Halogens in the Troposphere (HitT) is a project aimed at studying the sources, transformations and consequences of reactive halogen compounds in the troposphere. IGAC has endorsed HitT as an official task, which implies that projects and priorities for 3-year time periods need to be defined and that we are obliged to send annual reports to IGAC. SOLAS had already endorsed HitT in 2006 but has no strict requirements for reporting etc., however we plan to submit the reports to the SOLAS SSC as well. The goals for the implementation workshop in Vienna were to bring scientists together who plan research on halogen species in the troposphere, i.e. campaigns, laboratory experiments and/or model exercises in the next 3 years and beyond. In other words the goal was to “get HitT going”.

The two main topics of the workshop were (i) update on currently ongoing and planned HitT related projects, (ii) ideas for future work in phases 1 and 2 of the HitT task. Since the main foci of phase 1 are the polar boundary and the marine boundary layer many of these projects are part of the International Polar Year (IPY). Also, many projects are part of national Surface Ocean and Lower Atmosphere Studies (SOLAS) programmes. The workshop was held in Vienna, Austria, on April 21, 2007, it was funded by IGAC and attended by 31 scientists (see Appendix).

1 Ongoing and planned projects

The following list gives an – incomplete – overview of halogen-related projects that are in various stages of planning, implementation and completion. The list is somewhat biased to the work of the people present at the workshop. In many of these projects participation of additional scientists is still possible and welcome, therefore we have added the names of contact persons.

1.1 Field studies

1.1.1 Polar boundary layer

Many of the projects in this area are part of IPY. AICI (Air Ice Chemical Interactions) is an IGAC task coordinated by Eric Wolff and Paul Shepson and OASIS (Ocean-Atmosphere-Sea Ice-Snowpack) is an OASIS project coordinated by Harry Beine that both act as a platform for related field, laboratory and model studies. Many of the projects listed below are also endorsed by AICI and/or OASIS.

- Summit, “Radical Chemistry over Sunlit Snow: Interactions between HOx and Halogen Chemistry at Summit”, field campaign, May/June 2007, July 2008 (Jack Dibb)
- Tara, ice-drifting sailboat, BrO, O₃, 2007/8 (Udo Frieß)
- ASCOS (Arctic Summer Cloud-Ocean Study), Icebreaker Odin (OASIS), August 2008 (Harry Beine)
- O-Buoy Project, autonomous buoys frozen in Arctic Ocean, O₃, BrO, CO₂ – to be deployed early 2009 (Jan Bottenheim)
• CFL (Circumpolar Flow Lead) Amundsen icebreaker – date? (Jan Bottenheim)
• OOTI, “Out on the ice”. Ongoing series of field campaigns on the Arctic pack-ice (Jan Bottenheim)
• COBRA (Impact of combined iodine and bromine release on the arctic atmosphere), Kuujjuarapik/Hudson Bay, field campaign (incl. artificial leads); lab studies on frost flowers (Lucy Carpenter)
• Barrow field campaign (OASIS), winter/spring 2009; workshop 09/10 July 2007 (Harry Beine)
• ARCTAS: NASA IPY contribution (so far no halogen component but Hg) - NASA DC-8 in Kiruna during March/April 2008, May 2008 Fairbanks/Alaska (Chris Holmes, Daniel Jacob); part of POLARCAT
• NIWA: Antarctic spring sea ice off Cape Byrd, BrO, Hg, O₃, August – Oct. 2007 (Karin Kreher)
• CEFAC, BAS campaign at Halley, austral spring 2007, BrO, IO (Anna Jones)
• Particles, aerosols and ice nuclei from the sea ice zone, BAS (H. Atkinson, Howard Roscoe)

1.1.2 Marine boundary layer

There is a number of ongoing SOLAS related projects (UK-SOLAS, D-SOLAS) and an EU project. Some of these are still in planning state.

• MAP (Marine Aerosol Production), 2nd campaign at Mace Head, Ireland mid-August-mid-September 2007 (Colin O’Dowd, Katja Seitz)
• RHaMBLe (Reactive halogens in the marine BL), finished: Roscoff (France) field campaign: very high inorganic I but little organic-I, upcoming: field campaign on Cape Verde and cruise in the vicinity of the islands, gaseous (XO, x₂, XY) and particulate halogen speciation, May 2007 (Gordon McFiggans)
• INSPIRE (Investigation of near-surface production of iodocarbons: rates and exchanges), ship cruise: bio, seawater, air, late 2007 (Gill Malin)
• Bermuda Campaign: Production of marine aerosol in “bubbler” with ocean water strong OC and Ca²⁺ enrichment in small particles, (Bill Keene)
• SOPRAN (Surface ocean processes in the anthropocene), German SOLAS, ca. 30 groups involved, several ship cruises (around Cape Verde and Mauretanian upwelling areas as well as in the Baltic Sea) and long-term measurements (Cape Verde); very broad but several halogens related projects (Hermann Bange, Doug Wallace)
• MAPHINS (Marine Multi-Phase Halogen Chemistry and its Coupling to Nitrogen and Sulfur Cycles), German SOLAS, pot. 3x4 years, to be submitted (Uli Platt)

1.1.3 Other

• HALOPROC, “Natural halogenation processes in the environment – Atmosphere and soil” (incl. salt surfaces, dust, HULIS): iron catalysis, formation of organic and inorganic
halogens, 8 groups, lab, smog chamber, field (Russian salt lakes) and model studies (funding decision soon; Heinfried Schöler)

- Hg emissions by salt lakes, Prof. Mae Gustin (U Nevada-Reno)
- Measurement of bromoacetone as indicator of bromine chemistry (Cornelius Zetzsch)

### 1.1.4 Longterm observatories

The following list comprises a number of networks that have not exclusively been set up for halogen measurements but can/do provide some halogen data:

- NDACC (Network for the Detection of Atmospheric Composition Change), new name for NDSC – now also includes tropospheric components.
- NOVAC (volcano gas emission network), focus on SO$_2$ but BrO will also be measured (Bo Galle, Uli Platt)
- MAX-DOAS networks (U Heidelberg, U Bremen): Kiruna, Surinam, Neumayer, Kenia, Cape Verde, Lauder (NIWA) and other locations (Uli Platt, Udo Friess, John Burrows, Karin Kreher…)
- Satellite instruments, GOME, SCIAMACHY, OMI, GOME-2: BrO, IO
- CARIBIC (2004-2014), measurement container aboard commercial aircraft, VSLS measurements by UEA (Dave Oram, Carl Brenninkmeijer)
- Cape Verde observatory (Lucy Carpenter)
- “Longer-lived” halogen containing gases (incl. very short lived (VSL) according to WMO definition: lifetime less than 6 months); several networks e.g. NOAA which has a intercalibrated data set including many ship cruises and ground stations, also other groups like NCAR/U Miami (Jim Butler, Elliot Atlas)
- A protocol to intercalibrate and compare the measurements of organo-halogen gases has to be established in order to ensure that data from different labs is comparable and that trends can be deduced from the data (Jim Butler).

### 1.1.5 Upper Troposphere/Lower Stratosphere

- Several ongoing balloon and aircraft (Geophysica, BAe 146, CARIBIC) experiments, focus on “very short lived” (VLS, lifetime less than 6 months) compounds; main science question: additional injection of about 5ppt of bromine into stratosphere (see WMO 2006 report) (Klaus Pfeilsticker, Bill Sturges)
- Iodine budget in the tropical tropopause layer is not closed: organic iodine is present at ground level and in the troposphere but not in the UTLS region (Klaus Pfeilsticker)

### 1.1.6 Halogens and mercury
• Strong indications that Br might be important for the global budget of Hg, many Hg measurements are ongoing, the link to halogen measurements often weak/absent (Chris Holmes, Arnout ter Schure)
• Mercury deposition is an important topic for environmental agencies (esp. EPA in USA), halogens might be key
• Laboratory work on Hg – halogen oxide interaction is ongoing (Parisa Ariya)
• Modelling is ongoing

1.1.7 Volcanoes

• Regular measurements of halogen oxides at Mt Etna and other volcanoes (Nicole Bobrowski)
• NOVAC network will likely provide BrO measurements as well (Bo Galle, Uli Platt)

1.2 Model development/application

1.2.1 Global models

• Max-Planck-Institute for Chemistry, Mainz; ECHAM-MESSy, detailed treatment of sea salt aerosol source and aqueous chemistry, detailed gas phase chemistry (Astrid Kerkweg, Rolf Sander)
• York University, Toronto, GEM-AQ, core: Canadian weather forecast model with detailed gas and aerosol chemistry (Kenjiro Toyota, Jack McConnell)
• Cambridge Univ, p-TOMCAT (John Pyle)
• Univ. Leeds, GLOMAP, inclusion of halogen chemistry in progress (Ken Carslaw)

1.2.2 Process models

• Max-Planck-Institute for Chemistry, Mainz, MECCA, box model with detailed gas and size resolved aerosol chemistry (Rolf Sander)
• Univ. of East Anglia, MISTRA, 1D model with detailed gas and aerosol chemistry; size resolved treatment of aqueous chemistry is currently being expanded; applied for marine boundary layer, polar BL, volcanic plumes, salt lakes (Roland von Glasow)
• JPL, (Alfonso Saiz-Lopez)

1.2.3 Molecular modelling

UCI, PNNL, Czech Academy of Science; foci: Ions from salts & salt mixtures at the air/water interface, Interaction of gas phase species with aqueous interfaces, Alkyl halides at the air/water
interface; calculation of accommodation coefficients and comparison with measurements (Martina Roeselova)

1.3 Laboratory studies

1.3.1 Frost flowers

Laboratory studies of structure and chemistry ongoing at BAS and PSI (Manuel Hutterli), also AWI; details about the BAS project: laboratory measurements of frost flower growth and dispersal sufficient to provide a complete parameterisation of the production of frost flower area, aerosol mass, and aerosol surface area, as required by modellers dealing with sea salt aerosol and halogen activation processes

1.3.2 Gas phase kinetics

Gas phase kinetics studies are ongoing at U Leeds (John Plane, Dwayne Heard), the Hungarian Academy of Science (Sandor Dobe), University College Cork (Dean Venables), U Manchester (Carl Percival), Univ of East Anglia (Stephen Ashworth) (other labs as well?) but an important lab (MPI-Mainz) has stopped working on this. Data compilations are available from IUPAC and JPL (both on the web). A lot of work is being put in a regular update of these compilations which should be advertised more widely.

1.3.3 Heterogeneous reactions

- UCI, droplet train technique (John Hemminger)
- CalTech, surface chemistry (Agustin Colussi)
- TU Vienna, halogenation of HULIS (Hinrich Grothe)
- TU Vienna, Matrix isolation of halogen oxides (Anja Zoermer)
- UC Cork: froz-ozidation (John Sodeau)
- U Cambridge (Tony Cox)
- Several other labs

1.4 Instrument development

- U Leeds, Laser-Induced Fluorescence detection of halogen oxides (Dwayne Heard)
- Cavity Ring-Down (CRDS) and Cavity Enhanced Absorption Specroscopy (CEAS) (Stephen Ball, U Leicester)
- DOAS Variants: Long-path DOAS, Multi-Axis DOAS (MAX-DOAS), Imaging DOAS, CEAS-DOAS (Uli Platt)
- UC Cork, Incoherent Broad-Band Cavity Enhanced Absorption Spectroscopy (IBBCEAS): I₂ (Dean Venables)
Satellite algorithm development, ongoing focal points at U Bremen, U Heidelberg, MPI-Mainz, Harvard U, BIRA (Belgium), ESRON and KNMI (The Netherlands)

2. Requirements for future research and suggested directions for Phases 1 and 2

Please use the White Paper as reference for ideas and research needs as well. The need for a close collaboration of scientists working in the field, laboratory and those who are using numerical models is crucial to make progress and to link the available knowledge. In order to improve the efficiency of model-field intercomparisons, modellers should be involved in the planning of field campaigns.

In general one should try to achieve as broad a picture as possible during field campaigns, as halogen chemistry is obviously not separated from the “rest” of the chemistry and it is these links that we are most interested in. This implies that many measurements in addition to halogens have to be made and/or that halogen measurements should be added to other field campaigns that can provide the “background” data.

2.1 Main research questions

Closure of halogen budget
- Sources (vegetation, salty surfaces, (marine) aerosols, ..)
- Transport
- Transformation
- Sinks
- Globally and regionally (e.g. tropics)

Oxidation processes
- Impact on O₃
- OH/HO₂ partitioning, HOₓ budget
- NO/NO₂ partitioning, NOₓ/NO₃ budget, nitrate formation (make use of isotope studies)
- DMS oxidation (see also “climate”)
- Role of Cl-atoms

Climate impacts
- Oxidation of DMS by esp. BrO
- Change in oxidation products when BrO is active
- Formation of particulate sulphur, esp. MSA
- Increase in size of existing particles and decrease of new particle formation potential from S if halogens are active (via aq. Phase oxidation of S(IV) and BrO-DMS pathway)
- New particle formation from iodine oxides (mainly (?) coastal BL)
- Growth of clusters to nucleation mode particles by iodine oxides (poss. over open ocean?)
- Oxidation of CH₄ by Cl-atoms
Hg budget
- Strong indications that gas phase Hg lifetime might be shorter than assumed due to tropospheric background of halogens (esp. bromine)
- Increased deposition and bioavailability of Hg due to halogen reactions

2.2 Foci for phase 1

Main foci:
- Polar boundary layer
- Marine boundary layer

Additional foci:
- Free Troposphere (FT)
- Upper Troposphere Lower Stratosphere – region (UTLS)
- Halogens in plumes esp. volcanic plumes and biomass burning (release of Hg and halogens); direct measurements in plumes are desirable but difficult for obvious technical reasons; sondes and UAVs might be a solution
- Hg links
- Instrument development for projects for phase 2
- Piggy-back on other other campaigns (e.g. VOCALS (aerosol cloud-climate forcing off south America, Barry Huebert, Roberto Mechoso) for open ocean MBL)

2.3 Foci for phase 2

- Free troposphere: Ubiquitous presence of BrO? This is very relevant for O$_3$ and Hg budgets
- UTLS: VSL, relevance of breakdown products for FT, UTLS, input to stratosphere (esp. tropics): close (tropical) halogen budget from source to UTLS (poss. EU project, Klaus Pfeilsticker)
- Coastal Mega-Cities; Data mining as first activity? Coastal sea-salt effects on polluted atmospheres; if this is to be expanded we need to involve in the air quality community.
- Clean, remote MBL (relevance for O$_3$ and chemistry-cloud-climate interactions)
- Halogens in plumes (volcanoes, biomass burning, dust); Cape Verde site might be useful for dust and poss. aged biomass burning plumes
- Salt lakes: halogens, links with Hg

2.4 Requirements for future research

Instrument development:
- Improve detection limit for gas phase halogen compounds to 0.1 ppt level
- Develop techniques for better gas phase speciation (HOX, XNO$_2$, XONO$_2$, ..)
• Develop techniques for better aerosol phase speciation (specific, fast, size resolved, including salt aerosol)
• Develop affordable mercury speciation instruments to investigate Hg – X links
• Develop/improve isotopic techniques (others as well?) to investigate production pathways based on final products
• Miniaturize instruments for easier deployment on ships, aircraft and eventually airship/zeppelins for Lagrangian studies; also for UAVs for plume studies
• Use existing campaigns for instrument testing!

Laboratory studies
• Ensure that expertise in gas phase kinetics is not lost and that active research in kinetics is being done (esp. for radical-radical reactions, ..)
• Gas phase: I₂ + NO₃; OIO loss/recycling processes (in the presence of NOₓ); IONO₂ + O₃ (or net reactions consuming both poss. involving particles as well), XO + ROO
• Heterogeneous reactions: several labs work actively in this important field
• Aqueous phase reactions/equilibria and precipitation reactions: information about highly concentrated and acidic solutions (low pH) required; temperature dependencies required esp. for understanding of polar boundary layer chemistry
• Snow/ice photochemistry: reactive “pockets”? Acidity in/on ice/QLL/unfrozen parts of snow pack??
• Freezing of solutions: changes in compositions, pH
• Make use of WP5 of ACCENT: “access to data” (Tony Cox, Christian George, Hartmut Hermann, Gordon McFiggans, Jens Hjorth)

Long-term measurements
• There are (except for halocarbons) no long-term measurements in the Southern Hemisphere and very few data (except Antarctica)
• Urgent need for common standards and intercalibration for measurement of VSL gases (Jim Butler)
• There are no long-term measurements on “really” remote islands (Cape Verde is only under certain conditions in clean air)
• Re-evaluate existing hydrocarbon data with the “hydrocarbon clock” method to derive a bigger data set of indirect determinations of the concentration of chlorine atoms (esp. in the MBL)
• Use (existing) high mountain stations for BrO measurements in the free troposphere (e.g. Zugspitze, Mt. Bachelor (Daniel Jaffe), possibly ABC sites in Asia/Himalaya), easiest with MAX-DOAS but potentially also with long-path DOAS between two summits
• Global Atmospheric Watch (GAW) sites: potential for addition of halogen instruments

Model development
• The “bromine explosion” mechanism involves surfaces/particles; simplified but still inclusive chemical mechanisms have to be developed
• Snow chemistry module seems to be key for polar halogen chemistry
• Application of existing models to “new” domains/situations
• Develop small scale 3D models to investigate “hot spots”
• Improvement/development of global models to better assess the global consequences

Other

• Global budget: sources of organic-X and inorganic-X have to be known (terrestrial and ocean); this is key for more reliable global model studies
• Update of the Reactive Chlorine Emissions Inventory (Bill Keene et al.) would be very desirable; extension to other halogens would be even more desirable

2.5 Funding

HitT does not have funds to directly support research. We have received financial support from IGAC and SOLAS for workshops and IGAC hosts a HitT webpage (a more comprehensive webpage is being developed).

A goal of HitT is to bring international scientist together for joint research projects. The only large scale international research funding is currently provided by the European Union, several plans for EU projects are being discussed (7th Framework: Cooperation and Capacities), among them: Budget of halogens in the tropical tropopause from the surface to the UT/LS (contact: Klaus Pfeilsticker), halogens in volcanic plumes (prelim contact: Roland von Glasow), instrument/observatory development (prelim contact: Roland von Glasow). Furthermore, there is funding available from the ESF for workshops etc., which we will apply for in the future. Any non-EU collaborators are of course invited to participate in these projects with their own (national) funding. The idea of starting EU projects is NOT meant to exclude non-EU scientists, it is only a pragmatic approach. At any point we always try to encourage international collaboration on all scales. This implies that we strive to have a geographical balance also for halogen sessions at international conferences (e.g. EGU and AGU meetings).

Many countries have bilateral funding schemes which can be used in addition to national funding.

2.6 Publicity

• Organize halogen sessions at international conferences like the EGU or AGU meetings (with a geographic balance).
• HitT webpage in addition to IGAC page (Roland von Glasow)
• Entries about Ozone Depletion Events (ODE) etc on Wikipedia
• list of HitT references (or other topics) in docs.google.com

2.6 Implementation group

The following people have volunteered to help prepare the annual task reports to IGAC (and SOLAS):
field work:
  • long-term: Butler, Pfeilsticker, Sturges
  • campaign-based: McFiggans, Seitz

laboratory:
  Grothe (heterogeneous), Venables (gas)

model:
  Roeselova (MD), von Glasow

Hg:
  Holmes, ter Schure

Instrument development:
  Sjostedt, Venables

Attendees:

Cecilia Arsene (U Crete), Nicole Bobrowski (INGV), Jan Bottenheim (Env. Canada, Toronto), Jim Butler (NOAA), Agustin Colussi (CalTech), Terry Dillon (MPI-Mainz), Sandor Dobe (Hungarian Academy of Science), Marcel Dorf (U Heidelberg), Hinrich Grothe (TU Vienna), John C. Hemminger (UC Irvine), Chris Holmes (Harvard U), Astrid Kerkweg (MPI-Mainz), Eladio Knipping (EPRI), Alexander Laskin (PNNL), Gordon McFiggans (U Manchester), Klaus Pfeilsticker (U Heidelberg), Matthias Piot (U Heidelberg), Ulrich Platt (U Heidelberg), Martina Roeselova (Acad. Sc. Czech Rep.), Rolf Sander (MPI-Mainz), Robyn Schofield (AWI Potsdam), Katja Seitz (U Heidelberg), Steve Sjostedt (U Toronto), Linda Smoydzin (UEA), Bill Sturges (UEA), Arnout ter Schure (EPRI), Kenjiro Toyota (U York, Toronto), Dean Venables (UC Cork), Roland von Glasow (UEA), Cornelius Zetzsch (U Bayreuth), Anja Zoermer (TU Vienna)

This report was written by Roland von Glasow with input and comments from Ulrich Platt, Rolf Sander and Bill Sturges.