The 4th SHIVA newsletter reports on the activities performed within the EU project SHIVA (Stratospheric ozone: Halogen Impacts in a Varying Atmosphere, grant number 226224) during the first 6 months of 2011.

Thanks to all work package leaders and contributors.

With our bests regards,

Marcel Dorf and Klaus Pfeilsticker

**Report on activities within the individual Work Packages (WPs)**

**WP-1: Management**

**Meetings:** Summaries, minutes and presentations can be found on the Wiki

- A steering committee and campaign planning meeting was held at Kiel (IFM-GEOMAR) on January 6/7, 2011. Major issues regarding the deployment and instruments onboard the RV Sonne and the FALCON aircraft were discussed.
- January 26: FALCON aircraft planning meeting in Frankfurt/Certification of instruments for FALCON (Enviscope).
- April 19: Meteorological straw man flight planning meeting in Erding near Munich.
- May 3: SONNE cruise planning meeting at the IFM-GEOMAR, Kiel.
- July 3 -9: Visit of Miri airport, where the FALCON will be stationed during the campaign. Setting up cooperation with MMD (Malaysian Meteorological Department) (Frank Probst, Hans Schlager, and Marcel Dorf).
- The annual meeting 2011 and a half-day campaign planning meeting took place in Leeds on July 14/15.

**Administration:**

- In January 2011 we submitted the so called EPU (Economic Planning Unit) proposal, in order to obtain research permissions within Malaysia. By late February we already received first reactions from the EPU and the NSC (National Security Council).
• Individual EPU proposals by all campaign participants were collected and submitted in May 2011.
• The first periodic report was submitted to the EC in February, 2011.
• The interim payment was received from the EC and distributed to all partners in relative shares.
• The amendment No.1 of the CA (Consortium agreement) was signed by all participants.
• Another amendment to the Consortium Agreement is necessary due to the change in aircraft (HALO has to be replaced by FALCON in the document).

Reminder:

• The data protocol has to be signed by all participants. This is especially important for all campaign participants. You can download it from the Wiki. Please also remind newly hired students to sign it.

• Proper acknowledgement (using SHIVA-226224-FP7-ENV-2008-1) to the European Commission must be given in all SHIVA publications or publications using any SHIVA data.

• The SHIVA wiki-page (http://shiva.iup.uni-heidelberg.de/wiki/) will be a major tool of communication during the western Pacific campaign.

Timeline towards the western Pacific campaign 2011

• August 16-19: Instrument integration at DLR/Oberpfaffenhofen
• August 22-25: Test flights (only certified instruments)
• September 8/9: Steering Committee meeting in Kuala Lumpur
• End of September: Shipping of equipment

Campaign

Peninsular Malaysia campaign (UM, UEA, UCAM)

• Sept. 5th – end of Nov.: ground measurements at Bachok and Straits of Malacca, and lab work at Kuala Lumpur

November 15 – 29: RV SONNE cruise from Singapore to Manila

• Nov. 13 Arrival at Singapore
• Nov. 14 Container unpacking, air freight arrival
• Nov. 14 Set up on the ship, arrival of dangerous goods on Sonne
• Nov. 15 Departure from Singapore
• Nov. 29 Short cruise report (background and kind of obtained data)
• Nov. 29    Arrival at Manila and container packing
• Nov. 30    Container off board
• Nov. 30    (or Dec. 1) Departure from Manila

**FALCON schedule**

80 flying hours (38 for transit) allows for approximately 12 local flights of ~4hrs

• Nov. 2 - 8    Installation of racks
• Nov. 7 or 8   Test flight
• Nov. 9       Depart from DLR
• Nov. 11 (late)   Arrive in Miri
• Nov. 14      First possible science flight
• Dec. 6       Depart from Miri
• Dec. 9       Arrive at DLR
• Dec. 12/13   Instrument demounting in OP

**Borneo Ground campaign (UNIHB, UM, UMS, UNIMAS, UCAM, CIAC-Toledo, UHEI, UEA)**

• Measurement period: November 11 to December 8

**WP-2: Measurements**


A measurement container has been constructed in spring 2011 in the framework of the German research project SOPRAN (BMBF) and is now hosting a gas chromatographic/ mass spectrometric device, measuring halocarbons in seawater. A month-long campaign performing VSLS production studies in sea water was conducted in June 2011 also in the frame work of SOPRAN. SHIVA will benefit from the measurements. Logistical constraints and lacking operation of the observatory vessel make regular monthly measurements impossible. We thus perform individual campaigns in the tropical Atlantic. Also in SOPRAN a cruise (MSM 18/3) with MARIA S. MERIAN will be conducted from 22nd June -21st July 2011 (Mindelo (Cap Verde) to Libreville (Gabun), investigating biogeochemical cycles and feedbacks between atmosphere and ocean in the tropical Atlantic (Figure 2-1), where VSLS measurements of surface water and atmosphere, as well as depth profiles and some source experiments shall be performed.
Also in the tropical Atlantic the research expedition DRIVE (Diurnal and Regional Variability of halogen Emissions) had been performed from 31st May to 24th June 2010, from the IFM-GEOMAR with the RV Poseidon in the tropical eastern Atlantic (Las Palmas - Mindelo - Upwelling off Mauritania - Las Palmas – Vigo) to investigate air-sea fluxes of halogenated trace gases with oceanic sources in the SOPRAN project. The coastal upwelling off Mauritania is a significant source of climate relevant trace gases such as carbon dioxide (CO₂) and Nitrous oxide (N₂O) and for some VSLS. The major objective of P399/2 was to investigate the regional and diurnal atmospheric and oceanic variations of halogenated compounds in the eastern tropical North Atlantic Ocean with special focus on the Mauritanian upwelling. During the cruise short lived halocarbons were measured in seawater and atmosphere, with the special interest of diurnal variation of possible fluxes in coastal areas, influenced by local emissions and land-sea breeze fluctuations. Therefore, six 24-hour diurnal stations with hourly surface water and atmospheric sampling were conducted. In addition two atmospheric diurnal hourly sampling took place in parallel on Sao Vincente (Cape Verde). The cruise P399/2 took place during the decline of the coastal upwelling (upwelling off Mauritania is most pronounced during Feb/Mar). Therefore, upwelling was observed only north of 19°N. The upwelling could easily be identified by a drop in the sea surface temperature from 26°C to 18°C (Figure 2-2).
Figure 2-2: Cruise track of P399/2. 24h stations are indicated by numbers.

Figure 2-3: Bromoform (CHBr$_3$, blue lines) and dibromomethane (CH$_2$Br$_2$, red lines) atmospheric mixing ratios (open symbols) and ocean surface concentrations (filled symbols). The numbers correspond to the station numbering in Fig. 2-2.
During the 24h stations, when the ship was positioned against the wind at one fixed position, high resolved measurements of the atmospheric and dissolved halocarbons bromoform (CHBr₃) and dibromomethane (CH₂Br₂) were performed (Fig. 2-3). Dissolved surface concentrations and saturation anomalies were in the range from 1 to 43 pmol L⁻¹ and <0 to 225%, respectively, indicating that the Mauritanian upwelling is generally a net source of both compounds for the atmosphere during P399/2. Dissolved CHBr₃ and CH₂Br₂ concentrations as well as atmospheric mixing ratios of both compounds showed a clear increasing trend towards the coast which is in line with previous observations of near shore sources. The maxima of dissolved and atmospheric CHBr₃ and CH₂Br₂ (station 5) were not found at the station with the most intensive upwelling (station 6). Diurnal variability was observed for the atmospheric and dissolved concentrations, however, there seems to be no obvious correlation between both parameters. Computations of the sea-to-air fluxes of CHBr₃ indicated that they are not sufficient to explain either the observed elevated atmospheric mixing ratios or their rapid increases during the day and require additional sources, most likely from shallow coastal waters of the Banc d’Arguin area. The CH₂Br₂/CHBr₃ ratio in the atmosphere was constant whereas in the surface ocean it was increasing towards the open ocean indicating an enhanced loss of CHBr₃ from the surface layer compared to CH₂Br₂.

**Figure 2-4:** Ten minute average of wind speed and direction for every three hours, except 24 h stations during DRIVE.
Figure 2-5: Atmospheric mixing ratios of \( \text{CHBr}_3 \) and \( \text{CH}_3\text{I} \) during DRIVE.

Figure 2-6: Mixing layer height, deduced from 41 radio soundings during DRIVE (Fuhlbrügge).

Meteorological analysis during the cruise (diploma thesis Steffen Fuhlbrügge) reveals a strong influence of mixing layer height on the atmospheric mixing ratios of some VSLS and there with on their air – sea flux. Further analysis of the data is in progress.

Preparation for the SHIVA joint ship-aircraft campaign has advanced significantly. RV Sonne will depart Singapore on 15 November 2011 and arrive in Manila (Philippines) on 29 November. The route will hopefully include some diurnal stations along the coast line of Borneo where we hope to interact with scientists from local universities (exchange of samples, etc). The aircraft will be based in Miri (Sarawak, Borneo) for approximately 3 weeks, between 14 November and 3 December. The cruise was adjusted several times after meetings and new information from the captain, the ship’s owner and the ships funding agency, in order to minimize pirate incidents, avoid fishing activities and
insurance risk zones as well as in response to the Malaysian negative reply on our request for an escort. The current work version is generally following recommended shipping routes. The final decision how the actual track will be conducted and how and if the transects to the coast can be performed is with the captain. We will decide during the cruise, depending on the actual conditions and situation.

![Figure 2-7](image_url)

**Figure 2-7:** Proposed cruise track (version of 27th July 2011) for the SHIVA- Sonne campaign, RV Sonne cruise SO218 (15.-29. November 2011, Singapore-Manila).

### 2. Instrument development for the SHIVA joint aircraft-ship campaign

**2.1 SPIRIT:** LPC2E-CNRS has finalized the building of the new mid-infrared absorption spectrometer called SPIRIT (SPectromètre Infra-Rouge *In situ* Toute altitude) using three quantum cascade lasers for airborne measurements of several trace gases (N2O, CH4, H2O, CO2, CO, OCS). This instrument has been integrated in a Falcon rack. Flight certification is currently in progress.

**Publication:**

**2.2 WAS:** whole air sampler for Falcon (UEA)

The whole air sampling system we had intended to use for SHIVA has been designed for use on the HALO aircraft (University of Wüppertal) and is not compatible with the Falcon. It has therefore been
necessary to design and build an alternative sampler for the SHIVA campaign. This has been based on a glass sampling system used previously on the Falcon by colleagues at the University of York. However it has taken considerable time, effort and expense to build a fully-functioning set of samplers to aircraft specifications. We will have 4 samplers available for the campaign, each consisting of 30 x 1 litre glass flasks which can be filled to a pressure of around 2 bar. The samplers are currently being certified. The unexpected certification costs are likely to be met by DLR.

2.3 GHOST: University of Frankfurt

Certification for the airborne GCMS (VSLS analysis) is in progress. No problems have been reported.

2.4 LIF: University of Leeds

The LIF instrument was originally going to be installed on the new HALO aircraft. However with the delays in certifying HALO and the switch to the Falcon aircraft there was no room for this instrument on the aircraft. Consequently it was decided to operate the LIF instrument on the Sonne and detailed preparations for the SHIVA cruise are underway. The Leeds LIF and DLR CIMS instruments will be co-located in a 10ft shipping container on the "back-deck". The shipping container layout, air conditioning, power distribution and costs are nearly finalised, and pumps are to be housed in a nearby deck store room. Work is underway in the lab to optimise the Iodine Monoxide (IO) detection by LIF, and the possibility of simultaneous Glyoxal measurements will be explored in the coming weeks. Previous (as yet unconfirmed; Volkamer) ship borne observations by MaxDOAS has indicated a correlation between IO and Glyoxal and we hope to be able to test these previous observations. Work is underway to provide a means to obtain solar irradiance data during the cruise (via some as yet undetermined radiometer) to provide input for photochemical modelling of the IO observations.

3. Other VSLS sampling activities (UEA)

Regular long-term sampling for VSLS in the western Pacific has proven to be rather difficult. The intention of establishing regular flask filling at the Bachok station currently being built by the University of Malaya remains, but the site has experienced significant delays during construction and the availability of local people to fill flasks has been limited. We still hope to provide regular measurements from this site both during and beyond the November SHIVA campaign. Further sampling difficulties occurred when ~30 sample flasks went missing in Singapore customs before a NIWA cruise from Singapore to NZ. On a more positive note, a set of ~20 canisters have been sent to the Galapagos Islands in the eastern Pacific, which will complement previously-reported measurements in the western Pacific, eastern Atlantic and Indian Ocean. Regular analysis of samples collected by the CARIBIC aircraft in the UTLS has continued.
Publication:

4. Satellite observations

Recent developments can be found in the latest (July 2011) deliverables reports from the satellite groups involved in WP-2. These can be found on the SHIVA Wiki page.

D2.6: Consolidated monthly mean BrO and Br, fields in the TTL and stratosphere from satellite retrievals (Alexei Rozanov and René Hommel, UNIHB).

D2.7: Phytoplankton maps, Part II (Astrid Bracher and Tilman Dinter, AWI).

D2.8: Global maps of halocarbon primary source and transformation regions derived from GOME-2 BrO and IO fields (IASB).

WP-3: Emission inventories - Present and future scenarios

Birgit Quack, Franziska Wittke, IFM-GEOMAR  
Tilman Dinter, Astrid Bracher, AWI-Bremerhaven

Since the last Newsletter in January 2011, the HalOcAt database (https://halocat.ifm-geomar.de/) has slowly, but steady grown. Currently, the database contains 186 contributions with about 8,000 global oceanic and 135,000 atmospheric data sets from all depth and height levels, including 19 different compounds and thus ~44,000 oceanic and ~470,000 atmospheric data points.

Based on all surface data from the HalOcAt database from the year 1989 until today we started a new approach to calculate a global marine and atmospheric surface map of bromoform (CHBr₃) in order to derive global air-sea flux estimates from a bottom up approach. The existing data cover only about 4% of the ocean showing that more measurements are urgently needed. Parameterizations are currently tested, while we look for correlations of biological, physical and chemical parameters of individual cruises or the global data set, which however until now yield no satisfying results. The challenge of filling missing values for a global estimate, based on limited knowledge, is to find the best and most realistic way for inter- and extrapolation. We could however extract important information from the existing data sets, which are for instance higher concentrations in coastal and equatorial upwelling regions (> 15 pmol /L), coast lines (> 100 pmol /L) and close to islands, while generally lower and more homogeneous surface concentrations are found in the open ocean (< 5 pmol/L). Considering this, we divided all data into coast, shelf and open ocean regimes (coastal and
shelf seas are neighboring 1°x 1° each, rest is open ocean) and additionally the ocean into the Longhurst biogeochemical regions (Longhurst et al. 1995) and the atmosphere into climatological wind regimes (0-30, 30-60, 60-90°N and S). A Gauss-Marcow-Smoothing was used to transfer the data into the global 1°x 1° grid and to broaden the dataset. This technique calculates the grid point percentage of the surrounding data position, which is located in the discrete Gaussian bell area. Because of the homogeneity of the open ocean the Gaussian Bell area is wider (3°) than for the coast or shelf region (1°) (Figure 3-1).

**Figure 3-1:** With the Gauss-Marcow Smoothing technique calculated (Left panel) global marine surface CHBr₃ concentration map in pM/L. All concentrations above 10 pM/L are scaled down by a factor of 12. (Right panel) global atmospheric surface bromoform concentration in ppt. All concentrations above 5 ppt are scaled down by a factor of 7.

Open ocean surface CHBr₃ concentrations show a latitudinal variation. For the further extrapolation of the data, we divided the open ocean into 4 regions for each hemisphere in order to take the physical and biogeochemical character of the marine surface waters into account. The inner tropics (0-5°N) include the equatorial upwelling with high nutrients and biomass and higher CHBr₃ concentrations. The subtropical gyre with downward moving water masses hence lower surface biological production was identified as the second region (5 to 40°N). Third region is the temperate zone between 40 to 66° (~66.5° = polar cycle) with higher climatologically surface chlorophyll concentrations than in the gyre region and an increasing CHBr₃ concentration towards higher latitudes. The last region extracts the Arctic/Antarctic where the surface water is colder and polar microalgae are present possibly produce CHBr₃.

The classification of the atmosphere is different from the ocean. The inner tropical region (here from 0-10°N) is characterized by the trade winds, upward moving motion and high condensations. The atmosphere for each hemisphere is divided into the 3 wind regimes Hadley Cell (10-30°), Ferell Cell (30-60°) and Polar Cell (60-90°). A good classification for the fast varying atmosphere is difficult, but the wind regimes caused by earth rotation and solar altitude are characteristic for specific air masses, wind directions and weather conditions, thus meant to be a good extrapolation.

For the different oceanic and atmospheric regions a Robust Fit was calculated. Based on the produced regression equations every missing value was calculated. Figure 3-2 shows the new assessment of a) the global surface marine CHBr₃ concentrations and b) the global surface atmospheric CHBr₃ concentrations.

A classification for the coastal and shelf regions was not possible due to a lack of data. Here the fit was calculated over both entire hemispheres.
Currently we calculate global air-sea fluxes, compare them to existing maps and produce future fluxes as well. Furthermore, the same will be done for the compounds methyl iodide (CH$_3$I) and dibromomethane (CH$_2$Br$_2$).

In order to get proxies and parameterizations for VSLS concentrations and emissions, satellite products of different phytoplankton groups have been developed. Up to now it is thought that certain phytoplankton groups probably under certain conditions are responsible for bromoform emissions in the open ocean. The composition and concentrations of different dominant PFTs (Phytoplankton Functional Types) were derived from measurements of the satellite sensor SCIAMACHY on ENVISAT analyzed with PhytoDOAS, a method of Differential Optical Absorption Spectroscopy (DOAS) specialized for diatoms and cyanobacteria (Bracher et al. 2009). This method has been improved for detecting four different types of PFTs by using simultaneously fitting of the differential specific absorption spectra of each species to the satellite measurement (see Sadeghi et al. 2010). These PFTs are diatoms, cyanobacteria, dinoflagellates and coccolithophores. A 9-year dataset (2003-2010) as monthly averages in global 1°x1° grids for each PFT has been produced. Full calibrated SCIAMACHY Level 1c (version 7.03 and 7.04) data have been used. In addition, this SCIAMACHY PFT data base has been averaged into a monthly 1°x1° grid climatology (one example of this climatology for coccolithophores is given in Fig. 3-3). These datasets will be used by IFM-Geomar in order to calculate emission of CHBr3 over the oceans. The direct relationship between phytoplankton group abundance and CHBr3 emissions is studied using the campaign data measured and analyzed in WP2 of SHIVA.
**Figure 3-3:** Global climatology for April of coccolithophore biomass (given as chlorophyll-a concentration) derived from the average of all SCIAMACHY data retrieved via PhytoDOAS multtarget-fitting (according to Sadeghi et al. 2011). Source: T. Dinter, A. Bracher, Phytooptics, AWI-IUP.

**References:**


**WP-4:** Process studies - Transport and pathways

UCAM has finished adding a tropospheric bromine chemistry scheme into UKCA-CheT, which can be used to investigate the vertical transport of VSLS bromocarbons (e.g. CHBr3, CH2Br2) from the troposphere into the stratosphere. In addition, inorganic bromine chemistry in both marine boundary layer and over sea ice in polar region is modelled. The stratospheric halogen chemistry in UKCA-CheS has been improved by unlumping the two lumped CFCs and one lumped bromine species that have been used in the previous version. Now, seven Cl-containing species (CFC-11, CFC-12, CFC-10, CFC-113, HCFC-22, MeCCl3 and MeCl) and five Br-containing species (MeBr, CH3Br2, CF2ClBr, CF3Br and CHBr3) are explicitly considered in the model allowing exploration of their lifetimes in the
stratosphere. Further improvements of the heterogeneous reactions in the stratosphere are under investigation. Apart from UKCA model development, UCAM has run trajectory calculations to help with mission planning. UCAM has also investigated halocarbon emissions in the tropical marine boundary within pTOMCAT model.

UNIVLEEDS showed that the degradation of halogen-containing very short-lived (VSL) source gases (SGs), via oxidation with OH or by photolysis, ultimately leads to the production of inorganic halogen-containing species. For bromine-containing SGs (e.g. CHBr₃, CH₂Br₂), end inorganic bromine (Brᵥ) compounds include HBr, BrO and BrONO₂ etc. UNIVLEEDS has previously shown that organic intermediates in the oxidation chain (e.g. CHBrO, CBr₂O) are significantly shorter-lived than their parent SGs and thus instantaneous production of Brᵥ following SG loss is a valid assumption in model work (Hossaini et al., 2010). This assumption may not be the case for analogous chlorine-containing SGs, chloroform (CHCl₃) and dichloromethane (CH₂Cl₂). An expected major organic product following degradation of these gases is phosgene (CCl₂O). Unlike CBr₂O, phosgene has been observed in the tropical tropopause layer (e.g. Fu et al., 2007). There is currently large uncertainty as to how much phosgene in the TTL is produced from the in-situ photochemical degradation of VSL SGs. It is currently expected some (perhaps most) of the phosgene in the TTL is transported from the stratosphere (e.g. WMO, 2010). UNIVLEEDS has developed a detailed chemical degradation mechanism for CHCl₃ and CH₂Cl₂ for use in the TOMCAT/SLIMCAT 3-D chemical transport model (CTM). Future model work will assess the role of VSLS in maintaining CCl₂O and also HCl in the TTL/lower stratosphere. UNIVLEEDS will also quantify the total supply of inorganic chlorine from VSLS (ClᵥVSLS). Estimates of ClᵥVSLS (based on observations) are currently poorly constrained at 80(40-130) ppt in the upper TTL (WMO, 2010).

CNRS has studied the chemical conditions of CHBr₃ and CH₂Br₂ degradation (including tests on reaction constants) in the low troposphere without convective transport. 3D simulations with a fine resolution (~1 km) are currently run in a tropical atmosphere. Three scenario with tropospheric conditions ranging from clean to polluted air masses are tested, essentially determined by the NOₓ, HNO₃, CO, CH₄ and O₃ levels. All the simulations take place at the same latitude and longitude with Darwin as case study (12°S, 131°E). For each condition of pollution, the influence of the possible different chemical schemes is tested, in particular the influence of the RO₂ + NO and RO₂ + CH₃(O)₂ reactions, the influence of the branching ratios in the RO₂ + HO₂ reactions and the importance of the initiated-oxidation of organic compounds (including VSLSGs) by Cl atoms. In addition the Henry’s law constants for each intermediate degradation product are explicitly taken into account using an estimation method critically reviewed.

Secondly, additional fine scale simulations were run at CNRS for CHBr₃ in convection conditions taking into account in detailed interactions of organic and inorganic product gases (PG) with liquid particles, and in particular aqueous chemistry of Bry species. It was shown that the increase of the bromine content of the TTL after convection is approximately 80% coming from CHBr₃ and 20% from product gases (PG). Convection transports efficiently the organic PGs which are, for the most abundant of them, not very soluble. Inorganic PGs are not fully scavenged if aqueous chemistry in cloud droplets is taken into account as illustrated in Figure 4-1. A publication on these results was submitted to ACP (Marécal et al. 2011).
Figure 4-1: Profile of the ratio of the bromine atoms mixing ratio in total product gases over the bromine atoms mixing ratio in CHBr₃ averaged on the simulation domain at the end of the convective event (black); same for inorganic PG over CHBr₃ (red); same for organic PG over CHBr₃ (green). (left panel) for cloud pH =5, and (right panel) if the hydrolysis of BrONO₂ and the reactions in aqueous phase of HBr, HOBr and Br₂ are not taken into account.

At UNIHB the vertical distributions of the stratospheric bromine monoxide are continuously retrieved from SCIAMACHY/ENVISAT limb observations at the Institute of Environmental Physics. The SCIAMACHY BrO time series has been prolonged until May 2011 (Figure 4-2). This longer time series makes estimations of the inter-annual variability and of the trends more reliable. The updated data set was investigated and the trend in the tropical stratosphere as well as the mid-latitudes were determined by applying a multiple linear regression method. Comparing to earlier work, several higher order variability terms are used now to reduce the standard deviation of the fitted curve to the time series of observed zonal and monthly mean volume mixing ratios. This procedure also minimises the associated uncertainty in the trend determination. Comparing to previous trend estimates (see SHIVA newsletter # 3), the estimated trends in the extratropics are higher and in the tropics lower. The former do not differ from more than 55 % from the trends in the tropics.

Figure 4-2. Time series of zonal and monthly mean BrO volume mixing ratios as obtained from SCIAMACHY limb observations and estimated trends for three zonal bands at 17 km.
References:


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

A budget analysis of the stratospheric halogen loading including a trend analysis was carried out under the lead of IASB, including input from UNIHIB, UHEI and GUF. This analysis will be made available as Deliverable Report D-5.2 by the end of June 2011. UNIHIB updated the time series of stratospheric BrO from measurements of the SCIAMACHY instrument until May 2011 and performed a revised trend analysis (Fig. 4-2). This data set was also recently used to investigate the variability of BrO in the tropical tropopause region as part of WP4 and in the investigation of stratospheric bromine trends.

IASB has updated the trend analysis of stratospheric BrO using ground-based UV-visible observations at Harestua (60°N, 11°E) till October 2010. It is found that the BrO column continues to decrease with a rate of -0.7±0.2%/year since year 2001.

GUF has performed observations of the complete bromine budget in the western Pacific during the Sonne cruise and during a balloon campaign from Teresina, Brazil in 2008. The data from the cruise and the balloon flight have been finalised and submitted for publication to Atmospheric Chemistry and Physics (Brinckmann et al., 2011; at the time of writing the paper is still awaiting an editor). Concerning the stratospheric bromine budget a contribution of VSLS of 2.25 ppt has been derived from the species CHBr2, CHBrCl, CHBrCl2, CH2BrCl and CHBr2Cl. The main contribution is from CH2Br2 and CHBrCl. Further GUF has participated in a measurement campaign from Kiruna Sweden and measured stratospheric profiles of all major chlorine containing compounds. The data evaluation is still ongoing, but a complete data set of the stratospheric chlorine partitioning will be available.

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

All planned activities within WP-6 for this period are well under way. No milestones were scheduled for this period, and the detailed report from the groups involved with Deliverable 6.1 (CTM model calculations) are provided below (work of groups AWI and IFM-Geomar partially overlaps with other work packages, and may be discussed elsewhere in this report).
UCAM (Yang/Pyle): Partner UCAM has finished adding a tropospheric bromine chemistry scheme into UKCA-CheT, which can be used to investigate the vertical transport of VSLS bromocarbons (e.g. CHBr₃, CH₂Br₂) from the troposphere into the stratosphere. In addition, inorganic bromine chemistry in both marine boundary layer and over sea ice in polar region is modelled. The stratospheric halogen chemistry in UKCA-CheS has been improved by separating the two lumped CFCs and one lumped bromine species that have been used in the previous version. Now, seven Cl-containing species (CFC-11, CFC-12, CFC-10, CFC-113, HCFC-22, MeCCl₃ and MeCl) and five Br-containing species (MeBr, CH₂Br₂, CF₂ClBr, CF₃Br and CHBr₃) are explicitly considered in the model allowing exploration of their lifetimes in the stratosphere. Further improvements of the heterogeneous reactions in the stratosphere are under investigation.

Apart from UKCA model development, UCAM has run trajectory calculations to help with mission planning. We also investigated halocarbon emissions in the tropical marine boundary within pTOMCAT model.

UNIVLEEDS (Hossaini/Chipperfield): We have previously shown the TOMCAT/SLIMCAT 3-D chemical transport model (CTM) is able to simulate the chemistry and transport of very short-lived (VSL) source gases (SGs) and product gases (PGs) (e.g. Hossaini et al., 2010). Comparison of modelled and observed profiles of CHBr₃ and CH₂Br₂ in the tropical tropopause layer (TTL) show reasonable agreement. The modelled contribution from these species to stratospheric inorganic bromine (Brᵥ) was found to be ~2.4 ppt.

We have made two improvements to the model set up described in Hossaini et al. (2010). Firstly, we now model the wet deposition (wash out) of soluble Brᵥ species (e.g. HBr) in both large-scale and convective precipitation. The previously employed approach of assuming a uniform tropospheric Brᵥ lifetime of 10 days likely overestimated washout and thus underestimated the product gas injection (PGI) pathway (e.g. Aschmann et al., 2011). Secondly, we now include an option for offline convection within the CTM. This approach uses archived updraft and downdraft convective mass fluxes from the ECMWF Era-Interim reanalysis interpolated on to the model grid (e.g. Feng et al., 2011). As model convection is an uncertainty, it is useful to have this new approach available alongside the standard online Tiedtke (1989) mass flux scheme previously implemented in the model (e.g. Stockwell and Chipperfield, 1998).

Figure 6.1 shows the annual mean mixing ratio of an idealised tracer with a 6 hour lifetime at the cold point tropopause (CPT, ~17 km) for A.) offline convection and B.) online convection. The offline approach transports more tracer to the upper TTL / lower stratosphere due to deeper tropical convection and stronger convective mass fluxes in the lower atmosphere. For the relatively short-lived VSLS (e.g. CH₂I), the choice of convection scheme is clearly important. For VSLS such as CH₂Br₂, their local lifetime in the TTL can be large (>1 year, Hossaini et al., 2010) and thus the transport of these species to the stratosphere is less sensitive to model convection.

We have also now extended our model set up to include all known naturally occurring bromine-containing VSLS SGs (e.g. CHBr₂Cl, CH₂BrCl) and also anthropogenic species (e.g. C₂H₅Br, CH₂BrCH₂Br). Including these additional minor gases, our modelled contribution of very short-lived species (VSLS) to stratospheric Brᵥ (Brᵥ VSLS) is now 5.2-5.5 ppt – consistent with estimates derived from balloon-borne measurements (Dorf et al., 2008). Of this total, approximately 70% comes from the naturally-emitted species CHBr₃ and CH₂Br₂. The individual contribution from minor VSLS is small but their total
accounts for ~30% of the supply (~1.5 ppt). These species should therefore be included in model estimates of \( Br_y^{\text{VLS}} \) (Hossaini et al., 2011, in prep).

In addition to the above, we have also begun to add a treatment of VLS to the UKCA chemistry-climate model (CCM, e.g. Morgenstern et al., 2009). This work is still preliminary, however the model seems to perform well in reproducing observed profiles of \( CH_2Br_2 \). Figure 6-2 shows a tropical profile of \( CH_2Br_2 \) from UKCA, TOMCAT with online convection (labelled s_diag) and TOMCAT with offline convection (labelled s_archived) versus observations from the 2007 NASA TC4 campaign. The UKCA model exhibits slower transport through the TTL region than the p-coordinate CTM and appears to simulate the TTL distribution of \( CH_2Br_2 \) well. In future work, UKCA will be used to assess the impact of VLS on stratospheric ozone for present day and future scenarios.

**Figure 6-1:** Annual mean mixing ratio of idealised tracer (6 hr lifetime) at the cold point tropopause for (a) CTM with offline ECMWF convection and (b) CTM with online Tiedtke scheme. (Hossaini et al., 2011, in prep).
Figure 6-2: Modelled profiles of CH$_2$Br$_2$ versus observations from the 2007 NASA TC4 campaign.

References


