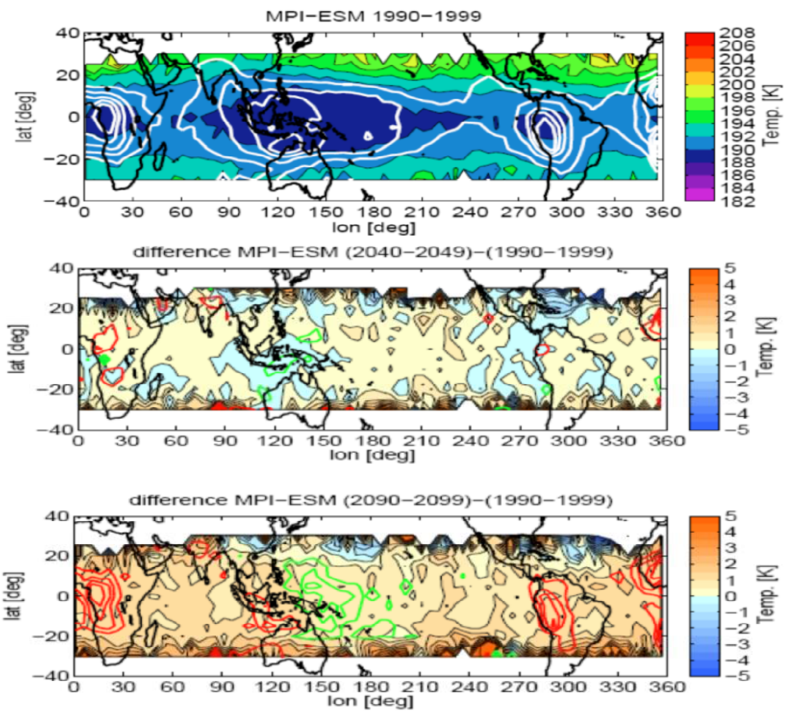

Figure 24: Climatology of LCP temperature and occurrence for MPI-ESM from past (1990-1999) and differences for the future (2040-2049 and 2090-2099) per 5° x 5°. Contour lines indicate the density of LCP occurrence in [%]; red, less than in 1990-1999; green, more than in 1990-1999. Color interval for LCP temperature differences is 0.5K, and for LCP occurrence 0.05% (V. Mohr, in preparation).

6. Specific results for AWI and UCAM

Trajectory model calculations in combination with a conceptual model were used to estimate the sensitivity of the stratospheric Br_y originating from VSLS to uncertainties in transport, source gas emissions, chemistry and microphysics (Schofield et al., 2011, Figure 16). The main processes are represented by simple equations governed by only one parameter to determine the approximate lower and upper bounds of stratospheric Br_y^{VSLS} due to the uncertainties in the input parameters. The parameterized processes were the rate of conversion of organic source gases to inorganic product gases, the efficiency of washout of product gases, the efficiency of convection and the boundary layer emissions. Figure 27 shows the resulting Br_y^{VSLS} for different sensitivity runs.

The model representation of TST is a major source of uncertainty for accurate estimates of VSLS delivery to the stratosphere. This uncertainty is related to very deep convection that may be poorly represented in global models, and also to uncertainties in models' mixing schemes. We found that mixing parameterizations employed in global models may play a non-negligible role for TST in models. Figure 27 shows the exchange coefficient calculated for two commonly used mixing parameterizations in the TTL; note the large difference in pattern.

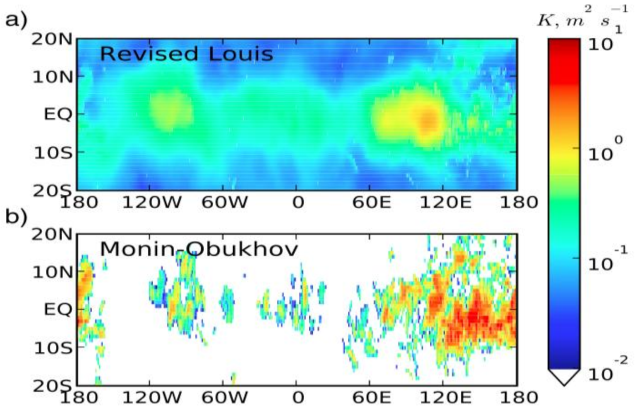

Figure 26: Mixing in the tropical tropopause layer due to shear-flow instability. Model calculations of the exchange coefficient at 104hPa calculated offline for two mixing schemes in use at ECMWF based on ERA-Interim data for the year 2000. (a) Results for the "revised Louis scheme", which is sensitive to conditions during passage of Kelvin waves. (b) Results for the "Monin Obukhov" scheme (adopted from Flannaghan and Fueglistaler, 2011).

4. Impact

Scientific results, impact and dissemination

1. Scientific Results

Within SHIVA considerable improvements have been achieved in the following areas:

1. VSLS emissions from the marine environment
   - Globally the important emitters of halogenated VSLS (primarily $CHBr_3$, CH_2Br_2 and CH_3I) are phytoplankton of various types (i.e. hapto-, chryso-, and chlorophytes), and VSLS emissions by natural or cultivated macroalgae in coastal regions. Emissions of VSLS from farmed macroalgae are likely to increase significantly in the future given the projected growth in seaweed farming. VSLS emissions of bacteria seem do not play a dominant role.
   - Cyanobacteria - besides photochemical production - seem to be potent CH_3I emitters, but the largest oceanic source of iodine to the atmosphere are emissions of I_2 and HOI, produced by inorganic reactions involving ozone, and in certain oceanic regions other iodinated VSLS such as CH_2I_2 and CH_2ClI play major roles for the atmospheric iodine cycling.
2. VSLS emission scenarios
   - For the major halogenated VSLS of stratospheric relevance ($CHBr_3$, CH_2Br_2, and CH_3I), best estimates of global sea-air fluxes (source/sink) based on in-situ observations are +2.96/-0.56, 1.09/-0.12, and 1.45/-0.0001 Gmol atoms/year, including oceanic sources and sinks for the first time.
   - Use of the bottom-up emission inventories (derived during SHIVA) in a global model leads to good agreement between simulated and observed $CHBr_3$ from independent ground-based and aircraft observations in the tropics
3. Atmospheric transport and transformation
   - Investigations performed within SHIVA indicate brominated VSLS concentrations of 4.1±0.6ppt in the (tropical) upper troposphere of the western Pacific (SHIVA-2011), which compares well with recent CARIBIC flights in the same region (4.2±0.6 ppt). These are slightly higher than the mean estimate of 3.5 ppt reported in WMO (2011), which may reflect the enhanced convection in this region.
4. Delivery to the stratosphere
   - Theoretical and experimental studies indicate that less than 0.3ppt of organic and inorganic iodine are transported into the stratosphere.
   - The SHIVA best estimate for VSLS bromine in the stratosphere is 4–5ppt based on the inorganic method, of which modeling suggests 75% is due to organic source gases and 25% due to inorganic product gas injection. Organic product gases are expected to make a minor contribution.
5. Past, present and future trend in stratospheric bromine
   - From its maximum (20-21ppt) reached in the stratosphere around 2000, total stratospheric bromine is presently decreasing at a rate of (0.8-0.9 ± 0.2)% per year and reached a level 19-20 ppt in 2011. This is primarily due to recent reductions in the atmospheric abundance (and emissions) of methyl bromide and the man-made halons.
   - In a future warmer world, VSLS emissions may increase. Furthermore, CCM simulations suggest that climate-driven changes to tropospheric transport and to oxidizing capacity may increase the SGI of bromine by 15-60% based on IPCC projections.
6. Consequences for past, present and future ozone
   - Theoretical studies indicate that VSLS-derived bromine presently reduce O_3 by several DU at low-latitudes to several 10s of DU at high-latitudes, and up to 20% O_3 in polar regions in winter.

- Radiative forcing due to reduced ozone by halogens released from VSLS also leads to modified stratospheric temperatures and transport. In future, the influence of brominated VSLS on the stratospheric ozone is expected to decrease however as stratospheric chlorine will decrease reducing the efficiency of combined ClO_x/BrO_x cycle for ozone destruction.

2. Impacts

Research within SHIVA has considerably reduced uncertainties in predicting global ozone and stratospheric transport (via radiative forcing of modified ozone) due to uncertainties related to the past, present and potential future delivery of VSLS derived halogens to stratosphere. This achieved reduction in uncertainty comprises a couple of areas: Firstly, investigation of VSLS emissions in the oceanic water body as a function of microalgae abundance, as well as incubation and laboratory experiments of macroalgae, are clearly indicating which species and their relative rank are important in this context. However due to the complexity of biochemical processes of which many act at the same time and at the same location in field, unambiguous conclusions on the relative importance on a regional or even global scale cannot firmly be made yet. Secondly, previous estimates of global emission fluxes of VSLS, primarily relevant in this context (i.e., $CHBr_3$, CH_2Br, and CH_3I) have been considerably improved but, primarily due to sparse coverage of the collected data to date and the dependence of emission fluxes on parameters like wind speed, salinity and sea surface temperature, some uncertainty remains. Next, atmospheric measurement of VSLS source gases made within SHIVA (but not exclusively) are clearly indicating the amount of VSLS-derived halogens present in the upper troposphere and lower stratosphere to be around 4ppt for bromine, and < 0.3ppt for iodine. Further, this finding is corroborated by the modeling work performed within SHIVA. In that respect, it appears that within SHIVA a closure between present day delivery of halogenated VSLS source and product gases and the total stratospheric bromine burden has been reached. The modeling work also predicts that in a changing climate potentially more VSLS derived bromine may reach the stratosphere in future, although it will be less harmful to ozone given the expected decrease in chlorine in the stratosphere. On the other hand, estimates of future VSLS emissions from the marine environment remain highly uncertain, since factors like a changing marine biology due to warmer waters, the oceanic acidification, or the changing nutrient supply into near shore waters is hard to predict. Further direct man-made impacts into marine life may also directly or indirectly matter in this context, such as the increasing cultivation of VSLS-emitting macro-algae, overfishing of algae based marine life, or the even by air pollution mediated emission of inorganic iodine, et cetera.

The result of SHIVA have also started to improve climate models, at least those considering in sufficient detail processes of stratospheric ozone and transport and their implications for the radiative forcing of the climate. By improving the knowledge on the future chemical composition of the stratosphere and its impact on global ozone, SHIVA largely contributed to improve the knowledge of some aspect of the future global socio-economic development, of which a detailed investigation was clearly outside the scope of the present project

The results obtained within SHIVA thus match excellently with the expected impact of sub-activity 6.1.1.2. in the FP 7 Theme 6 work programme, namely to “reduce the uncertainties in the evolution over the next decades of the stratosphere and improve estimates of time scales of ozone layer recovery” and to “provide information on the interactions of changes in the stratosphere and climate”. Finally, noteworthy are the remaining uncertainties regarding the magnitude of VSLS derived halogen emission in the future which, given that VSLS derived halogens will be observed to increase in the future stratosphere, may eventually require further attention and research.

3. Dissemination

To date (early Sept. 2013) 30 SHIVA related publications have already been published, 11 are submitted, and intentionally 28 more studies will be submitted to the peer-reviewed scientific literature in the near future. In order to keep the context of each individual publication to SHIVA, a joint special SHIVA issue has been organized among the journals (a) Atmospheric Chemistry and Physics, (b) Atmospheric Measurement Techniques, (c) Biogeosciences, and (d) Ocean Science journals of the publisher 'Copernicus Publications', see http://www.atmos-chem-phys.net/special_issue306.html, although publishing there is not mandatory for the SHIVA partners.

A project website http://shiva.iup.uni-heidelberg.de/ was installed early in the project period (August 2009) which contains information on the project and the consortium, as well as some background information about stratospheric ozone depletion. The website has been kept up-to-date with useful information and results, links to scientific papers, and any other news of relevance, and we will continue to update it regularly in the near future. In order to keep some (mostly non-scientific) information confidential, SHIVA partners and any colleagues signing the data protocol may have access to the internal password protected wiki page, and to the data ftp server: shiva.iup.uni-heidelberg.de

Extensive efforts were also undertaken to communicate SHIVA science to the wider public in Europe as well as in the host nations (Malaysia, Brunei and the Philippines) of the SHIVA western Pacific campaign. These included

1. Several press releases (http://shiva.iup.uni-heidelberg.de/press.html) issued by the coordinator and the partners lead to articles in local and regional newspapers and in a wider radio coverage.
2. Three press conferences were held in Malaysia at the beginning (at Kuala Lumpur on Nov. 11, 2011), in the middle (at Kuching on Nov. 22, 2011) and end (at Kota Kinabalu on Dec. 5, 2011) of the SHIVA western Pacific campaign. These led to a large number of articles in the written media of Malaysia, Brunei and the Philippines, and at a least to three interviews given by the coordinator and local partners to journalists from several local TV stations.
3. The SHIVA science was also presented by the coordinator or partners at various Malaysian universities (UM, UMS, and UNIMAS) and research institutions on the Philippines (University of the Philippines), or governmental organizations (Malaysian NOD, and MMD), as well as at European universities and different research institutions.
4. A report on the EU-SHIVA project was also published in the SPARC (*Stratospheric Processes and their Role in Climate)* newsletters (issue Dec. 2010; 24:25-28).
5. A SHIVA leaflet was issued and disseminated to authorities and media at dedicated meetings where reports on the SHIVA activities were given.
6. Finally, a report on the involvement of partner GEOMAR in SHIVA was broadcasted by the RTL news in January, 2012.

A complete list of activities in support of public awareness and dissemination is attached to this report.

Integrated approach

The SHIVA project has applied a unique integrated approach combining both experimental as well as theoretical studies. The experimental studies comprised investigations in the laboratory, and in the field, the latter combining for the first time measurements from ground-stations, research ships (local ships and the RV Sonne), the DLR Falcon aircraft and satellite observations. The theoretical studies not only used meso-scale dynamical models coupled to chemical codes (CATT-Brams), global chemical transport models (CTMs), chemistry climate models (CCM), but also state-of-the-art coupled atmospheric-oceanic global climate models (AOGCM) in order to provide a wider context of the SHIVA results for past, present and future ozone and climate.

For example, during the SHIVA western Pacific campaign, measurements taken in oceanic waters by local ships and the RV Sonne helped to characterize the physical, chemical and biological parameters in near shore oceanic waters, which are indispensable to unravel the source of halogenated VSLS. These in-situ measurements of likely VSLS sources were corroborated by laboratory measurements aiming at a specification and ranking of various marine bacteria, micro- and macro-algae and their potential to emit VSLS. The field studies were assisted by satellite observations of ocean color, which strongly relates to the near-surface concentrations of the pigments in various types of microalgae. Further, the atmospheric measurement of halogenated VSLS, and various inorganic source and product gases performed at ground-stations, the local ships, the RV Sonne and the research aircraft Falcon provided new information on the source strength, atmospheric concentration and the fate of halogenated VSLS.

Measurements of inorganic halogen gases, transport tracer and pollutants on the RV Sonne and the DLR Falcon aircraft provided further information on inorganic halogenated source (I_2, HOI) and product gases (IO, BrO), as well as on the atmospheric transport, primary and secondary pollutants in the investigated region. In part, these atmospheric observations were validated by measurements from satellite (e.g., BrO, NO_2 and CH_2O by ENVISAT/SCIAMACHY, or biomass plumes by GOES visible imagery).

Process modeling used to guide the field measurements and for post-campaign analysis comprised Lagrangian models, such as FELXPART, or HYSPLIT, as well as meso-scale process models such as CATT-Brams. Further, different Lagrangian (backward) air mass trajectory models helped to identify the origins (regions and seasons) for air masses crossing the Langrangian Cold Point (LCP) on their journey into the stratosphere. Last, but not least, these simulations assisted in locating where and when the SHIVA field campaign should be performed to maximize its outcome with respect to the given objectives.

Finally, simulation performed by different CTMs, CCM, and AOGCMs were used to provide the context and a deeper understanding of SHIVA results gained in WP 2 to 5 for global ozone in a climate change affected future world. The involvement of CTMs, CCM and AOGCMs partners has ensured a direct utilization of the knowledge gained from process studies, in order to improve our skills for the overarching goal of “improving the predictability of future ozone depletion”.

Publication of the various SHIVA studies and their presentation at international conferences and meetings is ongoing. In the coming months and years, a substantial impact and visibility of SHIVA in international global ozone and climate change research programs and reports (cf. below) in the larger scientific community can be expected. Finally results of the SHIVA report will be reported in the upcoming WMO (2014) report on stratospheric ozone.

Positioning in the international context of research

SHIVA has built on a number of successful past international research projects on global ozone depletion (e.g., SOLVE-THESEO, QUILT, VINTERSOL, RECONCILE, SCOUT-O3). At its core, SHIVA focused on some scientific questions related to the emissions of halogenated VSLS and their impact on past, present and future global ozone, which have not been directly, and never in as much detail, studied before. In this respect, the SHIVA project has continued in the successful tradition of “stratospheric ozone research” performed by European scientists.

The participation of leading institutions and research groups of different disciplines within the SHIVA project coming from different European countries as well as from Malaysia and the Philippines has demonstrated an unprecedented level of inter-disciplinary research in our field of research. Here the SHIVA project brought together experimental scientists with backgrounds in marine biology, oceanography, meteorology, atmospheric dynamics and photochemistry and finally theoretical scientists with backgrounds in mathematics, computer sciences and theoretical physics.

The co-operation with various partners and projects was established to bundle activities, such as project meeting, on campaign and post campaign workshops, exchange of scientists and finally even meetings with the interested public and media in the host country. In that respect, synergies among the knowledge of scientists working in different fields were fully used. Finally the collected data were jointly interpreted and comprehensively exploited.

The most important co-operations with external partners are listed in Table 7. Particularly fruitful for the European partners was the collaboration with several Malaysian institutions, namely with colleagues from the Universities of Malaya, Kuala Lumpur (UM), Malaysia Sabah (UMS), and Malaysia Sarawak (UNIMAS), the Malaysian Meteorological Department (MMD) and the Malaysia National Oceanography Directorate (NOD). Here the strong support given by Prof. Dr. Nor Aieni Binti Haji Mokhtar, Director of the Malaysian NOD, and by Mrs Munirah Abd Manan, Director of the Malaysian economic planning unit (EPU), needs to be strongly emphasized, without which the intended research would not have been possible.

The SHIVA consortium and the external collaborators together represent a significant part of the stratospheric research community, and many of the scientists involved in the project serve as co-authors of the past and upcoming

WMO ozone assessments and IPCC climate reports. The project results published over the past four years will directly contribute to the 2014 WMO assessment. The corroboration of many cornerstones of our knowledge of ozone depletion and the fine-tuning of those processes where significant uncertainties still existed will help to sustain and enhance the credibility of the ozone layer science and policy, with indirect implications for the credibility of the science and policy on global climate change.

Table 7: Important co-operations with other projects and scientists.

List of co-operations			
Project / Institute	**Contact person**	**Description**	**www**
EU-RECONCILE	Marc von Hobe (FZ-Jülich)	Reconciliation of essential process parameters for an enhanced predictability of arctic stratospheric ozone loss and its climate interactions	https://www.fp7-reconcile.eu/
HalOcAt	Birgit Quack (GEOMAR / Kiel)	Halocarbons in the Ocean and Atmosphere database project	https://halocat.geomar.de/
CARIBIC	Carl Brenninkmeijer MPI-Mainz	Access to air samples from passenger aircraft	https://caribic-atmospheric.com/
OP3	Nick Hewitt, (Lancaster), David Oram (UEA), Dwayne Heard (Univ. Leeds)	Oxidant and Particle Photochemical Processes above a South-East Asian tropical rain forest	http://www.es.lancs.ac.uk/op3/
SAMBBA	David Oram (UEA), Hugh Coe (Univ. Manchester)	South American Biomass Burning Analysis	
SCOUT-O3	Neil Harris (Univ. Cambridge) Martyn Chipperfield (Univ. Leeds)	Stratospheric-Climate Links with Emphasis on the Upper Troposphere and Lower Stratosphere	http://www.ozone-sec.ch.cam.ac.uk/scout_o3/
TROMPEX	Lucy Carpenter Univ. of York	Access to air samples collected by the UK BAe-146 research aircraft	
CHARLEX	Alfonso Saiz-Lopez CSIC, Toledo	Air samples collected on Galapagos Islands	
TransBrom	Kirstin Krüger (GEOMAR / Kiel)	Very short lived bromine compounds in the ocean and their transport pathways into the stratosphere	http://www.geomar.de/~transbrom
Envival Life	Mark Weber (Univ. Bermen)	Use of observational data for ENVISAT validation	
BREDOM	Folkard Wittrock (Univ. Bremen)	Passive remote sensing of reactive trace gases in the UV/Vis	www.doas-bremen.de
SHARP	Ulrike Langematz (FU-Berlin)	Stratospheric Change and its Role for Climate Prediction	http://www.geo.fu-berlin.de/v/sharp/
SOPRAN	Hermann Bange	Ships cruises and global modelling	http://sopran.pangaea.de/
Strapolété	Nathalie Huret (CNRS/LPC2E Orléans)	Summer Polar Stratosphere: dynamics, aerosols and bromine content – balloon observations	http://strapolete.cnrs-orleans.fr/
Enriched	Nathalie Huret (CNRS/LPC2E Orléans)	European collaboration for research on stratospheric chemistry and dynamics – balloon observations	http://www.lpc2e.cnrs-orleans.fr/~enriched/
NASA-Attrex	Eric Jensen (NASA-Ames)	Airborne Tropical Tropopause Experiment - measurements with the NASA Global Hawk unmanned aircraft system	http://www.espo.nasa.gov/attrex/

LPMAA	Claude Camy-Peyret (Univ. Paris 6)	Co-operation on stratospheric balloon-borne observations	http://www.lpmaa.jussieu.fr/ext
NIWA	Karin Kreher (National Institute of Water and Atmospheric Research)	Co-operation on ground-based DOAS observations	http://www.niwa.co.nz/
RSMAS	Elliot Atlas (Rosenstiel School of Marine and Atmospheric sciences)	Atmospheric trace gas measurements	http://www.rsmas.miami.edu
UM	(i) Azizan Abu Samah (ii) Siew-Moi Phang (Institute of Ocean & Earth Sciences, University of Malaya	(i) Collaboration on transport processes and climatology of the North East monsoon and its relation to primary productivity. (ii) Collaboration on halocarbon emission from tropical marine algae.	http://www.um.edu.my
UNIMAS (Universiti Malaysia Sarawak)	Po Teen Lim (Department of Aquatic Science)	Collaboration on oceanic research	http://www.frst.unimas.my/
UMS (Universiti Malaysia Sabah)	Ann Anton (Borneo Marine Research Institute/Biotechnology Research Institute)	Collaboration on oceanic research	http://www.ums.edu.my/ipb/ann.html
HGF_AWI project Phytooptics	Astrid Bracher (AWI)	Collaboration on biooptical and ocean color research	http://www.awi.de/en/go/phytooptics
Remote Sensing group HZG (before GKSS)	Roland Doerffer and Rüdiger Röttgers	Collaboration on biooptical research	http://www.hzg.de/institute/coastal_research/structure/operational_systems/KOF/index.html.de

Technological advance

The following technological advances have been achieved during SHIVA:

1. The algorithm, PhytoDOAS, aiming to retrieve the biomass of not only two but now four different phytoplankton types from space has been further developed, tested and evaluated. A global data set for the years 2002 to 2012 consisting of biomass data of diatoms, dinoflagellates, coccolithophores (a group of haptophytes) and cyanobacteria has been derived from the hyperspectral data of the satellite sensor SCIAMACHY (SCanning Imaging absorption spectrometer for Atmospheric ChartographY on ENVISAT) analytically and independent from a priori information.
2. Global emission data of VSLS have been added to the new database for 'Halocarbons in the Ocean and Atmosphere' (HalOcAt) https://halocat.geomar.de/de. The assimilation of these data to global circulation models have been supporting to establish global emission scenarios. These emission scenarios form the basis to analyze the past and present and to predict the future relevance of halogenated VSLS for global ozone and climate.
3. A first successful experiment has been performed with the novel Perfluorocarbon tracer release and sampling system (PERTRAS). During the RV Sonne, 9 kg of perfluoromethylcyclopentane (PMCP) were release and sampled downstream with the Falcon 5 and 25 hours after the release. The tracer plume was successfully intercepted with maximum PMCP mixing ratios of 300 fmol/mol.
4. Spectral structures from liquid water and their impact on the DOAS analysis were investigated. It was observed that over the remote ocean trace gases are often misfitted and tend to negative values. Correction spectra for currently available liquid water cross-sections were retrieved from ground-based measurements during TRANSBROM and SO218 and it was demonstrated that these correction spectra have the potential to improve space-borne DOAS measurements over the ocean.

Table 8: Students involved in SHIVA and its research themes.

#	Student's Name	Partner	Organisation	Date of defense
1.	Bieligk, Henner	GEOMAR	University of Kiel	March 2013
	Master thesis	Title: VSLS transport to the stratosphere during the DRIVE-POSEIDON campaign in the tropical East-Atlantic		
	Supervisor: Kirstin Krüger	This thesis investigated the VSLS transport to the stratosphere using VSLS fluxes from the DRIVE ship expedition in the tropical East Atlantic during May-June 2010 apllying the Lagrangian transport model FLEXPART.		
2.	Brinckmann, Sven	GUF	University of Frankfurt	2010
	PhD thesis	Title: Very short lived brominated gases: observations from source regions to the stratosphere		
	Supervisor: Andreas Engel	In the frame of this thesis measurement methods for brominated VSLS were improved and atmospheric measurements of VSLS from different source were performed, including balloon and ship measurements (TRANSBROM) which contributed to SHIVA.		
3.	Deutschmann, Tim	UHEI	University of Heidelberg	2010
	Diploma thesis	Title: Atmospheric Radiative Transfer Modelling with Monte Carlo Methods		
	Supervisor: Klaus Pfeilsticker	The thesis addressed the time-dependent profiling of important stratospheric radicals (O3, NO2, and BrO) by balloon-borne UV/vis limb spectroscopy. The measurements were used to infer J(N2O5).		
4.	Fuhlbrügge, Steffen	GEOMAR	University of Kiel	July 2011
	Diploma thesis	Title: Analysis of atmospheric VSLS measurements during the DRIVE campaign in the tropical East Atlantic		
	Supervisor: Kirstin Krüger	Within the thesis the relationship between meteorological conditions and VSLS abundances in the marine boundary layer was analysed in detail during the DRIVE ship cruise in the tropical East Atlantic.		
5.	Geib, Anika	GEOMAR	University of Kiel	2010
	Diploma thesis	Title: Transportprozesse in der Tropischen Tropopausenschicht im NH Winter mit ERA-Interim Assimilationsdaten		
	Supervisor: Kirstin Krüger	This work investigated transport processes in the TTL based on ERA-Interim data using a Lagrangian transport model.		
6.	Grossmann, Katja	UHEI	University of Heidelberg	Summer 2014
	PhD thesis	Title: Aircraft-borne DOAS measurements during SHIVA		
	Supervisor: Klaus Pfeilsticker	The thesis addressed the measurements, data retrieval and interpretation of aircraft-borne DOAS measurements with respect to halogen oxides (IO, BrO), photo-oxidants (C2H2O2, CH2O, HONO) and primary pollutants (NO2)		
7.	Grossmann, Katja	UHEI	University of Heidelberg	2010
	Diploma thesis	Title: Reactive Halogen Species in the western Pacific		
	Supervisor: Ulrich Platt	The diploma thesis addressed the measurement of IO in marine boundary layer of the western Pacific during the RV Sonne TransBrom cruise. Supporting modeling calculations suggested that in addition to the photochemical decay of CH3I an important source of iodine was missing the explain the measured IO concentrations		
8.	Kritten, Lena	UHEI	University of Heidelberg	2009
	PhD thesis	Title: Time dependent profiling of UV/vis absorbing radicals by balloon-borne spectroscopic Limb measurements and implications for the stratospheric photochemistry		
	Supervisor: Klaus Pfeilsticker	The thesis addressed balloon-borne limb measurements of some key radicals (O_3, NO_2, and BrO) in the tropical stratosphere, from which the photolysis frequency of NO2 (J(NO2)) was inferred.		
9.	Leedham, Emma	UEA	University of East Anglia	2013
	PhD thesis	Title: Emission of biogenic halocarbons in temperate and tropical coastal zones		
	Supervisor: Bill Sturges	Laboratory and field analysis of VSLS emissions from tropical seaweeds		
10.	Prados-Roman, Cristina	UHEI	University of Heidelberg	2010
	PhD thesis	Title: Aircraft-borne spectroscopic limb measurements of trace gases absorbing in the UV-A spectral range. Investigations of bromine monoxide in the Arctic troposphere		
	Supervisor:	The PhD thesis addressed first measurements of BrO profiles in the Arctic during so-called ozone		

	Klaus Pfeilsticker	depletion events in the troposphere		
11.	Rumpel, Verena	GEOMAR	University of Kiel	June 2011
	Bachelor thesis	Title: Meteorologische Auswertung der TransBrom Sonne Kampagne im tropischen Westpazifik		
	Supervisor: Kirstin Krüger	The bachelor thesis analysed in detail the TTL conditions during the TransBrom SONNE cruise in the tropical West Pacific.		
12.	Theys, Nicolas	BIRA	Université Libre de Bruxelles	2010
	PhD thesis	Title: Atmospheric Bromine Monoxide: multi-platform observations and model calculations		
	Supervisor: M. Herman and M. Van Roozendael	This study analyzed the BrO content in both the troposphere and stratosphere based on ground-based multi-axis and satellite nadir instruments (GOME and GOME-2) as well as model calculations.		
13.	Wache, Sebastian	GEOMAR	University of Kiel	2010
	Diploma thesis	Title: Transport of trace gases in the marine boundary layer in the tropical West Pacific during the TransBrom-Sonne campaign		
	Supervisor: Kirstin Krüger	The diplom thesis analysed the air mass origin of VSLS during the TransBrom SONNE cruise in the tropical West Pacific.		
14.	Werner, Bodo	UHEI	University of Heidelberg	2009
	Diploma thesis	Title: Case Study of stratospheric Limb measurements of O3, NO2 and BrO in the polar summer		
	Supervisor: Klaus Pfeilsticker	The thesis addressed the spectroscopic and profile retrieval of O3, NO2 and BrO measured during balloon-borne limb observations in the stratospheric over Kiruna on Sept. 9/10, 2009		
15.	Wisher, Adam	UEA	University of East Anglia	2010
	Master thesis	Title: Very short-lived halogenated substances in the upper troposphere / lower stratosphere		
	Supervisor: David Oram	Analysis of CARIBIC samples by negative ion, chemical ionisation mass spectrometry		
16.	Ihnenfeld, Verena	GEOMAR	University of Kiel	2012
	Bachelor thesis	Title: Methan-, DMS- und DMSP- Messungen während der SHIVA Sonne-Fahrt im November 2011		
	Supervisor: Hermann Bange	Analysis of CH4, DMS, DMSP data from the coastal western Pacific		
17.	Krysztofiak, Gisele	CNRS	Université Orléans	2013
	PhD thesis	Transport et chimie d'espèces soufrées et bromées dans la haute troposphère et basse stratosphère diagnostiqués par des mesures sous ballon et en avion et par modélisation (Transport and chemistry of sulfur and bromine compounds in the upper troposphere and lower stratosphere diagnosed by balloon-borne and aircraft measurements and modelling)		
	Supervisor: Valery Catoire	Development of a detailed atmospheric degradation scheme for CHBr_3 and CH_2 Br_2 and determination of the major pathways in the degradation scheme and the effect of air pollution on the pathways		
18.	Sadeghi, AliReza	AWI	University of Bremen	April 2012
	PhD thesis	Title: “Phytoplankton Functional Groups from Hyperspectral Satellite Data and its Application for Studying Phytoplankton Dynamics in Selected Oceanic Regions”		
	Supervisor: Astrid Bracher	This thesis further developed, tested and evaluated the PhytoDOAS algorithm to retrieve the biomass of four different phytoplankton types from space.		
19.	Reiter, Anja	DLR	Ludwig-Maximilians-University Munich	July 2012
	Diploma thesis	Title: First airborne SO2 Measurements in the West Pacific using IT-CIMS: Analysis of Regional Distribution, Sources and Transport		
	Supervisor: Prof.Dr.Bernhard Mayer Hans Schlager Heinfried Aufmhoff	CIMS measurements of SO2 from the Falcon aircraft were performed and analysed. Mean and median volume mixing ratios for the SHIVA investigation area were determined and compared with previous airborne SO2 observations in other regions. In the 8-12 km altitude range, the mean SO2 mixing ratios measured during SHIVA are higher than values observed in other tropical areas. Enhanced SO2 mixing ratios measured during several SHIVA flights were attributed to specific sources (anthropogenic emissions from the Philippines, shipping, volcanic emissions).		
20.	Walker, Hannah	UNIVLEEDS	University of Leeds	August 2013
	PhD thesis	Title: Field Measurements and Analysis of Reactive Tropospheric Species Using the FAGE Technique		

	Supervisor: Dwayne .E. Heard	Measurements during SHIVA of IO, by Laser-Induced Fluorescence spectroscopy, and I_2, and the sum of ICl + HOI, by the diffusion denuder method. Investigation of the relationships between IO and its potential precursors. Steady-state analysis of IO.		
21.	Mohr, Viktoria	GEOMAR	University of Kiel	August 2013
	PhD thesis	Title: Changes of the TTL in climate models and reanalysis data		
	Supervisor: Kirstin Krüger	This thesis analysed TTL changes in the past and future using ERA-Interim, CCMs and CMIP5 model data. For this a Lagrangian method is applied focussing on changes of the upper TTL.		
22.	Ziska, Franziska	GEOMAR	Helmholtz-Zentrum für Ozeanforschung Kiel	Summer 2014
	PhD thesis	Global and future modeling of oceanic VSLS emissions		
	Supervisor: Birgit Quack	Production of the first data-based global oceanic VSLS emission inventory and calculation of the future development of oceanic fluxes		
23.	Hepach, Helmke	GEOMAR	Helmholtz-Zentrum für Ozeanforschung Kiel	Spring 2014
	PhD thesis	Emissions, sources and budgets of oceanic halocarbons		
	Supervisor: Birgit Quack	Investigates the biological sources and the key controlling factors of the oceanic emissions of various brominated, chlorinated and iodinated compounds		
24.	Mroz, Julia	AWI	Hamburg University of Applied Science	2011
	Diploma thesis	Title: Bestimmung von eukaryotischen und prokaryotischen Photosynthesepigmenten in Phytoplankton mit Hilfe eines point-source integrating-cavity absorption meter. (“Determination of eukaryotic and prokaryotic photosynthetic pigments in phytoplankton using a point-source integrating-cavity absorption meter”		
	Supervisor: Astrid Bracher	Laboratory and field analysis of phytoplankton absorption data collected from cruises during SHIVA		
25.	Sala, Stephan	GUF	University of Frankfurt	Fall 2013
	PhD thesis	Entwicklung und Einsatz eines flugzeuggetragenen GC/MS - Systems zum Nachweis halogenierter Kohlenwasserstoffe in der Atmosphäre (development and deployment of an airborne GC/MS for the measurements of halocarbons in the atmosphere)		
	Supervisor: Andreas Engel	The thesis describes the development and the first operation of GhOST-MS during SHIVA and the bromine budget derived for the tropical upper troposphere during SHIVA.		
25.	Keng, Fiona Seh Lin	UM	University of Malaya	October 2013 (convocation)
	Master of Science (University of Malaya)	Title: Emission of selected halocarbons by seaweeds inhabiting a coral reef		
	Supervisors: Siew-Moi Phang & Noorsaadah Abdul Rahman	The emission of selected halocarbons by tropical seaweeds was investigated through field observations and laboratory experiments. Results showed that the tropical brown seaweed Turbinaria conoides emit higher levels of bromoform, $CHBr_3$ and other halocarbons than temperate and polar brown seaweeds, thus making it important to determine the contribution of tropical seaweeds to atmospheric composition of halocarbons. Irradiance and photosynthetic efficiency was found to be positively correlated to halocarbon emission by the seaweed.		
26.	Kuek, Felicity	AQUES	Swinburne University of Technology, Sarawak Campus	Convocation in October 2014 (already submitted for review)
	Master thesis	Coastal bacterial communities: their potential roles in dimethylsulfide (DMS) production and coral defence.		
	Supervisor: Moritz Müller	Samples collected during local cruises to culture bacteria and study microbial diversity as well as their potential involvement in DMS(P) cycling.		
28.	May Ling Onn	AQUES	Swinburne University of Technology, Sarawak Campus	Convocation October 2013 (degree already approved)
	Master thesis	SCREENING OF MANGROVE ENDOPHYTIC FUNGI FOR BIOACTIVE COMPOUNDS		
	Supervisor: Moritz Müller	Heavy Metal data collected during local cruises was used for thesis.		

29.	Song, Jessica	AQUES	Swinburne University of Technology, Sarawak Campus	Convocation October 2015
	Master thesis	MOLECULAR AND CULTURE-BASED ANALYSIS OF THE MICROBIAL COMMUNITIES IN SOUTH CHINA SEA WATERS		
	Supervisor: Moritz Müller	Samples for molecular work were collected by Dr. Aazani Mujahid during SHIVA cruise and are currently analyzed using NGS techniques.		
30.	Flöter, Sebastian	GEOMAR	Helmholtz-Zentrum für Ozeanforschung Kiel	August 2012
	Master thesis	Variability of sources of volatile halogenated organic compounds (VHOCs) in the Kiel Bight		
	Supervisor: Birgit Quack	Investigated the distribution of various brominated, chlorinated and iodinated compounds in different source areas of the Kiel bight as a coastal model		
31.	Ryan Hossaini	UNIVLEEDS	University of Leeds	October 2012
	PhD thesis	Title: Very short-lived halogenated species: modelling their tropospheric distribution, contribution to stratospheric bromine and impact on ozone		
	Supervisor: Martyn Chipperfield	Modelling VSLS chemistry and transport: Interpretation of VSLS observations in conjunction with model output.		
32.	Peters, Enno	IUP-Bremen	University of Bremen	October 2013
	PhD thesis	Improved MAX-DOAS measurements and retrievals focused on the marine boundary layer		
	Supervisor: John P. Burrows	Measurements of reactive trace gases during SO-218 and TRANSBROM, Evaluation of the effects of absorption and scattering in liquid water on the DOAS analysis		

Involvement of researchers from new EU member states

No partners from new EU members state were directly involved into the SHIVA project.

Involvement of researchers from non-EU member states

1. First of all, the SHIVA field observations required to use the knowledge of scientists from countries adjacent to the South China, notably from Malaysia and the Philippines. Among them the scientists from the Malaysian Economic Planning Unit (EPU) Prime Minister's Department, notably Mrs. Munirah Bt. Abd Manan, who patiently guided our approval process to conduct the intended research in Malaysia, and from National Oceanic Department (NOD, notably Prof. Dr. Nor Aieni Binti Haji Mokhtar supported us with their knowledge and unconditional support to make the SHIVA Western Pacific campaign happen. Further, scientists from the Malaysian Meteorological Department (MMD) support us in the SHIVA campaign related activities of weather forecasting, analyzing and the atmospheric sounding. Support and advice in biological questions were obtained from the Marine Science Institute of the University of the Philippines in Quezon.
2. Collaboration with Universiti of Malysia Sarawak (UMS), Universiti of Malysia Sabah (UNIMAS), and Swinburne University of Technology, Sarawak Campus (SUTS): Teams from UMS, UNIMAS and SUTS were largely involved to perform local ship cruises from Kuching, Kota Kinabalu and Semporna to take oceanic water samples for analysis of biological, chemical and physical parameter. Post mission analysis of the samples was jointly performed at UMS, SUTS and UNIMAS. In particular Emma Leedham (UEA), Dr. Marcel Dorf (Uni Heidelberg) and Klaus Pfeilsticker (Uni Heidelberg) presented their work to SUTS and UNIMAS students and staff. During the local cruises several Malaysian MSc and BSc students had the chance to get involved with preparations of the cruises as well as talk to visiting scientists. Microbiological diversity in the SCS and their potential impact on DMS release was studied by SUTS MSc student Felicity Kuek and the work has been presented in several conferences (i.e. SCS 2012, PD 2013; with acknowledgment to SHIVA) and 2 manuscripts are in the final stages of preparation. Another SUTS MSc student (Jessica Song) just started molecular work (Next-Generation Sequencing) on samples collected by Dr. Aazani Mujahid (UNIMAS) during the SHIVA cruise and the first two samples were sent to China (BGI) for analysis. A novel approach was used and if the initial analysis is successful, then this approach will be used for the remaining samples and will allow determination of biodiversity as well as gene activity (pending

funding as analyses are very expensive). Other data collected during the local cruises involved data on heavy metals and this data has been used in another MSc study (Onn May Ling, graduating in October 2013).

3. During the SHIVA-campaign in November 2011, rendezvous' between the research vessel Sonne with local boats launched from the University of Sabah in Kota Kinabalu and the University of Sarawak in Kuching have been organized and successfully conducted off the coast of Borneo. Most notably during the SHIVA-Sonne expedition, five Malaysian biologist and meteorologists and one Philippine planktologist were on board the research vessel conducting partly their own programs and also were involved with the meteorological and biological work conducted by the European partners on board. On the other hand, the crew members of the local boats were all from Malaysia but two scientists which were coming from the European partners. The coastal samples taken on the small boats cruises were transferred to RV Sonne where they were analyzed for VSLS and ocean color. In exchange samples taken by the RV Sonne from the open South China Sea were analyzed for biological and chemical parameters of our colleagues from the Malaysian Universities.
4. A post-doc and a student of MMD attended a one week training at DLR on the operation, calibration, and data analysis of three trace gas instruments: a CO_2/CH_4 cavity ring down spectrometer, an O_3 UV absorption detector, and a VUV fluorescence CO monitor. Both MMD members also operated these CO and O_3 instruments on the RV Sonne during SHIVA. Unfortunately, the cavity ring down spectrometer was damaged during the transport from Germany to the RV Sonne in Singapore and could not be operated during SHIVA.
5. Discussions of the data have followed and some posters were presented at national and international conferences. During the South China Sea 2012 International Conference organized by the University of Malaya, Kuala Lumpur, from 21 - 24 October, 2012, a session on the SHIVA expedition was convened by Azizan Abu Samah and Klaus Pfeilsticker. Eleven oral presentations and three posters were presented.
6. The emission of VSLS halocarbons by marine macro-algae was jointly investigated by the scientists from University of East Anglia (Emma Leedham & Bill Sturges) and University of Malaya (Fiona Keng & Siew-Moi Phang), and these studies in the field and laboratory of VSLS emissions due to macro-algae contributed to two scientific publications.
7. Ground-based measurements of reactive trace gases carried out of the University of Bremen on Boheydulang island were supported by several students of the University of Sabah in Kota Kinabalu (supervised by Justin Sentian) and rangers of the Tun Sakaran Marine Park. Students were trained to set-up and run a DOAS instrument.

The strong collaboration with the University of Malaya which developed during SHIVA has led to further planned research activity in 2014, based around the establishment of a new marine research station at Bachok (UEA, UCAM, UM).

Use and dissemination of foreground

As described in Section 3, a comprehensive set of observational data was acquired from the SHIVA western Pacific field campaign. All data were initially archived in a database maintained by the SHIVA coordinator University of Heidelberg and can be used for scientific exploitation by project beneficiaries and associated partners, leading to many of the scientific results and publications described above. Recently, the database has been transferred to an open access web server linked to the SHIVA web page (ftp server: shiva.iup.uni-heidelberg.de), and a user name and the password will be handed out upon request. Thus, the data has been put at the disposal of the atmospheric research community at large.

A special issue has been set up in Atmospheric Chemistry and Physics (ACP) (see http://www.atmos-chem-phys.net/special_issue306.html). This journal, run by the European Geosciences Union, provides open access to all its articles and currently has the highest impact factor of any journal dedicated to atmospheric sciences.

Global data were compiled in a novel database (https://halocat.geomar.de/), which created added value to the individual data sets by integrating them into a global framework. Many scientists in this field contributed to the initiative, which was launched in May 2009 within an EU-COST (European Cooperation in the field of Scientific and Technical Research) ACTION 735: “Tools for Assessing Global Air–Sea Fluxes of Climate and Air Pollution Relevant Gases” as part of the international SOLAS (Surface Ocean - Lower Atmosphere Study) research program. The data collection for HalOcAt is still ongoing and the database currently consists of 200 data sets comprising roughly 55,400 oceanic and 470,000 atmospheric data points of 19 different compounds.

An inter-comparison of available coupled Chemistry Climate Models (CCMs) was compiled within the SPARC CCMVal report (2010) focusing in particular on ozone chemistry and dynamical changes in the stratosphere of the past and future. Several SHIVA partners were involved in the compilation of this model report. Some of the CCMs were used for analyzing future changes of the TTL within WP6.

Research results of SHIVA will also contribute to future WMO assessments reports (e.g., the next one is expected to be released for end of 2014) and IPCC reports. We expect publications coming out of SHIVA to be cited in both these reports, and scientists involved in the present project are contributing to both reports directly as authors, contributors and reviewers.

The lifetimes of ozone depleting substances are a key parameter in estimating the future evolution of chlorine loading in the atmosphere and are also needed to determine ozone depletion potentials (ODP) and greenhouse warming potentials (GWP). Andreas Engel (GUF) has lead authored the chapter on “Inferred Lifetimes from Observed Trace-Gas Distributions” which summarized lifetime estimates based on observations and co-authored the summary chapter with new recommendations. One of the major outcomes of the report is that the atmospheric lifetime of CFC-11 (which is used as a reference in calculating ODP values) has been revised due to an improved lifetime uncertainty estimates. New recommendations for the best-estimate atmospheric lifetimes have been made, which will be taken up in the upcoming WMO report to be released in 2014.

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