



The first SHIVA newsletter reports on the activities performed within the first half year (July 1 to Dec. 31, 2010) of the EU project SHIVA (*Stratospheric ozone: Halogen Impacts in a Varying Atmosphere*, grant number 226224). It is intended to provide relevant information on the project's progress to all consortium members, the advisory committee, our cooperation partners, a wider scientific audience interested in our work, and finally the funding agency. In that respect we hope that this and future newsletters may help to stimulate the necessary scientific discussion among the addressees in order to update our scientific objectives, to identify potential problems and finally to address all organizational issues relevant for SHIVA.

With our bests regards,

Marcel Dorf, Klaus Pfeilsticker, Karoline Thomas (Administration), and Tilman Hüneke (Webpage/Wiki)

In January 2010

Report on activities within the individual WPs

WP-1: Management

Summary of the main management and administrative activities:

Meetings:

- Shortly after the official start of the project on July 1, 2009, the kick-off meeting was organized and held at Heidelberg, Germany, on July 6./7., 2009. The contents and time-lines of the individual work packages were revised and action items were identified. The detailed minutes of the meeting can be downloaded from the SHIVA wiki.
- A Steering committee and campaign planning meeting will be held at Cambridge on March 25./26., 2010.
- The date for the next annual meeting was set to July 5./6. (Monday / Tuesday), 2010. The meeting will take place in Paris.

WWW page:

The SHIVA webpage (<http://shiva.iup.uni-heidelberg.de/>) and SHIVA Wiki page (<http://shiva.iup.uni-heidelberg.de/wiki/>) were set up and are maintained continuously. Unfortunately the **Wiki page** has been hardly used by any of the partners, although it is a very useful tool to share documents, contact information, publications, comments Furthermore, it should be used as a discussion forum, e.g. for preliminary work, or preliminary data analysis....

Publications:

- A **newsletter** has been written and submitted to SPARC, which will be published in early 2010, see <http://www.atmosp.physics.utoronto.ca/SPARC/Newsletters.html> .
- Additionally a **campaign white book** was compiled and is regularly updated. The white book contains important information and the latest knowledge necessary for our campaign planning. In particular, some work has been spent on collecting and analyzing available meteorological information and in model simulations (FLEXPART see WP 4) in order to identify the best season and location for our field studies. Moreover the white book already contains a growing body of logistic information relevant for the campaign in the Western Pacific. The most recent version can be downloaded from the SHIVA wiki.

Contacts to external partner & bodies:

Novel contact has been established to relevant cooperation partners in the countries surrounding the Warm Pool.

Administration:

The CA (Consortium Agreement) was signed by all participants. Therefore, the pre-financing (about 61.7% of the total EC-contribution) was distributed to the partners by the coordinator with the start of the project.

Reminder:

- a) Unfortunately the **data protocol** has still not been signed by all participants. It can be downloaded from the Wiki. It also contains information about how to acknowledge SHIVA in publications: **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. In case that other agency supported the work, they must also be acknowledged.
- b) Each partner is responsible to administrate a **timesheet** for each employee working within SHIVA. An exemplary timesheet, of the University of Heidelberg can be downloaded from the SHIVA wiki-page.

WP-2:

Measurements

1. Fieldwork Activities

A number of SHIVA-related fieldwork activities have taken place during the first 6 months of the project. These include a dedicated cruise of the German research ship *RV Sonne* in the western Pacific, and the analysis of air samples collected during a 2nd cruise around the coast of Borneo, and from an aircraft detachment to Cape Verde.

1.1. Ship cruise: TransBrom Sonne (IFM-GEOMAR, AWI, GUF)

From October 9 to 25, 2009 the IFM-GEOMAR (Kiel, Germany) conducted a cruise with the RV Sonne in the tropical western Pacific to investigate trace gas emissions on a 4030 nm (7,500 km) and 60

degrees latitude covering transit between Tomakomai (Japan, 42°35,4'N/ 141°37,5'E) and Townsville (Australia, 19°06,6'S/ 146°50,5'E). The ships cruise crossed various biogeochemical regimes of the northern and southern western Pacific Ocean, which differ in seawater properties, currents, productivity and atmospheric dynamics (e.g. Kuroshio Front, Northern Pacific Gyre, Pacific warm pool and Coral Seas). The SONNE expedition, officially titled TransBrom-Sonne, has been funded by the Federal Ministry for Education and Research (BMBF) and is part of the "Wissenschaftsgemeinschaft-Leibniz" project TransBrom (www.ifm-geomar.de/~transbrom) lead by Prof. Dr. Kirstin Krüger (IFM-GEOMAR). Its results also contribute to SHIVA. The first measurements of a suite of halogenated very short lived species (VSLs) in the surface waters of the western Pacific were conducted and a variety of other chemical and physical parameters within the surface waters as well as between the atmospheric boundary layer and the stratosphere, with the purpose of analysing different biogeochemical regimes and their stratospheric contribution.

Ten halocarbons, in both seawater and air, were measured *in situ* using gas chromatography – mass spectrometry (GC-MS). More than 70 anthropogenic and natural trace gases, isotopes and aerosols within the marine boundary layer will be analyzed in air samples collected for partners from the Universities of Hamburg, Frankfurt, Norwich and Utrecht as well as the 'Rosenstiel School of Marine and Atmospheric Sciences' in Miami following the cruise. Biological sampling included parameters of organic carbon and nitrogen as well as pigments, cell sizes, the amount of small cells and the composition and activity of the phytoplankton. Other marine trace gases (inc. N₂O, DMS, CO₂, O₂) were also measured and possible relationships between these compounds and the VSLs will be investigated. Atmospheric profiles of temperature, humidity and selected trace gases (e.g. ozone, hydrogen, nitric oxide, bromine oxide, carbon monoxide and organic photo oxidation products) were examined using optical techniques and by launches of research balloons. Satellite measurements of phytoplankton groups, obtained by special retrieval methods from the SCIAMACHY and GOME-2 satellite instruments, and of total phytoplankton biomass from SeaWiFS/MODIS/MERIS gave further information about biogeochemical conditions during the cruise (see below).

1.2. Atmospheric measurements in the tropics (UEA)

In collaboration with scientists from the Universities of Malaya and Cambridge, 30 air samples were collected during a voyage of a Malaysian naval vessel in the coastal waters of peninsular Malaysia and northern Borneo in June 2009. These have been analysed at UEA by GC-MS for a range of halocarbons, including many VSLs. Additional air samples, collected during a short detachment of the UK FAAM aircraft to Cape Verde in September 2009, have been made available to SHIVA by the University of York. Approximately 100 marine boundary layer samples have been analysed for the same species.

1.3. Laboratory studies (UEA)

Initial steps are being taken to investigate emissions of halocarbons and other reactive gases from seaweeds, including tropical and farmed species. Wild collected samples and axenic cultures are being examined, initially to develop *in vitro* laboratory cultivation procedures and analytical protocols. These presently include mostly temperate species, but one tropical one (*Asparagopsis* sp.; *falkenbergia* stage) is being grown in the laboratory. The latter is reportedly one of the highest known emitters of brominated compounds. Experiments will include measuring the emissions rate response of multiple gases to changing environmental conditions such as irradiance, temperature, salinity, air exposure, desiccation, wounding, grazing, etc. Once successfully developed it is intended

to extend this to tropical wild and farmed seaweed species, through links with the University of Malaya, and to examine the effect on emissions from both intensive aquaculture and post-harvest processing.

1.4. Satellite observations (AWI)

Since there is no direct relation between phytoplankton total biomass and VLSL emissions in the ocean, it is necessary to investigate if certain phytoplankton functional groups (PFTs) under certain environmental conditions are responsible for VLSL emissions. To study the direct relationship between PFTs and VLSL emissions, during the recent TransBrom cruise in addition to the chemical and meteorological measurements described above, the composition and bio-optical characteristics of phytoplankton were also investigated. During the cruise satellite images of ESA's GlobColour Chlorophyll-a (case 1 water) product were provided to the ship on a daily basis to inform on the phytoplankton total biomass distributions in the sampled waters. To get reasonable coverage, because of excluding measurements which were contaminated by clouds and glint effects, the data were averaged over 5 days. Within the current reporting period all on board phytoplankton measurements (filtration of water samples, absorption measurements via PSICAM) and post-cruise lab measurements (HPLC, PABS, fluorometric, POC analyses) have been completed. The data analysis will be done within the next reporting period. Results will be used to derive relationships between PFTs and VLSL emissions and furthermore, the in situ PFT data will be used to validate the PFT satellite maps derived using the PhytoDOAS method of Bracher et al. (2009). The global PFT satellite maps and the derived parameterization of PFT composition and VLSL emission are necessary input for the work in WP3 to construct a global VLSL emission scenario.

2. Future fieldwork activities

2.1 Aircraft Campaign

The SHIVA field activities will largely depend on aircraft-borne observations of relevant atmospheric parameters (VLSL, product gases, transport tracers,...) planned in the Western Pacific during the convective season (Jan. to March) (see SHIVA's DoW and white book). For this purpose it has been planned to deploy the novel DLR-HALO aircraft into this region in early 2011, or 2012. However, the final preparation of the HALO aircraft has been severely delayed due to certification issues related to modifications to the aircraft itself. Mainly these are (a) novel sensors for the monitoring of basic atmospheric parameters (e.g., basic sensors for T, P, wind, humidity, ..), and (b) dedicated gas inlets, wing pods, and a belly pod. The expected final approval from the LBA (LuftfahrtBundesAmt – German agency for aviation security) for the basic sensors in late 2009 was not obtained. Presently the HALO aircraft is with the manufacturer for routine checks and it is expected back in Germany by late January 2010. Further information on the status and possible schedules of HALO are expected to become available by the next HALO WLA (Wissenschaftlicher LenkungsAusschuß – scientific steering committee for the usage of HALO) meeting (Feb. 10, 2010).

In the meantime a large number of staff within the DLR, MBL (MusterprüfLeitstelle – agency for certification issues) and LBA are working to develop procedures for flight certification of all parts/modifications relevant to render HALO into a research aircraft. It is anticipated that this process will take most of 2010. Since all scientific instrumentation used within the various demonstrations will also need flight certification, it can be expected that the first HALO flight carrying scientific instrumentation will not take place earlier than late 2010. In conclusion, using the HALO aircraft for a

Western Pacific campaign in early 2011 appears not to be a realistic option, and therefore other options are being considered.

The first option still depends on using the HALO aircraft, but would postpone the Western Pacific campaign until early 2012. This decision will allow us to wait until (a) further information and a firmer schedule for the usage of HALO will be available, and (b) the final decision is made for an additional requested national contribution in support of the Western Pacific campaign (e.g. additional funding for 45 hours, certification and campaign consumables requested within DFG SPP-1294/PF-384/7-1). With respect to the recent increase of costs for certification work related to HALO, it appears questionable as to whether we would be able to support a Western Pacific campaign purely from SHIVA funds, and therefore a national contribution to our activities is crucial. For the latter, the evaluation of the proposal will be on March 10 and 11, with a decision expected by March 15, 2010.

The second option builds on using the ENVISCOPE LearJet instead of HALO. This option would offer the advantage of being much cheaper and would allow a greater flexibility for scheduling the campaign. On the downside there would be a smaller payload capacity and a slightly lower maximum ceiling altitude as compared to HALO (see Table 1).

A third option is the use of the DLR Falcon aircraft (the precursor research jet of HALO). The deployment costs of the Falcon would be similar to those of the Learjet, and the payload, in terms of weight and installed rack volume, is slightly larger. The DLR-Institute of Atmospheric Physics has requested to keep the Falcon in operation until 2013, and a decision is expected by end of Feb. 2010.

It has been agreed with the EU that a final decision on which aircraft will be used for the Western Pacific campaign will need to be made in the first half of 2010, in order to be still able to meet SHIVA's milestones and deliverables within a reasonable timeframe. In appreciation of these matters, we should look forward to finally decide on the aircraft issue by the steering committee meeting to be held in Cambridge on March 25 and 26th, 2010.

Table 1: Aircraft Options

	Endurance (hours)	Payload (kg)	Range (km)	Air speed (m/s)	Max ceiling (ft)
HALO	11	max 3000	8000	235	51000
Learjet	4.5	1200	3000	236	45000
Falcon	4.5	1500	3500	240	42 000

2.2. Aircraft instruments

Several SHIVA partners (GUF, UNIVLEEDS, CNRS, UHEI, DLR) are developing instruments for installation on the HALO aircraft and good progress is being made. As with all HALO scientific instrumentation these have yet to be fully certified for aircraft use, although no problems are expected. Partners are also working on contingency plans such as refitting the instruments for

alternative aircraft. If the Learjet or Falcon options are chosen, there will have to be difficult decisions taken as the payloads of these aircraft are significantly less than HALO.

2.3. Future ship measurements

In June 2010 the IFM-GEOMAR will conduct another cruise with the RV Poseidon (31 May: Las Palmas – 18 June Las Palmas (Canary Islands) - 24 June Vigo (Portugal)) to the Mauritanian upwelling in context of the German joint project SOPRAN (Surface Ocean Processes in the ANthropocene) funded by the BMBF, where short-lived halocarbons will be measured in seawater and air, with a focus on the diurnal variation of possible fluxes in coastal areas, influenced by local emissions and land-sea breeze fluctuations. Therefore some daily stations in front of the coast are planned with frequent surface water and atmospheric sampling and, in addition, one or two days of atmospheric diurnal sampling may take place at Cape Verde and on Gran Canary in parallel.

Regular sea water sampling at Cape Verde is envisaged for 2011, since IFM-GEOMAR is currently constructing a measurement container hosting a GC-MS instrument for measuring halocarbons in seawater. This container is crucial for performing measurements of biogenic VSLS from ocean waters, as the samples have to be measured under controlled conditions immediately after collection. Regular measurements in Malaysia, in cooperation with the universities of Cambridge and Malaya, will be discussed at the next steering committee meeting.

For the joint SHIVA aircraft and ship campaign there are various possible options for cruises in the western Pacific, whether with the German research vessel Sonne or with the Taiwanese ship RV/OR1 in spring 2012. In summer 2011 the Sonne will be on a transit through Indonesian waters, which would provide an excellent opportunity for sampling in a region which is unexplored, difficult to access and potentially very important as a possible hot spot for VSLS emissions.

WP-3: Emission inventories - Present and future scenarios

Compilation of existing air-and seawater measurements of halogenated hydrocarbons, especially very short lived halogenated compounds (VSLS) into the project „HalOcat“, initiated in May 2009, started in SHIVA. The project aims mainly at the calculation of oceanic VSLS emissions. 79 datasets collected during research cruises, aircraft missions as well as coastal observations have already been submitted to <http://halocat.ifm-geomar.de> (accessible only for members). An overview of the current data base is given in the following.

The majority of the submitted data consists of atmospheric data (61 out of 79), 43 are taken from land based stations (mostly coastal), 7 from airborne missions and 11 collected during diverse research cruises, respectively.

Atmospheric compounds

The land based observations mainly took place in the US (Niwt Ridge, Park Falls, Trinidad Head, Barrow, Kape Kumukahi, Harvard Forest, Mauna Loa, Palmer Station, Tutuila). In addition, coastal observations were performed in Ireland (Mace Head), Barbados (Ragged Point), Australia (Cape Grim), Canada (Alert), Argentina (Tierra del Fuego), Italy (Lampedusa Island, Monte Cimone), American Samoa (Cape Motatula), Antarctica (South Pole) as well as Denmark (Summit). Most of the

above listed locations are sustained by the Global Monitoring Division (GMD, formerly CMDL) of the National Oceanic and Atmospheric Administration (NOAA), the Advanced Global Atmospheric Gases Experiment (AGAGE, i.e. Ragged Point, Trinidad Head, Mace Head and Cape Matatula) and the National Agency for New Technology, Energy, and Environment (ENEA, Lampedusa Island, Italy). Reported land based observations of halogenated compounds have been carried out since 1992 (i.e. Alert, Canada) until 2009. Some observations lasted only for one year (Lampedusa Island, Italy), several though for 16 years in total (e.g. Alert Canada). Some locations might still deliver data to date. Coastal observations included the following compounds: CH₃Cl, CHCl₃, CH₂Cl₂, CH₃Br, C₂Cl₄, C₂HCl₃ and CH₃I. Most data origin from the South Pole, Antarctica (1993-2009: CH₃Cl and CH₃Br, 55008 values in total), Monte Cimone, Italy (2000-2009: CH₃I and C₂Cl₄, 21752 values in total) as well as Niwot Ridge, USA (1993-2009, CH₂Cl₂, CH₃Br, CH₃Cl: 21382 values in total), while from Summit, Denmark and Ragged Point, Barbados only about 120 values are available.

Aircraft campaign data "ARCTAS", "INTEX A", "INTEX B" and "TRACE-P", carried out by NOAA, cover a wide range of latitudes and longitudes. They cover measuring periods of 3-6 months and took place during 2001 to 2008. Those airborne missions include a variety of compound measurements, i.e. CH₃I, CH₃Br, CHBr₃, CH₂Br₂, CH₃Cl, CHCl₃, CH₂Cl₂, C₂HCl₃, C₂Cl₄, CHBr₂Cl, CHBrCl₂, C₂H₅I. Total measured values: 22022-48057, respectively (depending on mission), with data often been collected every minute and partly covering areas of extraordinary high altitudes.

Air samples were also taken during the following research cruises: M55, P320-1, BLAST 1-3, GAS-EX 98, CLIVAR 01, PHASE 1-04, M60-5, OOMPH 2007 MD 158, MAP cruise as well as GOMECC. Measured compounds include CH₃I, CH₃Br, CHBr₃, CH₂Br₂, C₂HCl₃, CH₃Cl, CHCl₃, C₂Cl₄, CHBr₂Cl, CH₂Cl₂. GAS-EX 98, CLIVAR '01 and PHASE 1-04 comprise the most available data (6318, 5614 and 4457, respectively).

Of the atmospheric compounds of interest among the HalOcaT initiative, most data (by far) are available of CH₃Cl (107800), followed by CH₃Br (35414) and CHCl₃, CH₂Cl₂, C₂Cl₄ and CH₃I (about 30000 each). Bromoform (CHBr₃) values exist to around 19000.

Oceanic compounds

Measurements of dissolved compounds in ocean waters are also available from 19 research cruises in all major ocean basins: Sa Agulhas, M55, M60-5, P320-1, BLAST1-3, GAS-Ex 98, RB 99-06, CLIVAR 01, PHASE 1-04, DISCO, OOMPH, MAP CRUISE, ASCOE, ANT 18 ½, ADOX, NSP and GOMECC. Measured compounds during the cruises were: CHBr₃, CH₂Br₂, CHCl₃, CH₃I, C₂HCl₃, C₂Cl₄, CH₂I₂, CHBr₂Cl, CHBrCl₂, CH₃Br, CH₂I₂, CH₂I₂, CH₃NO₃, C₂H₅NO₃. Most values are provided from the NOAA-campaigns PHASE 1-04, CLIVAR 01 and BLAST 3 (4480, 3906 as well as 3651, respectively), while only a few hundred come from cruise missions like ASCOE, MAP CRUISE and P 320-1 (63, 100, 230, respectively), which is due to different analysis techniques that have been used which will need careful evaluation.

The distribution of collected data is different to the one of air given above. Total numbers of currently available data range from around 50 (CH₂I₂, C₂H₃Cl₃, CH₃NO₃ and C₂H₅NO₃) up to almost 5000 (CHBr₃, CH₃I, CH₂Br₂).

Miscellaneous

Data have either been sent or are provided online (<http://agage.eas.gatech.edu/data.htm>, <http://gaw.kishou.go.jp>, <http://doi.pangaea.de>, <ftp://ftp.cmdl.noaa.gov/hats/ocean>, http://www-gte.larc.nasa.gov/trace/TP_dat_alt.htm, www.bodc.ac.uk).

Despite several submitted datasets, the overall contribution has been rather sparse to date. All information concerning a contribution to HalOcat can still be found online (<http://halocat.ifm-geomar.de>). Submitted datasets can be downloaded and examined by members of the HalOcat-initiative.

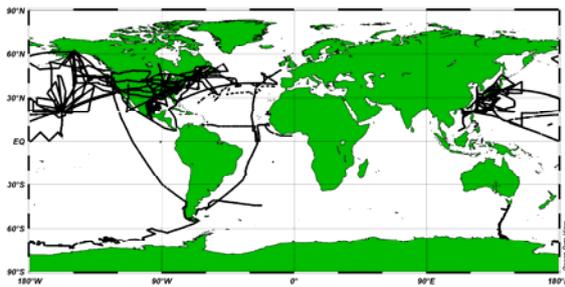


Figure 1: HalOcat airborne data.

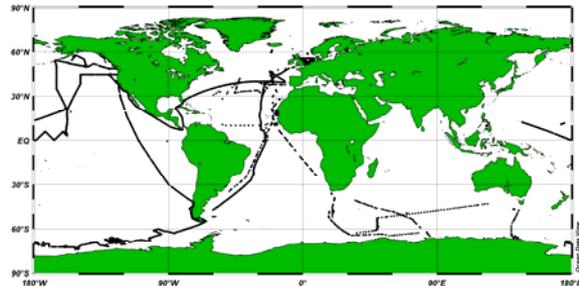


Figure 2: HalOcat ocean data.

Locations of airborne and ocean data are shown in Figures 1 and 2. Land-based observations are distributed worldwide, while cruise tracks cover all major ocean basins (Atlantic-North : 9, South : 4) as well as Pacific -North: 3, South: 4), despite the Indian Ocean, which only contributes with one dataset). Apart from the Indian Ocean, there have been a variety of research cruises in the

At this point: Many thanks to all scientists having contributed so far! Here a list of active participants and corresponding data values: Elkins (79044), Carpenter (291), Butler (7120), Smith (58), Williams (233), Quack (716), Atlas (827), Reeves (63), Montzka (2611), Turner (847), Yvon-Lewis (560), Liss (96), Maione (12445), Blake (14239), Abrahamsson (78), Artuso (15) and Prinn (1217).

Outlook

Apart from contributions to date, there have been several data promises for the upcoming months. Concerning this issue, individuals are currently reminded by Birgit Quack and Tom Bell (key contacts within the HalOcat project) of sending suitable data in order to provide a better basis for upcoming flux calculations starting in the next months.

Astrid Bracher and Tilman Dinter from AWI-Bremerhaven will in the next months construct global phytoplankton functional group (PFT) satellite maps, with emphasis on regions of interest, where we will try to derive parameterization of PFT composition and VLS emission to construct VLS emission scenarios of large regional and temporal extensions.

WP-4: Process studies - Transport and pathways

WP4 work for this first period was on the planning of the aircraft campaign (contributions to the white book), on the development of tools necessary for forecasting/analysis during and after the aircraft campaign and on first modelling studies.

NILU has made an atmospheric transport simulation, using emission data provided by B. Quack, for tracers of different lifetime and for one winter/spring season. The results of this simulation, provided to project partners through an interactive tool, helped to decide on the best region and time period for the aircraft campaign. CNRS and UCAM also provided a contribution to the aircraft planning document based on satellite meteorological data analyses.

UCAM has started development of a suite of tools to study transport of VSLs into the stratosphere from trajectory calculations. These tools include a simple cloud box model, and integration of observations of brightness temperatures with output from the trajectory module. Model runs are currently performed and analysed. CNRS has started including halogen chemistry (not VSLs yet) in the C-CATT-BRAMS mesoscale model. In parallel, UnivLEEDS has developed a degradation scheme for CHBr₃ and CH₂Br₂ which have been used in TOMCAT/SLIMCAT CTM in WP6 simulations (Hossiani et al. ACP 2010). This scheme will also be included in the C-CATT-BRAMS model.

UNIHB has conducted studies on the transport of VSLs into the tropical tropopause region. It is based on Chemistry Transport Model simulations forced by ECMWF convective updraft mass-fluxes and by diabatic heating rates for large-scale vertical velocities. The results are published in Aschmann et al. (2009).

AWI has worked on further developing and validating the new lagrangian model of transport and chemistry ATLAS. The transport scheme is now fully validated and published (Wohltmann and Rex 2009). The chemistry scheme is now also fully functional and under validation. A number of seasonal global runs of the overall system have been carried out for validation and a publication of the overall system including its validation is in preparation. Work on implementing VSLs chemistry has started.

A key parameter for VSLs chemistry in the tropical troposphere and tropopause region is the oxidizing capacity of the air. To better constrain this parameter for the modeling work in WP4 AWI has carried out ozonesonde measurements in the tropical West Pacific as part of the SHIVA-TRANSBROM campaign with RV SONNE. This vast area has so far been a blind spot in the global ozonesonde observation coverage and the oxidizing capacity of the troposphere in this region is a major uncertainty. Near zero ozone concentrations have been observed consistently throughout the troposphere over vast regions in the inner tropics of the West Pacific. Consistent with a small number of individual previous observations from the central Pacific ozone below or close to the detection limit of the sonde was found in the boundary layer and the tropopause layer in all our tropical observations. But in most observations in the inner tropics of the West Pacific these extremely low values extended throughout the free troposphere (Figure 3). These observations suggest an unusually low oxidizing capacity of the troposphere there. The background and implication of this will be investigated in more detail.

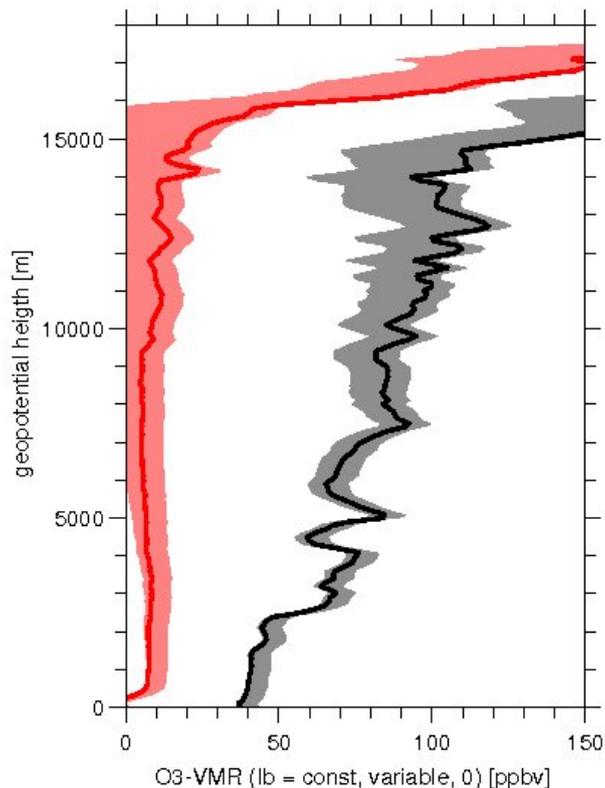


Figure 3: Normal (black, 11 Oct. 2009, ~33° N) and unusually low (red, 16 Oct. 2009, ~11° N) tropospheric ozone mixing ratio profile measurements during TRANSBROM. The shaded areas indicate uncertainty due to background current subtraction and uncertainties in its decay timescale. The upper envelop of the uncertainty ranges assumes immediate complete falloff of the background current and is a robust upper limit for the ozone mixing ratios. Ozone is below the detection limit of the sonde where the lower envelop of the uncertainty range (assumption: constant background current) overlaps with zero.

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

For WP-5 the analysis of stratospheric halogen trends from past measurements is proceeding as planned. According to the DoW no milestones have been reached and no deliverables have been provided at this stage.

Bromine

The analysis of the stratospheric bromine trend from past DOAS balloon observations by University of Heidelberg is updated using the most recent balloon flight at Kiruna, Sweden, on September 7./8., 2009 (see Figure 4).

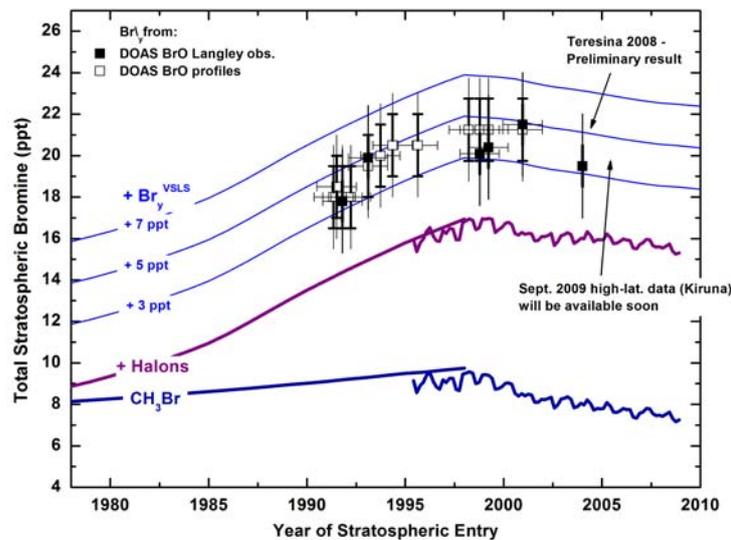


Figure 4: Measured trends for bromine (ppt) in the near-surface troposphere (lines) and stratosphere (squares). Update of Dorf et al. (2006).

The analysis of stratospheric BrO from the SCIAMACHY limb satellite observations is continued by University of Bremen and validated against ground-based observations in collaboration with BIRA. In particular, a trend analysis has been performed of stratospheric BrO columns retrieved from SCIAMACHY limb (version 3.2 of the IUP-Bremen scientific product) and ground-based UV-visible measurements. We focused on SCIAMACHY limb observations collocated with three NDACC (Network for the Detection of Atmospheric Composition Change) stations 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°N). The periods covered by the ground-based observations are 1998-2008 for Harestua and OHP, and 1995-2005 for Lauder. The SCIAMACHY data set extends from 2002 to 2008. Before 2001, a positive trend of about +2%/year is inferred over the three stations from ground-based UV-visible observations while after 2001, a negative trend of about -1%/year is 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 (methyl bromide and halons) observed at the Earth's surface since 1998. These findings provide therefore strong evidences that the effects of the Montreal Protocol restrictions on brominated substances have now reached the stratosphere.

Iodine

Results of balloon-borne solar occultation spectra (UHEI) of IO and OIO in the tropical UT/LS are reported by Butz et al. (2009). The observations were performed during 2 balloon flights in 2005 and 2008, in northeastern Brazil. Table 2 summarizes the upper limits of IO and OIO for various tangent heights. Furthermore, a photochemical model is used to derive the corresponding upper limits for the total gaseous inorganic iodine burden (I_y), which yields 0.17 to 0.35 (+0.20/-0.08) ppt in the tropical upper troposphere (16.5 km to 13.5 km) and 0.09 to 0.16 (+0.10/-0.04) ppt in the tropical lower stratosphere (21.0 km to 16.5 km). The findings of Butz et al. (2009) at low-latitudes complement the high and mid-latitude observations from Bösch et al. (2003), which were performed with the same instrumentation. Bösch et al. (2003) reported on an upper limit of I_y of 0.1 ppt.

Table 2: IO and OIO upper limits (in ppt)^a at several tangent heights (in km) inferred from LPMA/DOAS solar occultation observations conducted at Teresina (5.1° S, 42.9° W), Brazil. Adopted from Butz et al. (2009).

Date	Geophysical condition	IO upper limit/ppt					OIO upper limit/ppt				
		30km	24km	20km	16.5 km	13.5km	30km	24km	20km	16.5 km	13.5 km
17 June 2005	tropics, sunset	0.57	0.19	0.12	0.19	0.14	0.61	0.30	0.14	0.07	0.05
27 June 2008	tropics, sunrise	0.31	0.14	0.09	0.08	–	0.52	0.40	0.21	0.10	–
27 June 2008	tropics, sunset	–	–	0.04	0.09	0.07	–	–	0.06	0.05	0.06

^aAbsorber volume mixing ratios are estimated from slant column densities under the assumption that the absorber volume mixing ratio is constant along individual lines-of-sight.

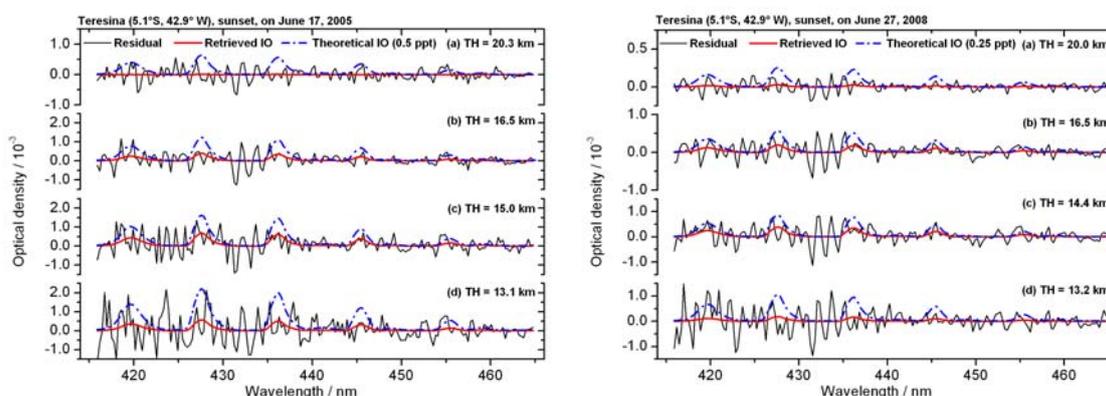


Figure 5: Residual optical density (black thin solid), retrieved IO optical density (red bold solid), and theoretical IO optical density (blue dash-dotted) in the IO retrieval window for sunset on June 17, 2005, (left panel) and sunset, on June 27, 2008, (right panel) at the indicated tangent heights (TH) for subpanels a to d. The theoretical IO optical density is calculated assuming 0.5 ppt (left panel) and 0.25 ppt (right panel) IO along the lines-of-sight. The tropopause is at roughly 16.5 km. Adopted from Butz et al. (2009).

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

All groups with funding and activities planned for this period have started their projects.

AWI (Rex/Wohltmann): AWI have continued model development for the Chemical Transport Model “ATLAS”, and have implemented the modules for transport and mixing (published in Wohltmann and Rex, 2009). Planned activities for next period include a tropospheric chemistry module, and, in collaboration with IFM, a convection module.

IFM (Krueger/Tegtmeier): No tasks/activities for this period.

U Bremen (Sinnhuber): U Bremen have carried out modeling studies with a Chemical Transport model in conjunction with archived convective updraft mass fluxes from ECMWF (published in Aschmann et al., 2009). Calculations focus on brominated compounds, in particular bromoform (CHBr_3), with simplified distributions in the boundary layer.

U Cambridge (Pyle): No tasks/activities for this period.

U Leeds: U LEEDS have used the TOMCAT/SLIMCAT off-line 3-D chemical transport model to study the transport of CHBr_3 and CH_2Br_2 through the TTL. Several model experiments have been performed to investigate the impact of model formulation on VLS transport and to obtain an estimate of source gas injection (SGI) and product gas injection (PGI) pathways. In order to quantify PGI a detailed scheme for CHBr_3 and CH_2Br_2 degradation has been included in the CTM (this scheme has also been supplied to CNRS Orleans as part of WP4). Results from these studies have been published in Hossaini et al. (2010). Briefly, the CTM results show that (i) organic degradation products of CHBr_3 and CH_2Br_2 are themselves quite short-lived with low predicted abundances, (ii) SGI and transport of inorganic Br_y are the most important transport pathways to the stratosphere and (iii) running the model with isentropic levels in the TTL ('SLIMCAT' mode) tends to improve tracer profile comparisons with observations compared to the pressure level model. On this last point, the p-level model, with vertical motion from analysed winds, tends to overestimate vertical transport in the TTL.

Publications directly related to SHIVA:

Aschmann, J., B.-M. Sinnhuber, E. L. Atlas, and S. M. Schauffler, Modeling the transport of very short-lived substances into the tropical upper troposphere and lower stratosphere, *Atmos. Chem. Phys.*, 9, 9237-9247, 2009.

Butz, A. H. Bosch, C. Camy-Peyret,, M. P. Chipperfield, M. Dorf, S. Kreygy, L. Kritten, C. Prados-Roman, J. Schwärzle, and K. Pfeilsticker, Constraints on inorganic gaseous iodine in the tropical upper troposphere and stratosphere inferred from balloon-borne solar occultation observations, *Atmos. Chem. Phys.*, 9, 14645–14681, 2009.

Bracher A. Vountas M., Dinter T., Burrows J.P., Röttgers R., Peeken I. : Observation of cyanobacteria and diatoms from space using PhytoDOAS on satellite sensor SCIAMACHY data. *Biogeosciences* 6:751-764, 2009.

Hossaini, R., M.P. Chipperfield, B.M. Monge-Sanz, N.A.D. Richards, E. Atlas, D.R. Blake, Bromoform and Dibromomethane in the Tropics: A 3D Model Study of Chemistry and Transport, *Atmos. Chem. Phys.*, vol 10, (in press), 2010.

Pfeilsticker et al., The EU project SHIVA (Stratospheric ozone: Halogen Impacts in a Varying Atmosphere), SPARC newsletters, 34, (in press), 2010.

Pfeilsticker et al., The SHIVA campaign white book, update see <http://shiva.iup.uni-heidelberg.de/wiki/>

Wohltmann, I. and M. Rex, The Lagrangian chemistry and transport model ATLAS: validation of advective transport and mixing, *Geosci. Model Dev.*, 2, 153-173, 2009.