Halogens in the Troposphere
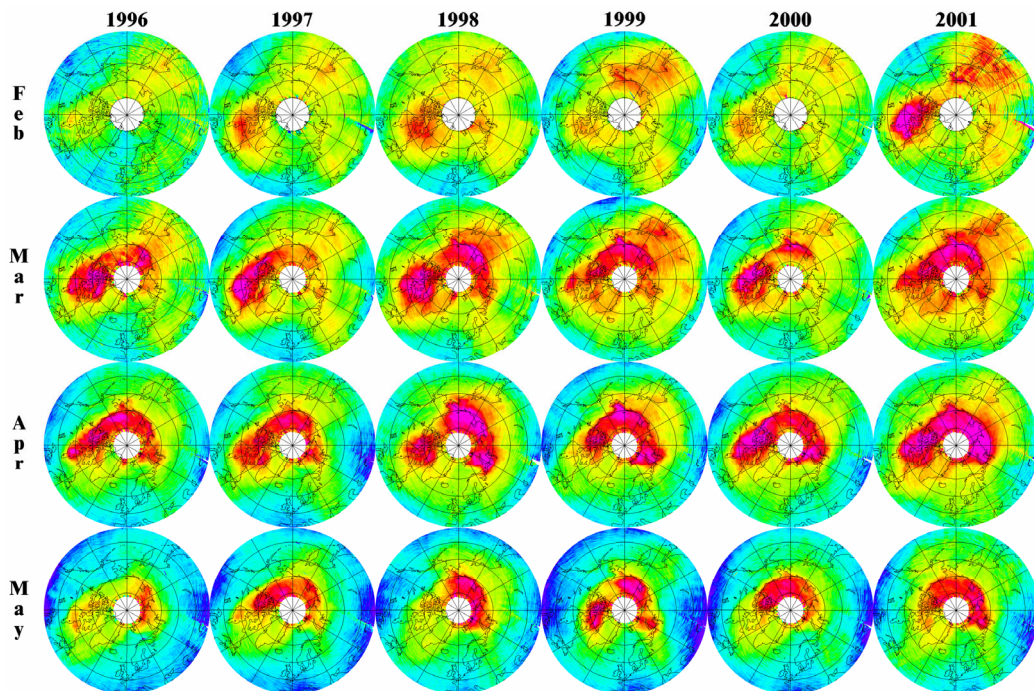
An international task

Science and Implementation Plan

Cover: Interannual variation of the vertical BrO columns for the Arctic (data from GOME, courtesy of J. Hollwedel).

1) Summary

1.1) Objective

Reactive halogen compounds (X, XO, X_2, XY, OXO, HOX, $XONO_2$, XNO_2, where X,Y=Cl, Br, I) – in particular halogen oxides - are present in various domains throughout the troposphere. The primary objective of the project HitT – Halogens in the Troposphere - is to determine the importance of RHCs in tropospheric chemistry and climate forcing. Key themes are the influence of RHC on the oxidative capacity of the atmosphere, the ozone budget, as well as in aerosol nucleation and growth.

1.2) The need for an international research framework

The characterization, quantification, and understanding of the abundances and cycles of RHC has already begun in many parts of the troposphere. However, beyond the present, often only pioneering and exploratory efforts, a comprehensive approach is needed, which is beyond the national scope and requires international and interdisciplinary cooperation.

The envisioned tasks of HitT are to suggest comprehensive field campaigns that usually require know-how, instrumentation, and logistics from several countries. Our efforts will be combined with existing/planned activities by e.g. IGAC, SOLAS, iLEAPS, OASIS, AICI and others. We aim to bring scientists from different fields (chemists, physicists, meteorologists, (micro-)biologists; laboratory, field, model, different focus on topics) and countries together to identify, discuss, and publish the most important topics with regard to reactive halogen chemistry. We want to make use of synergies between different fields/domains (e.g. measurement techniques and models developed for one domain can be applied to others as well) because of the interdisciplinary and international nature of the subject.

1.3) Priority topics

The following research topics should receive priority in the next years (see details in chapters 2 and 3):

1) Sources and distribution of RHC:

Determine the emission fluxes of and key release processes for RHCs and their precursors from the open and coastal oceans, polar regions, land surfaces, volcanoes, and urban-industrial areas. In order to achieve this goal

existing techniques have to be refined and new, faster and more sensitive methods for measuring RHCs have to be developed.

2) Transformation and transport:

Develop a detailed understanding of the multiphase chemical processes that determine the distribution of RHCs and their precursors at different spatial and temporal scales throughout the troposphere and the physical processes including aerosol- and cloud-microphysics and transport. This effort should ultimately lead to a realistic representation in numerical models.

3) Implications of RHC:

Integrate different measurement techniques and models to determine the regional and global role of RHCs in a series of physico-chemical processes in the troposphere, including: tropospheric oxidation processes (esp. sulfur), the ozone budget, HO_x and NO_x radical cycles, and aerosol nucleation and evolution.

1.4) Implementation

In sections 2 and 3 we propose initiatives that would help address the open questions. These initiatives are planned to be explored over the next 9 years, divided into three 3-year periods. In section 4 we list proposals for field campaigns and long-term observations, which will be accompanied by and closely coordinated with laboratory and modeling studies.

2) Halogen domains

Historically, reactive halogens have first been recognized to be of importance for stratospheric chemistry. In the early 1980s the discovery of "ozone depletion events" (ODEs), drastic ozone depletions in near-surface air during polar sunrise in the Arctic boundary layer (BL) have triggered us to rethink the usually held notion that inorganic halogens in the troposphere would mainly be in the form of hydrogen halides (HX, where X=F, Cl, Br, I) and rapidly be removed by wet and dry deposition.

The dramatic increase in our knowledge and the appreciation of the details of reactive halogen chemistry in the troposphere is reflected in the number of reviews that dealt with this topic in the last 10 years: Graedel and Keene (*1995*) summarized inorganic chlorine chemistry in troposphere, whereas Wayne et al. (*1995*) compiled the relevant reaction kinetics. Among other campaigns, the Polar Sunrise Experiments [*e.g., Barrie et al., 1994*] and ARCTOC were dedicated to studying halogen chemistry in polar BL [*Platt and Lehrer, 1996*]. The pH of (sea salt) aerosol and its importance for halogen release was assessed by Keene et al. (*1998*). The "Reactive chlorine emissions inventory" by Keene et al. (*1999*) collected the current knowledge about the main sources for atmospheric chlorine. In 2003 a variety of reviews was published ranging from an assessment of iodine chemistry in the marine boundary layer [*Carpenter, 2003*] to the details of the chemistry of sodium chloride and sodium bromide particles [*Finlayson-Pitts, 2003*] and in general heterogeneous reactions on salts [*Rossi, 2003*]. Quack and Wallace (*2003*) summarized the current knowledge on $CHBr_3$ concentrations and processes in the ocean and atmosphere, whereas the review of Sander et al. (*2003*) was dedicated to inorganic bromine chemistry in the marine boundary layer. Platt and Hönninger (*2003*) and von Glasow and Crutzen (*2003*) covered the broader topic of halogen chemistry in the troposphere whereas O'Dowd and Hoffmann (*2005*) reviewed the iodine-related new particle formation in the coastal boundary layer.

In the following section we give a brief summary of sources and distributions of RHC, their transformations, and the atmospheric implications. In sections 2 and 3 we summarize the current knowledge for the tropospheric domains where halogen chemistry was found to be of importance (see Fig.1).
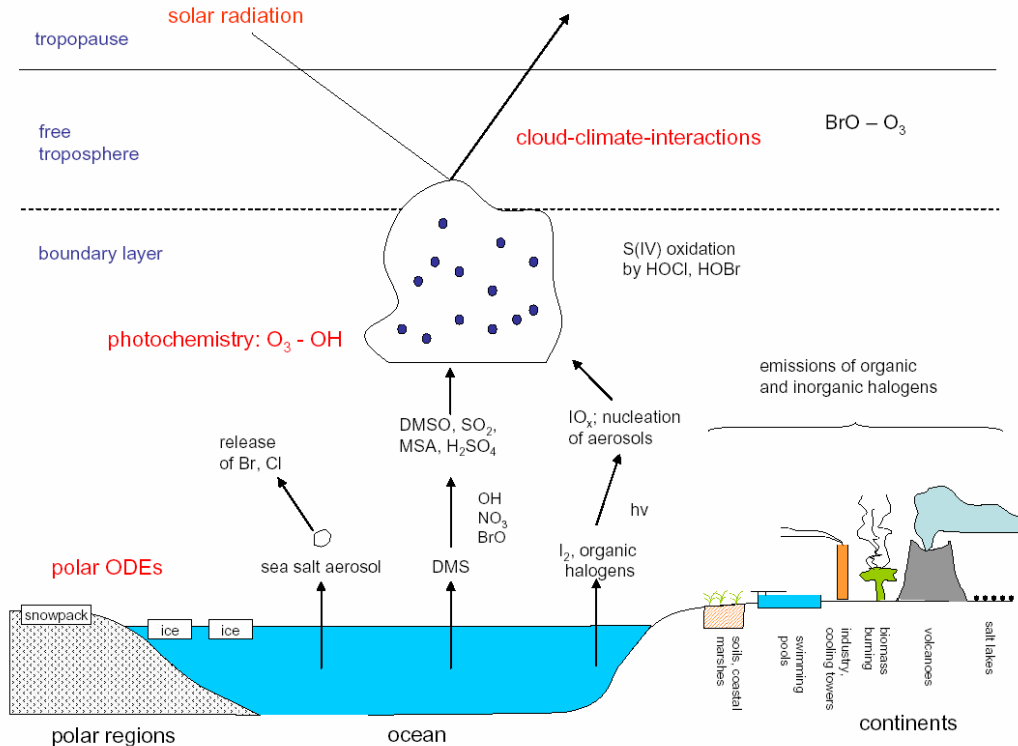
Figure 1. Tropospheric halogen domains.

i)   Sources and distribution

The sources for tropospheric RHC can be classified into five categories: direct release of inorganic halogens (e.g. I_2), breakdown (mainly through photolysis) of organic halogens, release from salt surfaces (salt aerosol, brines, salt lakes, deposited salt, for example) by the so-called 'bromine explosion' mechanism as detailed below, activation of hydrogen halides, and downward transport from the stratosphere.

In the following list we summarize the main origins of halogens for the different domains:

- polar boundary layer: fresh sea ice, frost flowers, aerosol
- salt lakes: salt surfaces, aerosol
- marine boundary layer: precursor (bio-)chemistry in the ocean and subsequent emission of halogen containing gases, sea salt aerosol
- volcanoes: direct emissions of inorganic halogens
- biomass burning: organic and inorganic halogen gases, aerosol
- dust plumes: aerosol
- other continental sources: aerosol, soil (biotic and abiotic formation of organo-halogens), vegetation, fungi, bacteria, coastal marshes, agriculture, industry, cooling towers, swimming pools, other ?
- free troposphere: breakdown of $C_iH_jX_kY_l$, halogens released from sea salt, downward transport from stratosphere, volcanoes, "spillout" from polar boundary layer, biomass burning, - but the relative importance of each process is unknown.

The basic source processes in the different domains involve similar physico-chemical processes so that important synergy can be achieved if the respective communities dealing with the different domains collaborate closely. In order to understand reactive tropospheric halogen chemistry and especially to properly assess the regional and global effects with numerical models, a thorough qualitative and quantitative understanding of these sources is essential.

Several of the above listed reviews contain a detailed list of the distribution of RHC [*e.g. Keene et al, 1999, Sander et al., 2003*], to complement this we list in Table 1 the locations at which halogen oxides have already been detected in the boundary layer.

Species	Location	Max. mix. ratio [ppt]	Error ±(2σ) [ppt]	Reference
ClO	Great Salt Lake	15		Stutz et al. [2002]
ClO	Volcanoes	$\sim 10^4$		Lee et al. [2005], Bobrowski et al. [2006]
OClO	Mt. Etna volcano	~ 100		Bobrowski et al. [2006]
BrO	Mace Head, Ireland	6.0	0.8	Saiz-Lopez et al. [2004]
BrO	Mid.Lat. MBL (30-37N, 13W)	2.3	-	Leser et al. 2003
BrO	Salt lakes (Dead Sea, Great Salt Lake, Caspian Sea, Salar de Uyuni)	176	-	Hebestreit et al. [1999], Matveev et al. [2001], Wagner et al. [2001], Stutz et al. [2002], Hönninger et al. [2004]
BrO	Antarctic, Arctic	30	-	Hausmann and Platt [1994], Tuckermann et al. [1997], Hegels et al. [1998], Martinez et al. [1999], Avallone et al. [2003], Hönninger et al. [2004], Frieß et al. [2004]
BrO	Volcanoes	~ 1000	-	Bobrowski et al. [2003,2006], Oppenheimer et al. [2006]
IO	Mace Head, Ireland (1997)	6.7	0.5	Alicke et al. [1999]
IO	Mace Head (1998)	7.2	0.3	Hebestreit [2001]
IO	Mace Head (2002)	7	0.5	Saiz-Lopez and Plane [2004], Saiz-Lopez et al., [2006a]
IO	Tasmania (1999)	2.2	0.4	Allan et al. [2000]
IO	Tenerife, Can. Islands (1997)	3.5	0.4	Allan et al. [2000]
IO	Kerguelen, Ind. Ocean (2002)	9.8	1.4	Hönninger [2002], Sebastián [2004]
IO	North Sea, Germany (2002)	2.1	0.5	Peters et al. [2005]
IO	Atlantic Coast, France (2003)	7.7	0.5	Peters et al. [2005]
IO	Crete, Greece (2003)	≤D.L. (0.8)	0.8	Hönninger [2002]
IO	Appledore Island (2004)	6		Pikelnaya et al. [2005]
IO	Dead Sea, Israel (2000)	10	2.4	Zingler and Platt [2005]
IO	Antarctic and Arctic	-	10	Frieß et al. [2001], Wittrock et al.

				[2000]
IO	Alert, Arctic (2000)	0.73	0.23	Hönninger [2002]
IO	Halley Bay, Antarctic (2004/5)	20		Plane et al. [2005]
OIO	Cape Grim, Tasmania (1999)	3.0	0.5	Allan et al. [2001]
OIO	Mace Head, Ireland (1998)	6.7	0.5	Hebestreit [2001]
OIO	Mace Head, Ireland (2002)	3.0	0.5	Saiz-Lopez and Plane [2004], Saiz-Lopez et al., [2006a]
OIO	Appledore Island (2004)	15		Pikelnaya et al. [2005]
I_2	Mace Head, Ireland (2002)	93	3	Saiz-Lopez and Plane [2004], Saiz-Lopez et al., [2006a]
I_2	Mace Head, Ireland (1998)	61.3	12	Peters et al. [2005]

Table 1: Measurements of halogen oxides and I_2 in the boundary layer (after Peters et al. 2005, updated).

ii) Transformation

To provide the context for the chemical transformations of RHC we start with a brief overview of the main reaction cycles (see also Figure 2).

Once released to the troposphere RHS undergo a series of reaction cycles. Primary organic and inorganic halogen species (e.g. CH_2I_2, $CHBr_3$, I_2, BrCl), will rapidly be photolysed to form halogen atoms, e.g.:

$$RX/XY + h\nu \quad \rightarrow \quad R/Y + X \quad\quad\quad (R1)$$
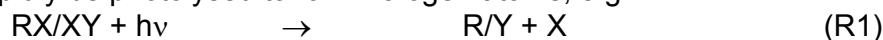
which – in turn – are most likely to react with ozone:

$$X + O_3 \quad \rightarrow \quad XO + O_2 \quad\quad\quad (R2)$$

Halogen atoms are regenerated in a series of reactions including photolysis of XO, which is of importance for X = I, Br and to a minor extent Cl:

$$XO + h\nu \quad \rightarrow \quad X + O \quad\quad\quad (J3)$$

In the parts of the troposphere affected by pollution rapid reaction with NO also produces halogen atoms:
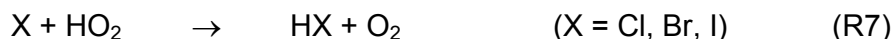
$$XO + NO \quad \rightarrow \quad X + NO_2 \quad\quad\quad (R4)$$

In addition to that the self reactions of XO (or reaction with another halogen oxide YO) also play a role, like:

$$XO + YO \quad \rightarrow \quad X + Y + O_2 \quad (\text{or } XY + O_2) \quad\quad (R5)$$
$$\rightarrow \quad OXO + Y$$
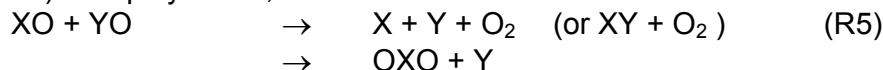
In addition chlorine atoms can react with hydrocarbons to form hydrogen halides, e.g.:

$$RH + Cl \quad \rightarrow \quad R + HCl \quad\quad\quad (R6)$$

Here R denotes an organic radical. For unsaturated hydrocarbons addition (of Cl, Br) is the most likely reaction, but some HCl can be produced via addition-elimination channels. Reaction of Cl with CH_4 is the major sink for the radical. An alternative is the reaction of halogen atoms with formaldehyde (or higher aldehydes) or HO_2 also leading to conversion of halogen atoms to hydrogen halides:

$$X + HO_2 \quad \rightarrow \quad HX + O_2 \quad\quad (X = Cl, Br, I) \quad\quad (R7)$$
$$X + HCHO \quad \rightarrow \quad HX + CHO \quad\quad (X = Cl, Br) \quad\quad (R8)$$

Bromine atoms can add to the C=C double bond of olefins leading to organic Br species, but – at least partly – also to HBr. Of the order of 1% of the Br-atoms are thus converted to HBr, while roughly 99% of the Br atoms react with O_3 [*Wayne et al. 1995, Platt and Janssen 1995*]. Since HX is highly water soluble it is either irreversibly removed from the atmosphere by wet or dry deposition or taking part in recycling reactions involving aerosols (see below). The only relevant gas phase 'reactivation' mechanism of HX is reaction with OH:

$$HX + OH \rightarrow X + H_2O \qquad (R9)$$

Other key inorganic halogen species besides HX are HOX and $XONO_2$, where HOX is formed via the rapid reaction of peroxy radicals with XO:

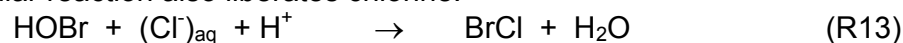$$XO + HO_2 \rightarrow HOX + O_2 \qquad (R10)$$
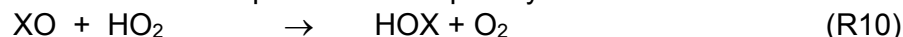
An analogous reaction involving CH_3O_2 is also likely to (ultimately) produce HOX [*Aranda et al. 1997*]. Photolysis of HOX:

$$HOX + h\nu \rightarrow X + OH \qquad (J11)$$
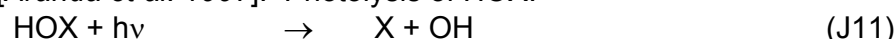
leads to a photo-stationary state between XO and HOX with [HOX]/[XO] ranging from roughly 1 to 10 (if heterogeneous reactions are neglected), depending on the oxidation capacity of the atmosphere. An interesting reaction cycle involving HOBr [*Fan and Jacob 1992, Mozurkewich, 1995, Tang and McConnell 1996, Vogt et al. 1996*] is the liberation of gaseous bromine species (and to a lesser extent chlorine species) from halides by the following heterogeneous mechanism:

$$HOBr + (Br^-)_{aq} + H^+ \rightarrow Br_2 + H_2O \qquad (R12)$$

A similar reaction also liberates chlorine:

$$HOBr + (Cl^-)_{aq} + H^+ \rightarrow BrCl + H_2O \qquad (R13)$$

The required H^+ (the reaction appears to occur at appreciable rates only at pH < 6.5 [*Fickert et al. 1999*]) could be supplied by strong acids, such as H_2SO_4 and HNO_3 originating from man made or natural sources. In the case of X = Br the above reactions followed by photolysis of Br_2, oxidation of Br by O_3 (R2) and conversion of BrO to HOBr by HO_2 (or CH_3O_2), R10, complete a cycle with the net result:

$$\textbf{BrO} + O_3 + (Br^-)_{aq} + (H^+)_{aq} \xrightarrow{Surface, HO_X} \textbf{2 BrO} + \text{products}$$
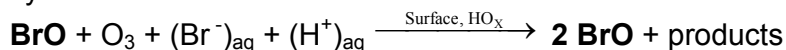
Effectively one BrO molecule is converted into two by oxidising bromide at or on aerosol particles (e.g. sea salt aerosol). This process leads to an exponential growth of the BrO concentration in the atmosphere, which led to the term 'Bromine Explosion' [*Platt and Lehrer 1996, Platt and Janssen 1995, Wennberg 1999*]. As a consequence BrO rather than HBr can become the dominating Br species. Since Cl_2 does not appear to be released from the liquid phase there is no 'chlorine explosion', however Cl atoms may be formed as 'by-product' of the Br-explosion via R13.

In polluted areas halogen nitrate, $XONO_2$ may form:

$$XO + NO_2 \xleftarrow{\quad M \quad}\rightarrow XONO_2 \qquad (R14)$$
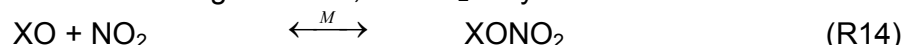
Halogen nitrates are readily photolysed and may be converted to HOX by heterogeneous hydrolysis [*e.g. Sander et al., 1999*]:

$$XONO_2 + H_2O \xrightarrow{Surface} HNO_3 + HOX \qquad (R15)$$
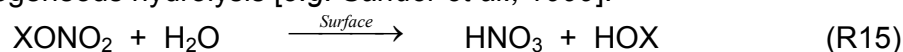
or to Br_2 or BrCl by heterogeneous reaction with HY:

$$XONO_2 + HY \xrightarrow{Surface} HNO_3 + XY \qquad (R16)$$
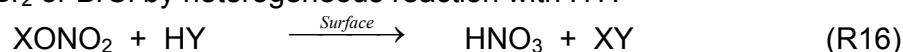
Under conditions of high NO_X halogen release from sea salt aerosol can occur via the reactions:
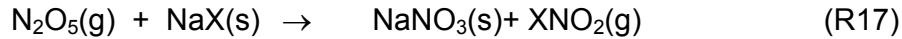
$$N_2O_5(g) + NaX(s) \rightarrow \quad NaNO_3(s)+ XNO_2(g) \quad\quad (R17)$$

[*e.g. Finlayson-Pitts et al. 198*9]. The XNO_2 formed in the above reaction may photolyse to release a halogen atom or possibly further react with sea salt [*Schweitzer et al. 199*9]:

$$XNO_2(g) + NaX(s) \rightarrow \quad NaNO_2(s)+ X_2(g) \quad\quad (R18)$$
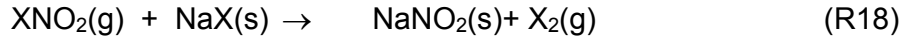
The above reaction sequence would constitute a dark source of halogen molecules under polluted conditions. Another possible reaction involves the NO_3 radical.

$$NO_3(g) + NaX(s) \rightarrow \quad NaNO_3(s)+ X(s) \quad\quad (R19)$$
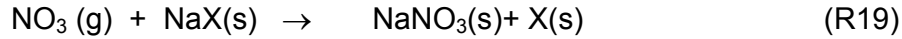
[*Seisel et al. 1997, Gershenzon et al. 1999*].
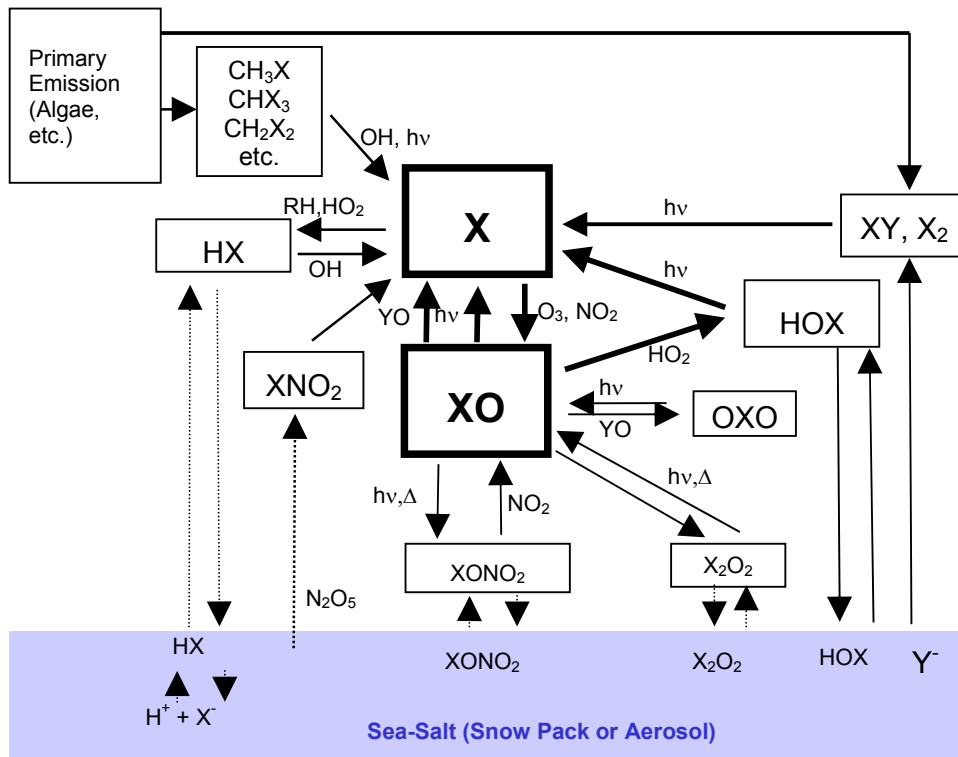
Figure 2. Simplified Outline of the XOX (=X + XO, X = I, Br, Cl) Cycles (based on Wayne et al, 1995).

According to our current knowledge fluorine is unimportant for tropospheric chemistry because it very rapidly reacts to HF, which is the reason why we did not consider it in this paper. However, we should keep an open eye for possible reactions/processes involving fluorine as well, to avoid missing important chemistry as has happened in the past with the reactive halogens that this paper describes in detail. Perhaps fluorine holds some surprises in the future?

iii) Implications

The main implications of RHC for the troposphere are:

- catalytic ozone destruction and therefore change (decrease) in oxidation power of the troposphere and its radiative forcing
- change in HO_2:OH and NO:NO_2 ratios with implications for many photochemical reaction cycles including a decrease in ozone production
- increase in CH_4 and NMHC oxidation by the chlorine radical, therefore increasing the oxidation power of the atmosphere for these compounds
- new particle formation and particle growth by iodine compounds with potential consequences for cloud formation and lifetime and inland transport of particulate iodine
- deposition and enhancement of bioavailability of mercury especially in polar regions
- increase in DMS oxidation and shift in the final products potentially leading to a decrease in cloud albedo

In the following sections we give for the various domains a brief description of the current knowledge and list the open scientific questions in three categories of importance: i) most important questions, ii) important questions, iii) further questions. Furthermore we propose initiatives to address these open questions.

2.1) Polar boundary layer

Current knowledge

In the 1980s sudden ozone depletion events (ODEs) were discovered in the Arctic boundary layer (BL) after polar sunrise [*Bottenheim et al. 1986, Oltmans and Komhyr 1986*]. These events were well-correlated with high levels of filterable bromine [*Barrie et al. 1988*]. Subsequently bromine monoxide (BrO) was measured directly by the Differential Optical Absorption Spectroscopy (DOAS) technique at up to 30 ppt during ODEs [*Hausmann and Platt 1994, Tuckermann et al. 1997, Martinez et al. 1999, Hönninger and Platt 2002, Hönninger et al. 2004a, Frieß et al. 2004*]. First year sea ice appears to be the major source for halogen release via the bromine explosion mechanism, with a likely role of frost flowers in providing sea salt surfaces [*Richter et al. 1998, Wagner and Platt 1998, Wagner et al. 2001, Rankin et al., 2002, Hollwedel et al. 2004, Kaleschke et al. 2004*]. Br_2 and BrCl have been found above the snow pack at up to 30 ppt, Cl_2 could not be detected above the detection limit of 2 ppt [*Foster et al. 2001, Spicer et al. 2002*]. The levels of Cl inferred from indirect methods indicate a minor role in ODE, however hydrocarbons and radical budgets may be affected considerably [*Jobson et al. 1994, Ariya et al. 1998, 1999, Solberg et al. 1996, Ramacher et al. 1997, 1999*]. Oxidation of elemental mercury correlates well with ozone depletion indicating strongly interrelated radical chemistry. Furthermore, an increase in oxidized mercury in snow was observed [*Schroeder et al. 1998, Steffen et al. 2002, Lindberg et al. 2002, Ariya et al. 2002*]. Iodine oxides have also been observed in polar regions but their importance for ODEs is yet to be

determined [*Frieß et al., 2001, Wittrock et al., 2000, Hönninger, 2002, Plane et al., 2005*].
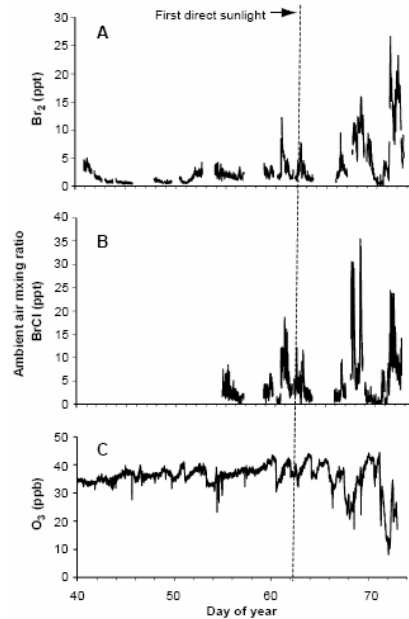
Figure 3. Ambient mixing ratios of Br$_2$, BrCl, and O$_3$ during at Alert in 2000 (Foster et al., 2001).
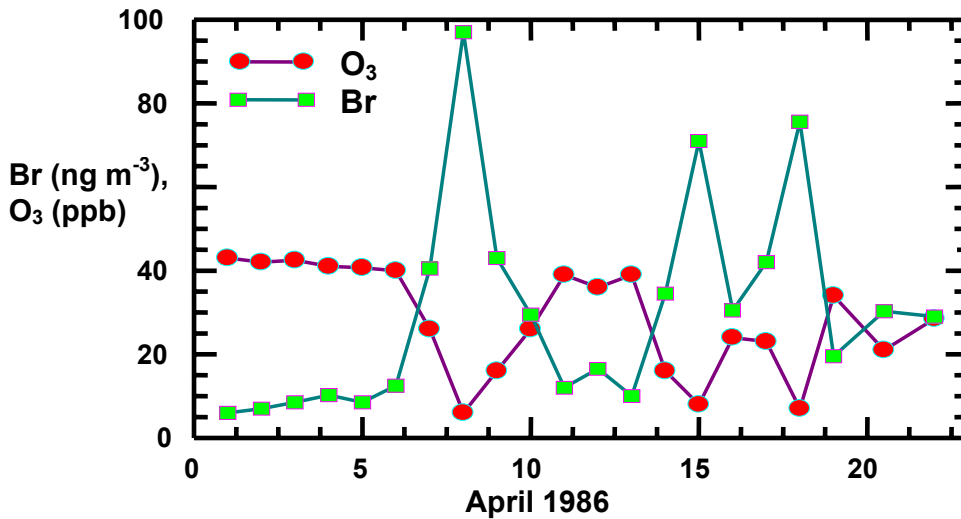
Figure 4. O$_3$ depletion vs. filterable bromine (Barrie et al., 1988).

Open questions

i) Most important questions

The major question still is: what triggers bromine explosion events in polar spring? Are available spot measurements representative, indicating sporadic occurrence? Is there a continuous bromine source, thus do other parameters sometimes start the bromine explosion/ODE? In case events are of a stochastic nature, is a new approach necessary to study these chemical

instabilities and oscillations of bromine chemistry? The fate of mercury in the polar environment needs to be addressed, especially what the extent of halogen reactions on Hg redox processes is and its effects on the speciation of mercury at the snow-air interface.

ii) Important questions

Can we understand the occurrence of bromine explosion events (measured at ground stations and from satellite) by including knowledge on frost flowers, sea ice, boundary layer inversions etc. in a 3D-model? Sensitivity studies should try to determine what the prerequisites are to start a bromine explosion, including a detailed description of frost flowers. What is the role of the snow pack in the production and recycling of reactive halogens? How can the release of chlorine be explained quantitatively and how important is the chlorine (photo-) chemistry? The significance of halogen recycling on aerosols and the fate of bromine should be investigated. The importance of deposition to snow, ice or ocean surfaces versus transport to the free troposphere needs to be better understood to determine the ultimate sink of reactive halogens. Is transport to remote continental regions important? What are the regional and global effects? What is the role of iodine?

iii) Further questions

What is the temporal and spatial extent of bromine explosion events and how can differences between the Arctic and Antarctic be explained? Why are events restricted to springtime? How does synoptic and local scale weather relate to bromine and ODEs and do trajectories explain the evolution of BrO clouds? What are the sources and the possible role of organic halogens in Polar Regions? Is bromine catalyzed ozone destruction accelerated by iodine chemistry and what are the iodine sources and release mechanisms? How can the seasonal cycle in aerosol iodine be explained?

Initiatives that would improve current understanding:

- Increase the number of stations with timeseries of O_3, BrO and other compounds (currently existing at Alert (Arctic), Ny Alesund (Arctic), Neumayer (Antarctic), being implemented at Halley).
- Complement coastal measurements with studies on the sea ice away from the coast to investigate the large regions where BrO is seen from the satellite (already started with the Canadian and Alaskan "Out on the ice" (OOTI) campaigns, 2004/5), e.g. upgrade drifting buoys for atmospheric measurements.
- Do spatial and temporal correlation studies with satellite BrO observations.
- Investigate the vertical characteristics of ODEs, maybe with the help of tethered balloons, unmanned aerial vehicles (UAV) or an airship.
- Do Lagrangian studies to investigate the complete timespan of an ODE event from the start to the end (once a good way of identifying potential start conditions has been found).

- Investigate model systems esp. for frost flowers in the laboratory.
- Study evolution of frost flowers with time in the field (acidity, composition of halides, physical transformation), determine processes governing the deposition and redistribution of halides on/in the snowpack.
- Use numerical models of different complexity (0D, 1D process models to 3D regional/hemispheric models) to test if our understanding of the involved processes is complete, to test possible parameterization for the release of bromine from salt surfaces and finally to try to predict the occurrence of ODEs.

2.2) Salt lakes

Current knowledge

In recent years reactive halogen species were found in the atmosphere above several salt lakes and salt pans. Field studies by active DOAS and passive MAX-DOAS showed, that salt lakes (Dead Sea, Israel; Great Salt Lake, USA; Salar de Uyuni, Bolivia) release reactive halogens into the atmosphere. In particular at the Dead Sea, Israel up to 200 ppt BrO [*Hebestreit et al. 1999, Matveev et al. 2001*] and 10 ppt IO were found [*Zingler and Platt, 2005*]. The BrO appears to originate not from the surface of the Dead Sea, but from the salt pans (dry salt) south of the lake. The BrO events recorded at stations along the shore of the lake always coincide with loss of ozone [*Tas et al., 2005*]. While one would expect halogen catalysed ozone destruction, the estimated transport time (1-2 hours) from the salt pans to the site appears to be somewhat shorter than the calculated time for complete ozone destruction (about 4 hours). Aircraft observations showed situations where the entire Dead-Sea valley was apparently free of ozone [*Matveev et al. 2001*].

In the case of the IO release it is interesting to note that the formation of biogenic precursers is not entirely impossible, but unlikely at the Dead Sea, while all other reported IO events at coastal regions are thought to be caused by degradation of biogenic precursors (see section 2.3).
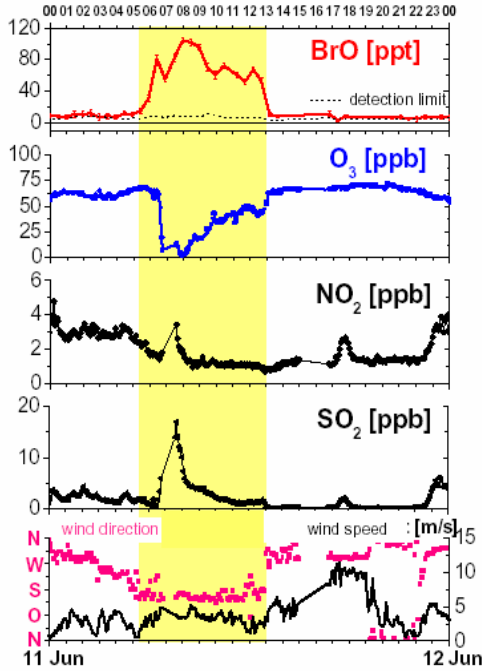
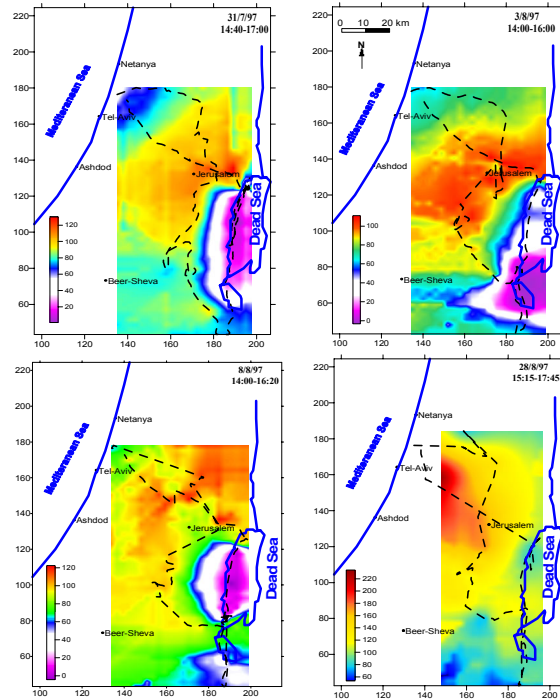**Figure 5. First measurements of BrO over a salt lake (Hebestreit et al., 1999).**

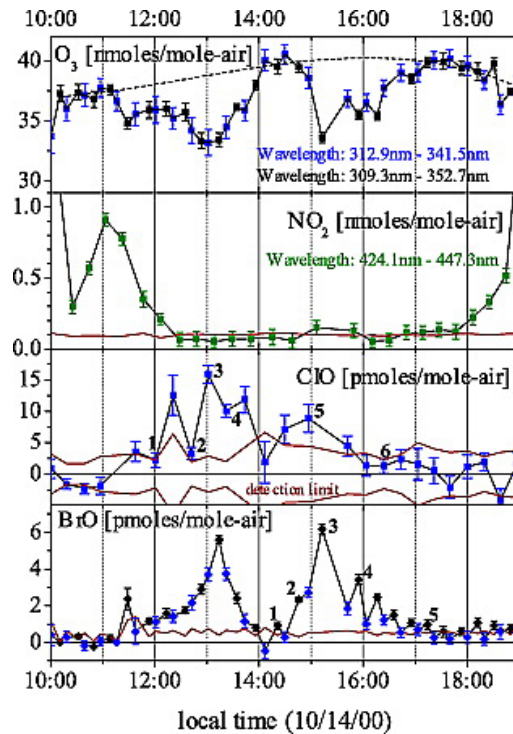**Figure 6. O$_3$ depletion in the Dead Sea area (Matveev et al., 2001).**

Figure 7. Identification of ClO and BrO at the Great Salt Lake (Stutz et al., 2002).

15

Lower levels of BrO (up to 6 ppt), but also ClO (up to 15 ppt) were discovered at the Great Salt Lake, USA [*Stutz et al. 2002*]. Similar amounts of BrO (up to about 15 ppt) were found at the salt pan of the Salar de Uyuni, coincident with indications for ozone loss [*Hönninger et al., 2004b*]. It is also interesting to note that the salt pans in the Andes mountain range are at high elevations (around 3600m), thus transport of the released reactive halogen species to the free troposphere could be efficient. In addition, satellite measurements found elevated BrO columns over the northern part of the Caspian Sea during spring [*Wagner et al. 2001, Hollwedel et al. 2004*] and also BrO plumes in the Dead Sea area [*Kurosu et al., 2005*].

In all cases the likely source is release from the exposed salt pans or sea ice by the "Bromine Explosion" mechanism.

Open questions

i) Most important questions

What is the global and regional significance of this release process? This includes the following additional questions: Are reactive halogens, in particular BrO, released from all salt lakes (or salt pans) or is the phenomenon only occuring at specific salt lakes? What is the source strength per unit area of salt lake (salt pan)? To what extent are the released reactive halogens reaching the free troposphere?

ii) Important questions

What are the details of the release process: Is actually the bromine explosion mechanism active? Are reactive halogens always released from dry salt, if so, why not from the lake surfaces? Is there a possibility of involvement of bacteria in I_2 formation in the brine [*see Amachi et al., 2005*]?

iii) Further questions

What is the significance of the topography (deep valley like the Dead Sea)? What is the importance of meteorological parameters (e.g. nighttime inversion)? How much ClO and IO is actually being released? Is there an abiotic formation mechanism for iodine? Are there interactions between the halogens like the reaction of BrO + IO $\rightarrow$ Br + OIO? Is the release of halogens limited to salt lakes or is it also possible from salty soils/evaporate deposits like Lake Aral (note that BrO has been observed over the Caspian Sea)? Is the release of halogens important for halogen ratios in salt deposits; are there links to geochemistry that would allow conclusions on paleo-climate (compare the vertical salt profile in salt lake crust observed in Salar de Uyuni)? To what extent can these processes be observed from satellites, (relatively high spatial resolution required)? What is the role of wind-blown (salt containing) dust as

reactive surface (see also section 2.4.3)? What is the night time chemistry at salt lakes (salt pans) in view of the laboratory results on non-photochemical release of halogens from halides?

Initiatives that would improve current understanding:

- Laboratory studies to investigate the release of halogens from salt deposits for the temperature and pollution range observed over salt lakes/deposits.
- Perform "in-situ smog chamber" experiments (e.g. "tent" over salt surface).
- Statistical analysis of existing satellite observations.
- Make use of new satellite instruments with increased resolution (e.g. OMI).
- Joint field and model experiments in the Dead Sea basin to understand the chemistry as a function of distance (and therefore time) from the likely release points.
- Use numerical models to test our understanding of the involved processes, taking the orography (esp. Dead Sea) into account.

2.3) Marine boundary layer

2.3.1) Coastal regions

Current knowledge

Coastal regions have significance for halogen-related chemistry for two main reasons. First, macroalgae are often abundant which are strong emitters of reactive halogen compounds. Due to the sometimes extensive presence of macroalgae at coastal regions, the emissions are several times higher than over the open ocean [*e.g. Carpenter et al., 1999, Quack and Wallace, 2003*]. In the case of iodine, massive bursts of new iodine-containing particles can be formed during daytime low tide [*e.g O'Dowd et al., 1998, 2002a,b*]. Extensive field deployments at Mace Head, Ireland, and associated laboratory work have revealed that this particle formation is associated with the emission of molecular iodine (I_2) and organic compounds such as diiodomethane (CH_2I_2) and their subsequent photolysis in the atmosphere [*Carpenter, 2003; McFiggans et al., 2004; Saiz-Lopez and Plane, 2004*]. The resulting atomic iodine reacts with ozone to yield iodine monoxide (IO) that self-reacts to form iodine dioxide (OIO) which is thought to play a major role in cluster formation and particle nucleation which occurs most likely in "hot spots" [*Hoffmann et al., 2001, O'Dowd et al., 2002, Jimenez et al. 2003, Burkholder et al., 2004, Saiz-Lopez et al., 2006b, Pechtl et al. 2006*]. Iodine oxides have been detected at Mace Head, Ireland [*e.g. Alicke et al., 1999*], in Brittany, France [*Peters et al., 2005*], Tenerife, Canary Islands, at Cape Grim, Tasmania [*Allan et al., 2000, 2001a*], and at Appledore Island, Bay of Maine [*Pikelnaya et al.,*

2005]. Recent thought is that OIO reacts to form higher oxides, leading to cluster formation and particle nucleation. The second characteristic of coasts is that they provide an interface between marine halogen emissions and anthropogenic pollutants, allowing the interaction of halogens with NO_x to form halogen reservoir species, and with acidified aerosol which can enhance halogen recycling and hence the rate of halogen activation.
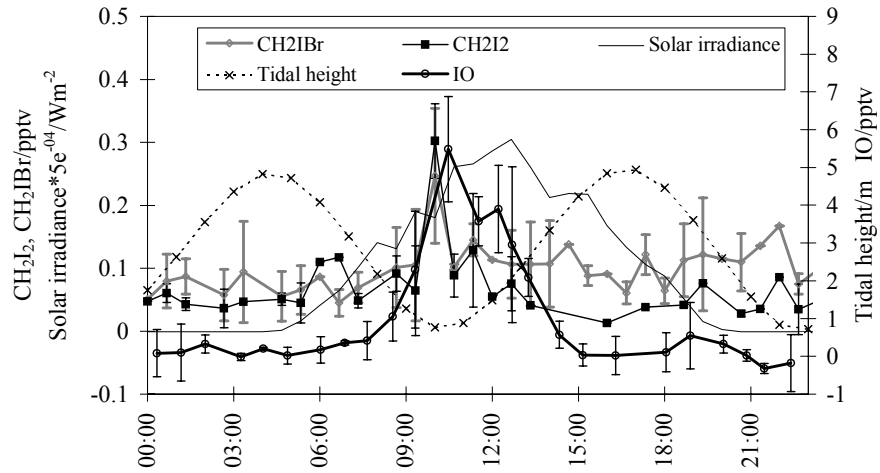

Figure 8. The main requirements for iodine oxide formation in coastal regions: iodine precursors, low tide, and sun light (Carpenter et al., 1999).
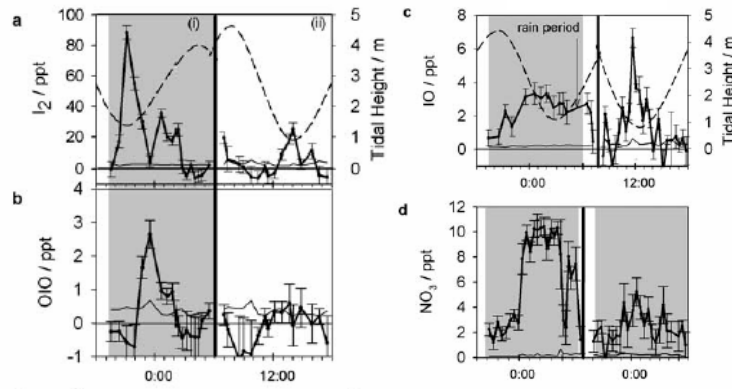
Figure 9. Iodine compounds (I_2, OIO, and IO) and NO_3 radicals at Mace Head (Saiz-Lopez and Plane, 2004).
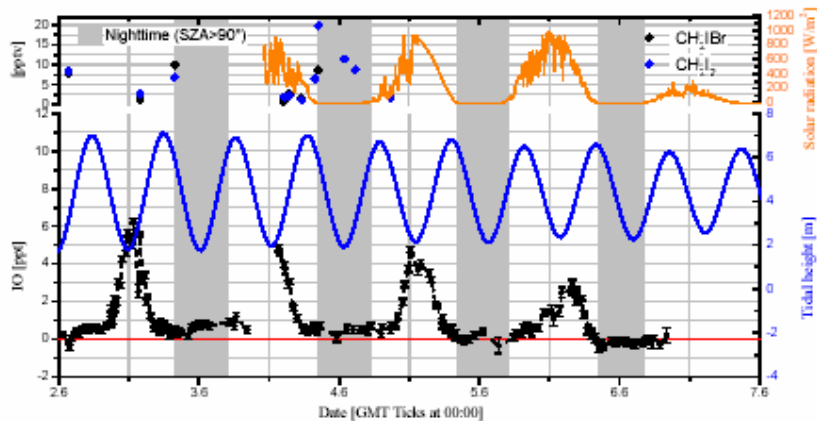
Figure 10. Time series for IO in Brittany 2003 Brittany. The blue line indicates the tidal height and grey shaded areas indicate dark conditions (SZA > 90°, Peters et al., 2005).

The recent detection of up to 6 ppt of BrO at Mace Head was the first for coastal regions [*Saiz-Lopez et al., 2004a*], its presence can also be inferred from measurements at Hawaii [*Pszenny et al., 2004*]. Chlorine compounds have been measured at several locations [*Pszenny et al., 1993, 2004, Keene et al. 2004*] with Cl_2 mixing ratios during night of up to 150 ppt on Long Island, USA [*Spicer et al., 1998*]. In later publications they also report the likely presence of Br_2 at this site [*Foster et al., 2001, Spicer et al., 2002*]. It has been postulated that NO_x and OH reactions with sea salt (especially on the interfaces) can lead to the release of chlorine near coastal cities [*Finlayson-Pitts et al., 1989, Knipping et al., 2000, Knipping and Dabdub, 2003*].

Furthermore, coastal salt marshes have been shown to emit significant amounts of a variety of organic halogens [*Rhew et al., 2000, Yokouchi et al. 2000, 2002 and Lee-Taylor et al. 2001*].

Open questions

i) Most important questions

The most important scientific question is the regional and global importance of the halogen events in coastal regions, where a clear distinction has to be made between the regional impacts for remote coastal regions and for coastal cities.

ii) Important questions

Further important questions include the investigation of the significance of the new particles formed in coastal areas for radiative transport and atmospheric photochemistry. What are the most relevant gaseous iodine precursors? What are the formation and growth mechanisms for the new aerosol particles? There appear to be important differences between Brittany, Mace Head, and Appledore Island in this regard which leads to the next question: How representative is Mace Head, the location where the majority of studies have

been conducted to date? Furthermore, what is the temporal and spatial scale of the iodine events, how heterogeneous are sources of reactive halogens? What are the details of I_xO_y kinetics? What's the relative importance of biogenic compounds vs. sea salt aerosol as a source for inorganic bromine and chlorine?

iii) Further questions

The details of new particle formation as well as: "when, where, what triggers it?" remain to be explored. What are the production mechanisms of the iodine precursors and what are the final sinks for iodine? What are the interactions between new particle formation and iodine photochemistry? Is I_2O_2 present in the marine boundary layer? What are the spatial distributions of coastal reactive iodine precursors in the horizontal and vertical and how does this relate to their effects on the atmosphere? Is I_2 volatilised from the ocean surface or just from seaweeds? What is the influence of the presence of large amounts of fresh sea salt aerosol in the surf zone? Are the aerosols being acidified rapidly enough to be able to release bromine and chlorine via acid-catalyzed pathways or do they mainly act as scavengers for gas phase acidity? Is there release of halogens by other processes like reaction of nitrogen oxides or surface reactions?

What are the mixing ratios of Br_2, Cl_2, and BrCl in coastal areas, especially in coastal cities and what are the impacts on O_3, HO_x, NO_x and other air pollutants? How important is nighttime halogen chemistry, for example involving $ClNO_2$? Do interactions between NO_x, O_3, OH with sea salt aerosol play a role especially for polluted coastal regions?

Initiatives that would improve current understanding:

- Flux measurements of iodine compounds in coastal areas.
- More locations for coastal investigations.
- Increase the spatial resolution to gain 2D/3D info on patchiness of sources and IO/particle clouds.
- Polluted cities: measure chlorine (bromine, iodine) in the gas and aerosol phase with increasing distance from coast.
- Lab: what is the iodine flux (in I atoms) needed for new particle formation?
- How are the I precursors produced (lab, marine reaction chambers)?
- What are the final sinks for iodine?
- Retrieval of IO from satellites (e.g. SCIAMACHY).
- Use several instrumental techniques in parallel (e.g. DOAS, CRDS, denuder, mist chamber, AMS, cascade impactor) at the same location to comprehensively characterize multiphase halogen speciation.
- Use process and local/regional 3D models to investigate the importance of "hot spots" and the development of plumes with new particles and iodine compounds downwind of the coastline.

2.3.2) Open ocean

Current knowledge:
In contrast to coastal and polar regions, evidence for the presence of reactive halogens over open oceans at levels that may affect the ozone budget and the cycles of other elements is limited and mostly indirect. The broadest evidence for active halogen chemistry occurring in the open ocean MBL is the nearly universal depletion of Cl and Br and enrichment of I relative to seawater exhibited by the predominantly supermicrometer sea-salt aerosol [*e.g., Moyers and Duce, 1972; Rancher and Kritz, 1980; Graedel and Keene, 1996; Sander et al., 2003, Baker 2005*]. These departures can be only partly explained by acid displacement or redox processes that do not involve halogen radical chemistry or multi-phase reaction cycles; processes causing iodine enrichment are very uncertain.

Post-sunrise O_3 depletions that have been observed in the boundary layer ("Sunrise Ozone Destruction") at two marine sites [*Nagao et al, 1999, Galbally et al., 2000*] and over the North Pacific [*Watanabe et al. 2005*] might be indicative of halogen chemistry [*von Glasow et al., 2002a*].

Estimates of the concentrations of atomic Cl have been made with the hydrocarbon-clock technique and inferred from the ^{13}C/ ^{12}C ratio in CH_4 and yielded values between 10^3 – 10^5 atoms cm^{-3} [*Pszenny et al., 1993; Rudolph et al., 1996, 1997, Singh et al., 1996a,b; Wingenter et al., 1996, 1999, 2005, Platt et al., 2004, Allan et al., 200b, 2005*]. Numerous data for volatile inorganic Cl (i.e., not specific for HCl) have been published that are based on measurements with filter packs [*e.g., Rahn et al., 1976; Berg and Winchester, 1977*], denuders [*Vierkorn-Rudolph et al., 1984*] or tandem mist chambers [*e.g., Pszenny et al., 2004*]. These data indicate that HCl dominates the inorganic gaseous Cl pool and that mixing ratios in open ocean areas are of order 50-200 ppt. Neither HBr nor HI has been measured specifically anywhere in the MBL. Non-specific measurements of total volatile inorganic Br and I [*e.g., Moyers and Duce, 1972; Rancher and Kritz, 1980; Pszenny et al., 2004*] suggest upper limits of about 10 ppt. Models predict that HOBr and HBr are the most abundant inorganic Br gases during day and Br_2 and BrCl during night [*e.g., von Glasow et al., 2002a*] while HOI is probably the dominant inorganic I gas under open-ocean conditions (low organic I compound levels) [*e.g., O'Dowd et al., 2002b*]. O'Dowd et al., 2002b also suggested that over the open ocean iodine oxides might help overcoming kinetic limitations for the growth of clusters to aerosols of detectable size.
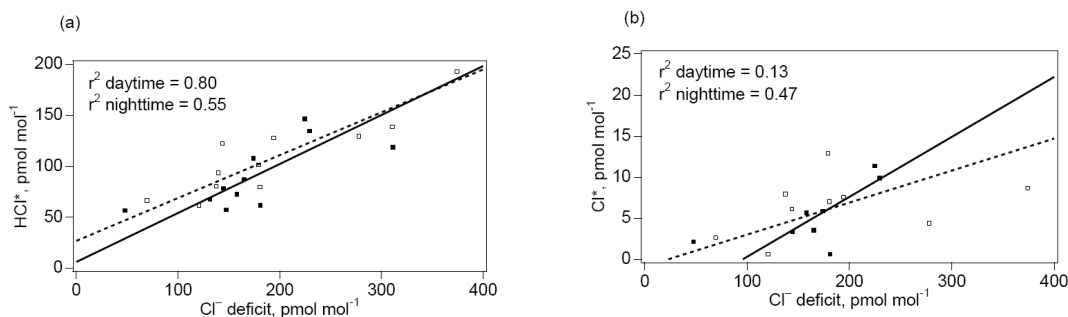
Figure 11. Mixing ratios of HCl (a) and Cl (b) averaged over impactor sampling intervals plotted against corresponding measured particulate Cl− deficits summed over all impactor stages (daytime: open squares; nighttime:solid squares; Pszenny et al., 2004).

The presence of BrO has been inferred from differential optical absorption spectrometry (DOAS) measurements in open-ocean surface air at Hawaii [*Pszenny et al., 2004*]. BrO has been quantified at mixing ratios of 1.0 to 2.5 ppt over the eastern subtropical North Atlantic [*Leser et al., 2003*]. Model calculations have shown that BrO mixing ratios below the current detection limit of optical instruments of about 0.5 ppt can have a significant impact on photochemistry, especially O_3 and DMS [*Toumi, 1994, von Glasow and Crutzen, 2004, von Glasow et al., 2004*]. The only measurements of iodine oxides that might reflect open ocean conditions have been made by DOAS at Tenerife, Canary Islands and Cape Grim, Tasmania at average daytime levels of about 1 ppt with maxima up to 4 ppt [*Allan et al., 2000*]. Allan et al. [2001] reported measurements of OIO at Cape Grim.

No direct measurements have been reported for any of the hypohalous acids despite their importance, particularly with respect to the roles of HOCl and esp. HOBr in the 'bromine explosion' mechanism.

The principal precursors for reactive Cl and Br are Cl^- and Br^- in the sea salt aerosol [*e.g., Finlayson-Pitts, 2003*]. Reactive I, in contrast, is derived mainly from organic I compounds produced in and emitted from the ocean [*e.g., Carpenter, 2003*] and possibly from I_2 [*Saiz-Lopez and Plane, 2004, Saiz-Lopez et al., 2006a*]. CH_3I is usually most abundant (at ~0.5 to ~3 ppt) but is less important as a source than more photolabile compounds such as CH_2I_2 (~0.05-0.5 ppt) and CH_2IBr ~0.05-0.10 ppt). It is important to note that of all these compounds, only CH_3I has been measured on a regular basis in open ocean locations. C_2H_5I has been observed in Asian seas [*Yokouchi et al, 1997*] and CH_2ICl in the Atlantic [*Carpenter, talk at HitT workshop, 2004*]. Other organic halogens like $CHBr_3$ are released at least from some open ocean regions [*e.g. Quack and Wallace, 2003*] and might be a source for inorganic bromine in the free troposphere [*e.g. Warwick et al., 2006*]. Amachi et al. (2005) isolated iodide-oxidizing bacteria in natural gas brines but also in sea water, the products were found to be I_2, CH_2I_2, and CH_2ClI.

Evidence from laboratory and modeling studies suggests that surface reactions may have important influences on MBL halogen chemistry [*e.g. Knipping et al., 2000*].

Open questions:

i)   Most important questions

What are the typical concentrations of halogen radicals (Cl, BrO and IO) over the open ocean and how do they vary with location, altitude, season and time of day? What are the production mechanisms and sea-to-air fluxes of gaseous halogen radical precursors (e.g., alkyl halides, X_2, XY, etc.)?

ii)   Important questions

How do halogens affect new particle formation and CCN formation and growth over the open ocean and what are the links to sulfur, organic and other condensable compounds? Is aerosol pH low enough over the open ocean to allow halogen activation (especially in unpolluted regions with high sea salt production)? Are NO_X oxidation products mainly responsible for acidifying sea salt and, if so, what are the NO_X sources over the open ocean? Is there an influence of I_XO_Y on growth of thermodynamically stable clusters (TSC)? What is the speciation of gaseous and particulate iodine? How do surface reactions affect the cycling of halogens and other key elements such as N and S? What's the relative importance of biogenic compounds vs. sea salt aerosol as a source for inorganic bromine and chlorine?

iii) Further questions

What is the speciation of halogens: XNO_2, $XONO_2$,HOX, X_2, XY? Are organic molecules important to "titrate" reactive halogens [*see idea by Toyota et al., 2004*]? Are there enough gaseous iodine precursors over the open ocean to lead to new particle formation like in coastal regions? A prerequisite for this and other questions is to improve our knowledge of the distributions and fluxes of alkyl halides. What is the importance of Cl for destruction of alkanes? Are there links between halogens and mercury as have been observed in the polar-regions? What are the interactions between I_2, organic material, and organic and inorganic iodine in seawater? Is there a tropical "hot spot" of alkyl halide emission? What is the reason for the observed and largely varying ratios I^-/IO_3^- ratio in aerosols? Is the incorporation into sea-salt aerosol of surfactant organic material from bulk seawater and the surface micro-layer important for the release (or delay thereof) of halogen from sea salt? Are halogens emitted from the combustion of fossil fuels by ships at sea? What is halogen content of bunker oil?

Initiatives that would improve current understanding:

- Design and conduct field studies to capture the expected variability ranging from very clean regions with high sea salt loadings (e.g.

Southern Ocean) to polluted areas with low sea salt loadings (e.g. off eastern Asia and eastern North America).

- Increase the number of marine stations with long time series to cover the range of atmospheric conditions: a) sites influenced by continental dust (e.g. Cape Verde); b) sites influenced by significant upwind anthropogenic pollution (e.g., Bermuda or N-Pacific); c) sites with long upwind fetch over open ocean; generally unaffected by significant anthropogenic emissions (e.g., Hawaii or stations in the Southern Ocean). Increase the number of halogen relevant measurements at existing sites (e.g. Cape Grim). Can available time series be used as proxies for halogens?
- Develop ship-going instrumentation to measure halogens, especially halogen oxides on the open ocean with detection limits of the order of 0.1 ppt.
- Develop techniques to measure hypohalous acids.
- Speciation of aerosol iodine: do more field studies in different locations to understand the relative importance of I^-, IO_3^- and other iodine reservoirs in the aerosol.
- To investigate if there is an influence of iodine on new aerosol particle formation (via I_xO_y rapidly increasing the size of TSC, see O'Dowd et al., 2002) model calculations should be performed to quantify how much I_xO_y would be needed and field studies should be designed in order to find out if iodine oxides are present at these levels.
- Study the fluxes and production pathways of organic precursors in biologically active and inactive regions.
- Measure the aerosol pH and gas phase acids under situations representative for large ocean regions, esp. in regions remote from combustion sources like the Southern Ocean.
- Continue use of process models (0D, 1D) with the latest kinetic information and develop regional and global 3D models to examine the relevance of the aforementioned processes on various scales.

2.4) Halogens in plumes

2.4.1) Volcanic plumes

Halogens are well known constituents of volcanic gases [*e.g. Sugiura et al. 1963, Oppenheimer et al. 1998*] with Br/Cl ratios ranging from $5 \cdot 10^{-4}$ to $6 \cdot 10^{-3}$ [*Kraft and Chaigneau 1976, Gerlach 2004*]. However, it was assumed that the bulk of these gases would be hydrogen halides (HCl, HBr), which should be readily removed from the plume due to their high water solubility, thus they would only have local effects (except for major eruptions, where the plume would reach the stratosphere).
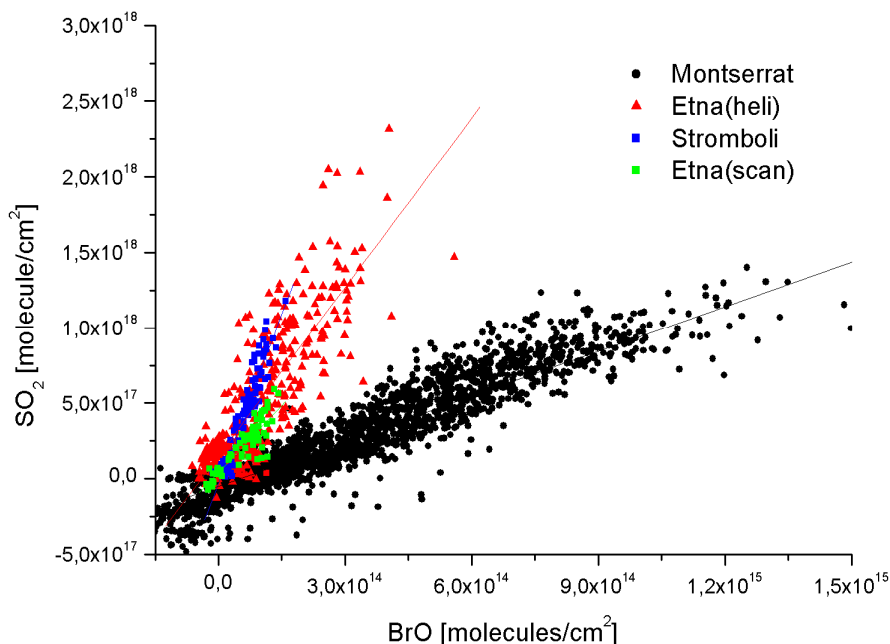
Figure 12. Correlation of the slant column densities of BrO and SO$_2$ in the plume of the Soufriere volcano on Montserrat, Stromboli and Mt. Etna (Bobrowski and Platt, 2006).

Only very recently it became clear that reactive halogen compounds like BrO, and possibly ClO can be quite abundant in volcanic plumes [Bobrowski et al. 2003, Gerlach 2004, Bobrowski and Platt 2006, Oppenheimer et al., 2006]. So far BrO has been detected in the plumes of Carribean, Southern American, as well as Italian volcanoes, where strong, though varying, correlations with SO$_2$ were observed [*Bobrowski et al. 2003, Bobrowski et al., 2006].* Satellite observations with GOME and Sciamachy could not detect enhanced BrO or strong BrO to SO$_2$ correlations on the scale of the satellite pixels [*Afe et al., 2004*], the new instrument OMI with significantly improved spatial resolution, however, did identify a BrO plume originating from a volcano [*Kuroso et al., 2005*]. Presently it is unclear, however, whether reactive halogen species are produced by high-temperature reactions during emission or subsequently by photochemistry in the plume but first comparisons between meaurements, kinetic, and thermodynamic model calcuations indicate that photochemistry dominates [*Bobrowski et al., 2006*].

In any case, as soon as ambient air and thus ozone mixes into the plume photochemical production of radicals will start and probably lead to a series of chemical processes. In particular the atmospheric residence times of halogen oxide radicals are much longer than those of the hydrogen halides, thus volcanoes could influence atmospheric chemistry over large areas, moreover, they could have yet unknown effects on the atmosphere. Central questions in this context are the physico-chemical processes in volcanic plumes.

In volcanic plumes very unique conditions can be encountered:
- High concentration of particles and thus a large surface available for (heterogeneous) chemical reactions.

- High levels of acids (H_2SO_4, HCl), thus low pH.
- High humidity (in the initial phase).
- Elevated temperatures (in the initial phase).
- Presence of reactive bromine and possibly chlorine.

The consequences have not been systematically explored to date, however it is likely that high levels of free radicals (OH, halogen atoms, halogen oxides) can be produced, which lead to regional ozone destruction and possibly to the formation of species not synthesised elsewhere in the atmosphere. In particular it is well possible that volcanoes provide an important contribution to free tropospheric bromine [*see Van Roozendael et al., 2002, von Glasow et al, 2004*].

Open questions

i) Most important questions

What is the total global source strength for reactive halogen species emitted by volcanoes? What are the details of the chemistry within a volcanic plume with respect to emission and transformation of halogen species?

ii) Important questions

What is the importance of high temperature chemistry of halogens during emission and of entrainment of ambient air into volcanic plumes? What is the regional loss of ozone in volcanic areas? Are other reactive halogens present in plumes as well?

iii) Further questions

What are NO_X – levels in volcanic plumes, is there a possible NO_X – formation at hot lava surfaces? Is formation of halogen containing organic species (like CH_3Br) occurring in volcanic plumes? How widespread are halogen emissions from volcanoes globally? Are only certain volcanoes emitting halogens? What are the halogen precursors especially oxidized vs. reduced compounds? How fast is plume chemistry? Plume chemistry as function of time/distance from crater. Can halogen emissions generally be scaled to SO_2?

Initiatives that would improve current understanding:

- Establish a network for long-term monitoring of volcanic emissions, in particular for halogen species.
- Study the evolution of volcanic plume chemistry at several points downwind the plume. Probably this has to be performed by ground based (possibly plus satellite) remote sensing techniques.
- Use satellite observations with increased spatial resolution and statistics of satellite observations for analysis of BrO.

- Characterize the halogen speciation (ratio of reactive/unreactive halogen species).
- Laboratory studies and literature search for high temperature oxic and anoxic halogen reactions.
- Study amount of NO_X produced at hot surfaces in/near volcanoes.
- Study of the oxidation of mercury species due to halogen initiated reactions in volcanic plumes (gas and aerosol phase).
- Conduct detailed model studies of the processes in volcanic plumes to test if our current understanding of the physical and chemical processes is complete.

2.4.2) Biomass burning plumes

Current knowledge

The role of reactive halogens in the chemical evolution of biomass-burning plumes is very poorly constrained. Chlorine is a major elemental constituent of important fuel types including savanna grasses, agricultural waste, and cow dung (typically ranging from 1 to 10 g kg^{-1} dry weight) and the corresponding Cl/Br ratios are similar to that in surface seawater [*e.g., Lobert et al., 1999; Keene et al., 2006*]. Most halogens associated with vegetation are emitted to the atmosphere during combustion [*e.g., Andreae et al., 1996; McKenzie et al., 1996*] and available, albeit limited, evidence suggests that inorganic volatile- and particulate-phase species dominate these emission fluxes [*Lobert et al., 1999; Keene et al., 2006*]. There is only one study that investigated reactive halogens in fresh biomass-burning exhaust in detail [*Keene et al., 2006*]. Their major findings are that most volatile inorganic Cl is associated with compounds other than HCl (presumably Cl_2 and HOCl) suggesting that, like other inorganic acids, HCl in aged plumes originates primarily from secondary reactions rather than direct emissions. To provide perspective, N contents of these vegetation types in southern Africa are about 4 times greater than those of Cl [*Keene et al., 2006*] but about half of this N is emitted as unreactive N_2 [*Kuhlbusch et al., 1991*]. The emission factors (g species emitted / kg dry wt. fuel burned) for NO are generally greater than those of inorganic Cl (volatile + particulate) by a factor of about 4 but the ranges overlap [*Keene et al., 2006*]. Because biomass-burning plumes contain high concentrations of inorganic halogens, acids, particles, and water, it is reasonable to hypothesize that halogen activation and multiphase cycling analogous to that in the MBL would proceed. The relative importance of these processes in the chemical composition and evolution of air influenced by biomass-burning emissions is virtually unexplored but could be significant.

Open Questions

i) Most important questions

What is the halogen content of the major biomass types that burn globally? What are the regional and global source strengths of major inorganic halogenated species emitted during biomass burning? What is the speciation

and multiphase chemical evolution of inorganic halogens in biomass-burning plumes?

ii) Important questions

Does the chemical processing of halogens in biomass-burning plumes significantly influence the cycling of other atmospheric species?

iii) Further questions

Are lab measurements of inorganic halogen release representative? Can halogens be of importance under these conditions and maybe lead to O_3 production like in polluted cities? Can halogen emissions from biomass burning be scaled to other gases, for example CO? What is the variability of the halogen content in the fuel? What is the ratio of inorganic vs. organic halogen emissions, are findings for chlorine (mostly inorganic other than HCl, i.e. Cl_2) extendable to other halogens? Can chemical composition of biomass burning plumes be characterized from satellites?

Initiatives that would improve current understanding:

- Measurements of the halogen (Cl, Br, and I) contents of major biomass types and the corresponding speciated emission factors over representative ranges of burn conditions.
- Develop regional and global burn models that are capable of simulating speciated halogen emissions as functions of burn conditions and the corresponding elemental contents of fuels.
- Measure time-series of halogen speciation in the vapor and particulate phases in parallel with related reactant and product compounds in aging biomass-burning plumes.
- Develop chemical models for biomass-burning plumes that include halogen activation chemistry.

2.4.3) Dust plumes

Current knowledge

Although crustal dust is a major component of aerosol mass on a global scale, influences vary substantially over seasonal, annual, and decadal time scales and are limited spatially to regions downwind from large arid land masses such as north central Asia and the Sahara [*e.g. Prospero et al., 1981*]. Dust scatters and absorbs incident solar radiation [*e.g. Li et al., 1996*] and is also an important source of trace elements in the MBL and surface waters of the western Pacific and equatorial Atlantic Oceans [*e.g. Arimoto et al., 1997*]. The availability of crustal Fe via atmospheric transport and deposition limits phytoplankton production in many marine regions remote from dust sources [*Boyd et al., 2000*]. Much atmospheric dust originates in arid but seasonally wetted regions subject to evaporative concentration of salts at the air-land

interface. Consequently, fresh atmospheric dust is typically enriched substantially in halogens relative to earth's crust [*e.g. Adepetu et al., 1988; Graedel and Keene, 1996*].

The chemical processing of mineral aerosol through the atmosphere is poorly understood but potentially very important. Available evidence indicates that multiphase reactions involving S and N compounds at mineral surfaces produce concentrated aqueous coatings [*Dentener et al., 1996*]. The associated removal of aerosol precursors and titration of atmospheric acidity have important implications for the chemical evolution of the multiphase system. In addition, cloud processing may lead to internal mixtures of dust with other aerosol types [*Andreae et al., 1986; Anderson et al., 1996*]. Reaction chamber experiments reveal significant Cl_2 production from photochemical transformations involving metal oxides and HCl in the presence of water [*Behnke and Zetzsch, 1989*], with potential implications for O_3 and S cycling, aerosol production, other important chemical processes in the multiphase MBL system [*e.g. Keene et al., 1998*]. It is reasonable to hypothesize that analogous activation reactions involving both crustal halogens and the recycling of halogens from other sources (marine, industrical, etc.) occur in acidic aqueous films coating aged crustal aerosol.

Open questions

i) Most important questions

What are the regional and global source strengths of major inorganic halogenated species emitted associated with dust and what is their relevance on a regional and global scale? What is the speciation and multiphase chemical evolution of inorganic halogens in aging dust plumes?

ii) Important questions

What is the halogen content and speciation of fresh dust in major source regions? Does dust act as a source/recycler of halogens? Are deposited halogens relevant for recycling or release processes and the ground/in the ocean surface layer?

iii) Further questions

What is the chemical composition and pH of aqueous coatings on aged mineral aerosol as a function of radiation, RH, exposure to combustion products, and exposure to marine air. What is the relative importance of transformations involving metal oxides versus conventional pathways in activating halogens in dust plumes. Does the chemical processing of halogens in dust plumes significantly influence the cycling of other atmospheric species? Are there dust–sea salt interactions leading to the recycling/release of halogens?

Initiatives that would improve current understanding:

- Quantify the halogen content and speciation of fresh atmospheric dust over major source regions.
- Reliably characterize the halogen content and speciation of individual dust particles in the MBL (this will require the development of new techniques for analyzing individual super-µm aerosols; see below).
- Simultaneously measure the chemical composition of major classes of aerosols in dusty regions downwind from major source regions (mineral dust, sea salt, combustion-derived aerosols, and internal mixtures) and mixing ratios of reactive trace gases with which they are chemically coupled. Apply thermodynamic relationships to infer the pH of aqueous coating on dust over relevant ranges of inferred water contents.
- Develop models of dust cycling air that consider halogen activation chemistry involving both conventional pathways and metal oxides.

2.5) Free troposphere

Current knowledge

The comparison of ground-based, balloon- and space-borne DOAS measurements and a stratospheric model, as well as the diurnal variation of ground based BrO column measurements indicate that a global background of BrO might be present in the troposphere with vertical columns of $1\text{-}3 \times 10^{13}$ molec cm^{-2} [*Fitzenberger et al., 2000, Wagner et al., 2001, Van Roozendael et al., 2002, Richter et al., 2002, Hollwedel et al., 2004*]. Direct evidence for free tropospheric BrO in the Arctic comes from balloon [*Fitzenberger et al., 2000*] and high altitude aircraft observations [*McElroy et al., 1999*]. Schofield et al. (2004) reported ground based measurements from Lauder, New Zealand (45°S) showing vertical tropospheric BrO columns of $0.2\pm0.4 \times 10^{13}$ molec cm^{-2}. Observations like this have not yet been published for lower latitudes. All observations are consistent with a free tropospheric BrO mixing ratio of about $0.5 - 2$ ppt.

The sources of RHCs for the free troposphere include: breakdown of CH_nX_m, halogens released from sea salt and transported into the FT, downward mixing of inorganic halogens from the stratosphere esp. in tropopause fold regions, volcanoes, upward transport from "ozone depletion events" in the polar boundary layers during spring ("spillout"), biomass burning, crustal dust but a quantification of these processes remains to be made.

Global 3D studies with chemistry transport models [*von Glasow et al., 2004, Yang et al, 2005*] showed that BrO mixing ratios of $0.5 - 2$ ppt can have a significant impact on the photochemistry by reducing photochemical ozone production and increasing its destruction (zonal annual mean: up to 18% reduction of O_3, regionally up to 40%). Yang et al., (2005) could reproduce BrO columns of up to 1.6×10^{13} molec cm^{-2} using only organic bromine and sea salt aerosol as precursors in their global CTM.
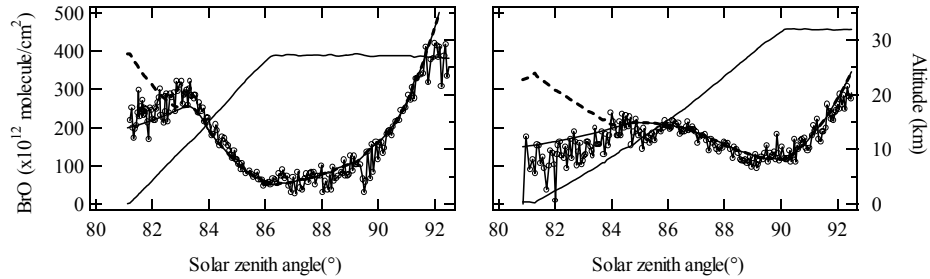
Figure 7. BrO slant columns during balloon flights on 02/03/98 at 69°N (left) and 11/08/98 at 68°N (right) together with balloon altitude. Solid line: model simulation for 0 ppt, dashed line: simulation for 2 ppt tropospheric BrO (Pundt et al., 2002).
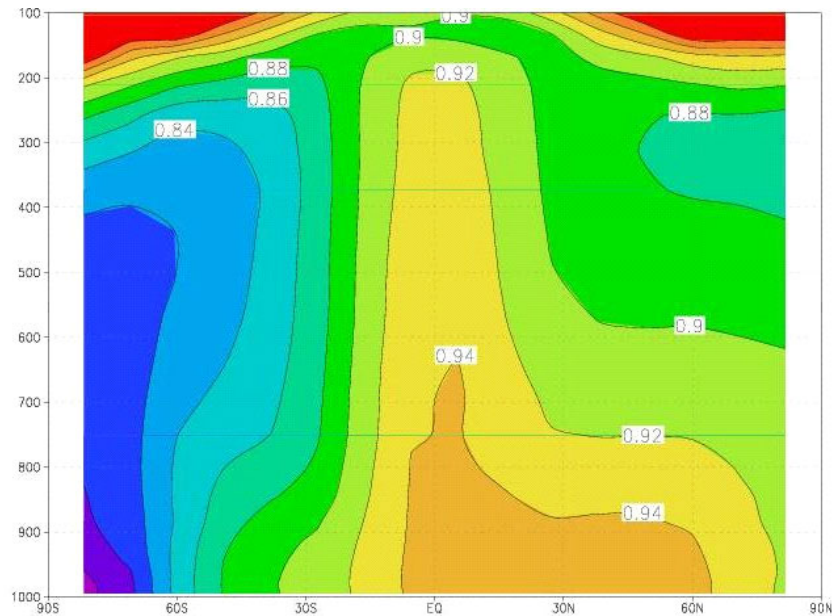
Figure 8. Ratio of O$_3$ in a model run with bromine chemistry to O$_3$ in a model run without bromine (zonally and annually averaged, ordinate is the σ-level multiplied by 1000 which is approximately the pressure in hPa and the abscissa is latitude in degrees.; von Glasow et al, 2004).

Open questions

i) Most important questions

The most important scientific question is how much X and XO (mainly BrO and Cl) is present in the free troposphere and what is the spatial and temporal distribution? The effect on O$_3$/oxidation capacity in the FT is probably globally the most important of all domains, but this has to be verified.

ii) Important questions

The strength and relative importance of the above mentioned halogen sources have to be quantified. How important are dynamics in this?

iii) Further questions

How important is the recycling on aerosols, cloud droplets, and ice particles?

Initiatives that would improve current understanding:

- Airborne measurements of halogens in free troposphere, esp. halogen oxides. Extension of these measurements to lower and southern latitudes.
- Further comparison of stratospheric BrO from models with total vertical column density from satellites.
- Compare stratospheric BrO profiles from satellites (SCIAMACHY, OMI etc.) with total vertical column density.
- Derivation of source inventories for organic precursors [*see e.g. Warwick et al., 2006]* and other source mechanisms (outflow of marine and polar boundary layers).
- Extension of ground based (e.g. direct sun and MAX-DOAS) measurements to achieve a greater temporal and spatial range of tropospheric BrO data, for example at top and bottom of high islands like Hawaii, Tenerife) to be able to differentiate between BrO located in the BL vs. the FT.

2.6) Other continental sources

2.6.1) Anthropogenic sources

Current knowledge

Anthropogenic sources of halogens include cooling towers, industry, water purification, public and especially private swimming pools, and road salts in winter. In coastal cities (note that many, particularly Mega-Cities are located in coastal environments) sea salt is present in the atmosphere and the polluted air will lead to rapid halogen release due to reactions involving NO_x and gas phase acids. In some areas leaded gasoline might still be in use which contains chlorine but especially bromine.

As described above, active halogen chemistry catalytically destroys ozone. However, under conditions of high NO_x in polluted cities, this loss can be compensated by the enhanced supply of odd hydrogen radicals from the rapid oxidation of alkanes by atomic Cl leading to net ozone production [*Tanaka et al, 2000, 2003, Chang et al, 2002, Knipping and Dabdub, 2003*].

Open questions

i) Most important questions

Quantify the pollution (NO_x) – sea salt interactions. If elevated levels of halogens exist in coastal urban areas (esp. Megacities), are there efficient transport mechanisms to export the halogens to less polluted regions (horizontally) or to the free troposphere (vertical transport including convection and urban heat island effects)?

ii) Important questions

None defined.

iii) Further questions

To our knowledge emissions inventories focusing on toxic compounds including halogens are available only for the USA. Inventories are needed on a global scale for all relevant reactive species, most importantly for XY, HX, HOX, XNO_x. They should include industrial point sources like cooling towers and large scale water treatment plants but also small scale or dispersed sources like private swimming pools, household cleaners, road salt. Are there regions where leaded fuel is still being used? Are there halogen sources from other combustion sources like small planes, ship fuel or during oil refining?

Initiatives that would improve current understanding:

- Prepare inventories of industrial and household emissions of halogens for all regions.
- Measure halogen compounds as a function of distance to the coast to investigate pollution-sea salt interactions in the field.
- Do smog chamber experiments for polluted air with sea salt aerosol (not only NaX) to quantify chemical interactions.

2.6.2) Soils, vegetation

Current knowledge

Several studies found coastal marshes and tropical wetlands to be important emitters for short-lived organic halogens [*e.g. Yokouchi et al., 2000, Rhew et al., 2000, Cox et al., 2005*]. These sources are most likely due to biological processes in the soil and/or root system. Laboratory studies showed that abiotic formation of short-chain organic iodines can also occur [*Keppler et al. 2000*], probably involving oxidation by compounds like Fe(III). Ectomycorrhizal fungi [*Redeker et al., 2004*] and bacteria [*Amachi et al., 2003, 2005*] have also recently been proposed to be of importance for the global methyl halide budget and even oxidation of iodide to I_2. Peatland as a source for organic halogens have been identified by Keppler et al. (2004) and Carpenter et al. (2005).
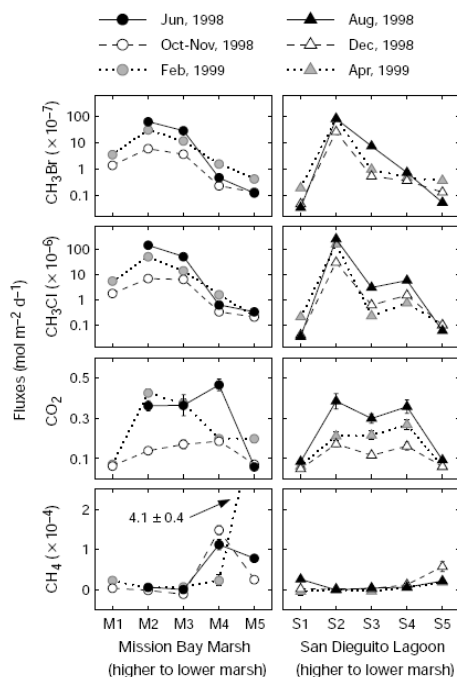
Figure 9. Daytime fluxes of CH$_3$Br, CH$_3$Cl, CO, and CH$_4$ from southern Californian coastal marshes (Rhew et al., 2000).

Open questions

i) Most important questions

What are the global source strengths of these emissions? What is the exact speciation, are shortlived organic or inorganic halogens also produced in these environments? What is the predominant production pathway for organic halogens in forests, soils, peat, swamp, rice paddies: biogenic or abiotic; are only organic halogens being produced? Is there production of short-lived organic and inorganic halogens?

Initiatives that would improve current understanding:

- Inventories of halide content of soils and vegetation to be able to upscale potential emissions.
- Quantify halogen emissions as function of halogen content of soil/vegetation (and other parameters).
- Conduct field studies with instrumentation to measure short-lived organic and inorganic halogens that might emanate from soils or vegetation (e.g. chamber studies).

3) General topics

In this section we list the more general topics that are of importance for all domains like kinetic data and measurement and modeling techniques and strategies.

3.1) Laboratory/kinetic studies

Many important chemical and photochemical processes involving halogen species in the MBL are associated with very large uncertainties, which impedes assessment of their role in e.g. ozone destruction, sulfur oxidation, liberation of sea-salt halides and particle formation. For gas-phase processes involving chlorine and bromine species, the kinetic / photochemical database is in good shape, for iodine species this is not the case. Our understanding of multiphase processes, aqueous phase processes and particle formation has large gaps for all halogens. A number of issues that require investigation in laboratory studies are listed below.

3.1.1) Gas-Phase processes

Chemistry and Photochemistry of OIO

OIO is formed in the IO self-reaction, [*Himmelmann et al.*, 1996; *Bloss et al.*, 2001] and in the reaction of IO with BrO [*Bedjanian et al.*, 1998; *Rowley et al.*, 1998], and has also been observed in the field [*Allan et al.*, 2001]. Its yield in the IO self-reaction, and especially its subsequent fate in the MBL are poorly characterized. Its potential formation in reactions between IO and O_3 or peroxy radicals is inadequately constrained.

Literature values of its absorption cross section in the visible vary by a factor of about 4 [*Himmelmann et al.*, 1996; *Cox et al.*, 1999; *Ingham et al.*, 2000; *Bloss et al.*, 2001]. The latest studies of its photolysis quantum yield (to form I atoms) agree that it is smaller than 0.15 *[Ingham et al., 2000; Joseph et al., 2005, Tucceri et al., 2006]*, however, this number would still be high enough so that photolysis were the main sink for OIO. Likely reactions of OIO in the atmosphere involve the OH radical, NO and other iodine oxides. There are presently no experimental data available for the reaction with OH, for which HIO_3 is the most likely product [*Plane et al., 2006*]. The potential formation of HIO_3 is interesting as it provides a chemical route to aqueous-phase IO_3^-. For reaction with NO a single data set is available [Plane et al., 2006]. Qualitative observations [*Ingham et al.*, 2000; *Bloss et al.*, 2001] suggest that OIO reacts with I_xO_y, but rate constants and products are unknown.

Chemistry and Photochemistry of I_2O_2

Indirect evidence supports dimer formation (I_2O_2) in the IO self reaction [*Sander*, 1986; *THALOZ*, 2005]. This species has never been unambiguously identified spectroscopically though some evidence for absorption in the actinic region has been obtained [*Bloss et al.*, 2001]. Consequently, its yield in the

IO self reaction is highly uncertain. Recent calculations [Plane et al., 2006] suggest that lifetime of IOOI with respect to thermal decomposition is too short for it to be considered as a stable reaction product, and its formation in the IO self reaction may be neglected. The lifetime of IOIO is sufficiently long for it to be detected in laboratory experiments, but short enough (about 1 s) that it will decompose to OIO + I under atmospheric conditions. These calculations need experimental verification. Thermochemical calculations suggest that IOIO is the more stable form [*Misra and Marshall, 1998*].

Photochemistry of $IONO_2$

$IONO_2$ is formed in the reaction of IO with NO_2 and is expected to be an important reservoir of inorganic iodine in the polluted MBL, which is mainly lost by photolysis. The available absorption cross sections of $IONO_2$ diverge by a factor of almost 10 at 300 nm [*Mössinger et al., 2001; THALOZ, 2005*], making calculation of its lifetime, and thus its role in heterogeneous reactions difficult to assess. Unpublished data on the relative quantum yield of the two photolysis product channels is available for a single photolysis wavelength [*THALOZ*, 2005].

Halogen and Sulfur cycles

The halogen-sulfur cycles are coupled in the gas-phase by the reaction of BrO and Cl with CH_3SCH_3. The reaction of IO with CH_3SCH_3 was recently suggested to be fast enough to be significant [*Nakano et al.*, 2003]. More recent examinations of this reaction, however, showed that the previously reported slow rate coefficients are correct [*Gravestock et al., 2005, Dillon et al., 2006*]. Important follow-up reactions of DMSO and esp. MSIA have uncertain product yields which are key to understanding the relative importance of the BrO + DMS reaction under cloud-free conditions, so that further laboratory investigation is warranted. [s*ee discussion in von Glasow and Crutzen, 2004*].

Halogen and Mercury cycle

The strong correlation observed between Hg and O_3 depletion and the anti-correlation between Hg and BrO indicate that either Br or BrO can efficiently remove Hg from the polar troposphere during ODEs [e.g. *Calvert and Lindberg*, 2003]. There are limited kinetic and product studies of reactions of $X/X_2/XO$ with elemental mercury [*e.g., Ariya et al., 2002; Shepler and Peterson, 2003; Balanabanov and Peterson, 2003; Khalizov et al., 2003; Raofie and Ariya, 2003 and 2004*]. At the same time, rapid reduction, followed by revolatilization of elemental mercury at the snow-air interface has been observed [*Poulain et al., 2004*], which merit further studies. One of the major uncertainties lies in lack of knowledge on the primary and secondary reactions leading to oxidized mercury, their chemical nature, and following photo-redox reactions in the snow-air interface which dictates the extent of mercury accumulation. Mercury aerosols are speculated to be formed via halogen initiated oxidation processes, but their chemical nature and their atmospheric fate should be identified through field and laboratory studies.

3.1.2) Multi-Phase / aqueous-phase processes

Iodine compounds

HOI and $IONO_2$ are the most important reservoirs of inorganic iodine. Both are photochemically active, but both can undergo heterogeneous reactions on sea-salt or sulfate aerosol. To date, data is only available for dry salt surfaces, which indicates that liberation of dihalogens takes place [*Holmes et al.*, 2001; *Mössinger and Cox*, *2001*] The relative efficiency of release of ICl (important for chlorine activation) versus IBr (important for initiating a bromine explosion) remains unknown as neither data on aqueous surfaces, nor the necessary aqueous phase equilibrium constants for reaction of ICl and IBr with Br^- / Cl^- are known. ICl and IBr have short photochemical lifetimes, but can be formed at night. Therefore information regarding their accommodation coefficients, solubilities and rate coefficients for reaction with Cl^- and Br^- are necessary, but not available.

There are no data on the interaction (accommodation coefficients, solubility, reactivity) of OIO or I_2O_2 with e.g. sea-salt or sulfate aerosol. These processes will however only be important if photochemical loss is slow.

Particle formation from I_yO_x reactions

The photooxidation of RI leads to particle formation in laboratory experiments [*Jimenez et al.*, 2003; *Burkholder et al.*, 2004]. A potential role of I_2O_2 has been proposed [*Hoffmann et al.*, 2001], but there are presently no measurements of the particle precursors. Further suggestions include particle formation via larger iodine oxide clusters like I_2O_3, I_2O_4, I_2O_5 [*e.g. Pirjola et al., 2005, Saunders et al., 2005*]. Experiments that simultaneously control the gas-phase and measure nucleation and particle formation are required to identify the clusters and derive the hygroscopic properties and growth rates of the particles under atmospheric conditions.

Bromine compounds

$BrONO_2$ is an important reservoir of BrO radicals. It may react with sea-salt aerosol either via hydrolysis (to form HOBr) or directly to form BrCl. If the direct mechanism is important, the uptake of $BrONO_2$ to the ocean surface may be a source of halogen liberation that does not require the presence of aerosols or their acidification [*Sander et al.*, 1999]. The accommodation coefficient and reaction of $BrONO_2$ on aqueous salt surfaces has recently been investigated, [*Deiber et al., 2004*] but the effect of acidity on the activation of halide has not been investigated.

The temperature dependence of many important aqueous phase reactions/equilibria (esp. involving Br_2Cl^-) is unknown. For quantitative studies of polar ODEs this data is crucial.

Halogen and sulfur cycle

The aqueous phase reactions of HOX/OX$^-$ (X=Cl, Br) with S(IV) has been suggested to be of major importance for the atmospheric sulfur cycle [*Vogt et al, 1996, von Glasow et al, 2002b, von Glasow and Crutzen, 2004*]. These model studies, rely however on a single estimation of the rate coefficient and assume the same reactivity for HSO_3^- and SO_3^{2-}. Given the potential importance of this reaction it should be reevaluated and measured for both S(IV) ions.

General aqueous phase points

For many aqueous phase reactions and equilibria involving halogens (esp. XY$^-$, XO$_2^-$, XO$_3^-$) we lack kinetic information. Furthermore, many existing rate coefficients have been measured in systems that are very different in composition from the airborne atmospheric aqueous phase, which is characterised by high ionic strengths and variable pH.

3.1.3) Molecular modeling

Recently, several molecular modeling studies (molecular dynamics and Monte Carlo simulations employing empirical force fields with atomic resolution) have shown that interesting heterogeneous processes can take place at interfaces. For homogeneous gas or liquid phase chemical processes the knowledge of rate constants and transport coefficients is often sufficient. However, for reactions at surfaces of aerosols atomic resolution is important already for qualitative considerations concerning possible heterogeneous processes. Molecular dynamics simulations showed that, contrary to the common wisdom, chloride, bromide, and iodide are present at the surfaces of these aerosols in quantities sufficient for potential heterogeneous chemistry to be plausible [*Knipping et al, 2000, Jungwirth and Tobias, 2001, 2002*]). Recent simulations showed that reactive gases such as O$_3$, OH, HO$_2$, or H$_2$O$_2$ adsorb at the air/water interface, increasing thus the probability of the surface reaction with the halides and other species (*Vacha et al, 2004*).

In the future, molecular simulations can continue to serve as a very useful tool for quantifying distributions of reactive species (such as halide and other ions, or inorganic and organic pollutant molecules and radical) at the air/solution interface of tropospheric aerosols. Simulations can also elucidate basic mechanisms of possible heterogeneous reactions on the surfaces of aerosols and provide thus parameters for atmospheric models.

3.2) Instrument development

3.2.1) Aerosols: Instrument Development and Analyses

Current state of the art

The production of super-µm sea-salt aerosols at the ocean surfaces is the dominant source of inorganic halogens and many other reactive condensed species to the overlying atmosphere. Subsequent wet and dry deposition of aged sea salt is the principal pathway by which many product species enter the surface ocean. Similarly, the production of super-µm crustal dust might be a major source for atmospheric halogens and sink for reaction products in many continental regions. These aerosols are also important media in which atmospheric chemical transformations proceed both in aerosol solutions and on aerosol surfaces. Many reactive trace gases in the MBL can be reliably quantified by various techniques on time scales of seconds to tens of minutes and composition of sub-µm aerosol size fractions can be quantified by aerosol mass spectrometers (AMS) [*e.g. Jayne et al., 2000*], aerosol time of flight mass spectrometers (ATOFMS) [*e.g. Prather et al. 1994*], and particle-into-liquid sampler (PILS) techniques [*e.g. Weber et al., 2001*] on similar time scales; aerosol mass spectrometers is a rapidly expanding field. In contrast, however, characterization of the super-µm aerosol size fractions (with which both reactive gases and sub-µm aerosols are chemically coupled) typically requires sampling with cascade impactors deployed over many hours to a day or more following by extraction and chemical analysis [e.g., Pszenny et al., 2004]. Such techniques obscure temporal variability in the composition of larger size fractions, constrain resolution in deconvoluting chemical dynamics of the multiphase system as a whole, preclude evaluation of internal versus external mixing of similarly sized particles, and exacerbate inherent problems associated with artifact reactions caused by mixing compositionally distinct but similarly sized particles in individual samples [*e.g. Keene et al., 1990*]. In addition to the above, reliable measurement techniques for many non-ionic and reactive-transient species associated with aerosols do not exist. Finally, inlets on most research aircraft do not pass super-µm aerosol efficiently [*Huebert et al., 1990*] and, consequently, vertical distributions of sea-salt and dust composition are very poorly constrained.

Future requirements

The poor temporal and vertical resolution of current measurement techniques for the chemical composition of super-µm-diameter aerosols is a major impediment to progress in resolving the nature and importance of halogen-radical chemistry in air.
What are the vertical profiles of sea-salt size distributions and associated compositions through the MBL over representative ranges of conditions?
What are the diurnal temporal variabilities and external (versus internal) mixing states of super-µm diameter aerosols over representative ranges of conditions?

Are photochemical reactions involving nitrate and marine-derived organic carbon significant sources for reactive transient species in sea-salt aerosols; if so, what are the associated implications for the chemical processing of other species?

What is the speciation of oxidized and particulate mercury compounds (also gas phase) – what fraction, esp. in polar regions, can be associated with halogen cycling?

Initiatives that would improve current understanding:

- Extend the analytical range of current aerosol mass spectrometers and PILS techniques to super-µm as well as to smaller size fractions and/or develop new approaches to reliably quantify the composition of aerosols at high temporal resolution and to determine their internal/external mixing state.
- Develop new and/or modify existing analytical techniques to reliably quantify non-ionic and reactive transient species in marine aerosols and to measure particle pH.
- Develop, rigorously characterize, and deploy inlets on aircraft that efficiently pass super-µm aerosols; quantify vertical distributions in the size-resolved number concentrations and compositions of atmospheric sea salt over representative ranges of meteorological conditions. Also, design instrumentation to measure the spatial (horizontal and vertical) variation of aerosol speciation on the ground (e.g. during iodine related particle production events in coastal regions.

3.2.2) Gases

Current state of the art

Adequate measurement techniques are the key to experimental investigation of reactive halogen species in the atmosphere. While measurement techniques for the relatively non-reactive halogen species like hydrogen halides and organo-halogens have been in existence for quite some time reactive species have been detected in the troposphere only during the recent decade.

Reactive halogen species, in particular Cl- and Br- atoms, IO, BrO, and ClO could be detected by several direct or indirect techniques in the troposphere, both, at polar and mid-latitude sites:

- Active Differential Optical Absorption Spectroscopy (DOAS) of BrO, IO, OIO, I_2, and ClO. This technique is being applied in ground based measurements [*e.g. Tuckermann et al. 1997, Hebestreit et al. 1999, Alicke et al. 1999, Allan et al. 2000, Matveev et al. 2001, Stutz et al. 2002, Saiz-Lopez et al. 2004, 2005, Zingler and Platt 2005*]. Active DOAS identifies and quantifies halogen oxides based on their strong narrow band absorption features in the UV/Vis radiation emitted from an artificial light source.

- Passive Differential Optical Absorption Spectroscopy (DOAS). This technique has been applied from the ground [*Kreher et al., 1997, Frieß et al. 1999, 2001, Hönninger et al., 2002, 2004, Bobrowski et al., 2003, 2006*], from aircraft [McElroy et al. 1999], balloons [*Harder et al. 1998, Weidner et al., 2005*], and from satellite [*Richter et al. 1998, Wagner and Platt 1998, Hegels et al. 1998, Wagner et al. 2001, Hollwedel et al. 2004*].

- Chemical conversion plus Atomic Fluorescence for the detection of XO with detection limits of about 0.1 ppt for BrO and IO and about 0.5 ppt for ClO [*Avallone et al. 2003*].

- 'Hydrocarbon Clock' observations of time - integrated amounts of Cl- and Br- atoms, where the term Hydrocarbon Clock refers to the observation of hydrocarbon ratios in air masses of known chemical age [*e.g. Jobson et al. 1994, Solberg et al. 1996, Ramacher et al. 1997, 1999*].

- Chemical amplification combined with the detection of NO_2 for the measurement of ClO_x by liquid-phase chemiluminescence. The method is commonly used for the detection of HO_x and RO_x radicals, but was also found to be sensitive towards ClO_x (Cl+ClO+OClO) [*Perner et al. 1999*]. ClO_x is converted to Cl by NO. In a reaction chain of known length added CO and NO is oxidised to CO_2 and NO_2 which allows to derive the ClO_x concentration.

- Sampling (mist chamber) and wet chemical detection of reactive chlorine [*Pszenny et al. 1993*]. In the alkaline part of a tandem mist chamber Cl_2 and a fraction of HOCl is trapped and subsequently analysed.

- Detection of Br_2, BrCl and Cl_2 by Atmospheric Pressure Ionization Mass Spectrometry (APIMS) [*Foster et al. 2001, Spicer et al. 1998, 2002*]. Using a chemical ionisation tandem mass spectrometer these molecules can be detected at high sensitivity by selecting specific parent/daughter ions for the respective species.

- Detection of photolysable bromine species (mainly HOBr, BrO) by Impey et al. [1999] using a Photolysable Halogen Detector (PHD) based on the conversion of reactive halogens to chloroacetone and bromoacetone and subsequent GC analysis.

- Detection of the presence of Cl atoms by observing the isotopic ratios of ^{12}C and ^{13}C in CO and CH_4 [*Röckmann et al. 1999, Allan et al., 2001b*]. Since Cl atoms react slower with $^{13}CH_4$ than with $^{12}CH_4$ the ^{13}C depletion in the resulting CO and the isotopical composition of CH_4, respectively, indicates a contribution of Cl atoms (in addition to OH) to CH_4 oxidation.

An emerging and promising technique for the sub-ppt detection of BrO is chemical amplification (by addition of DMS and O_3) combined with the detection of DMSO by chemical ionisation mass spectrometry.

Note, however that there is a number of relevant, reactive halogen species, where no adequate and specific measurement technology exists, these include: HOX (X = Cl, Br, I), $XONO_2$, XNO_2.

Future requirements

- Develop an algorithm for the detection of IO from satellites.
- Develop alternative/new measurement techniques for X, XO, HX, HOX, XY, $XONO_2$, XNO_2, oxidized Hg. Exact speciation will be needed as much as low detection limits. In particular for BrO detection limits well below 1 ppt would be required. The Chemical conversion/ Atomic Fluorescence technique should be deployed in boundary layer studies because it can already reach the required detection limits.
- Design instrumentation to measure high spatial (horizontal and vertical – meter-scale and BL) variation of XO.
- Increase the analytical resolution (detection limit) of (active and passive) DOAS techniques. Improve spectral information on O_4 and O_3 in 350nm region to improve BrO spectral fitting.

3.3) Promising measurement strategies

The following is a list of measurement strategies that are partly already being applied and that we think have potential to further our knowledge

- Do "closure" field campaigns, i.e. try to measure all relevant properties (meteorology and chemistry) at the same time.
- Plan and conduct field campaigns in conjunction with models to facilitate comprehensive interpretation of the results – be aware of the "field-model agreement trap", i.e. a disagreement is sometimes more useful than a "forced" agreement (e.g. by an overly constrained model that does not posses the necessary degrees of freedom anymore).
- Use "satellite" stations around bigger "supersites" in order to provide information about chemical and meteorological air mass history. This requires the existence of small, easily deployable yet comprehensive instrument packages.
- Simultaneous deployment of IC and NAA mainly for sub-micrometer aerosol to compare total particulate bromine with bromide.
- Conduct Lagrangian experiments (maybe using an air ship?).
- Develop/refine instruments that are small, reliable, autonomous, affordable so that they can be deployed in very remote location and in more than one place at a time.
- Ensure that the instrumentation is lightweight enough for airborne deployment, consider the use of tethered balloons.
- Combination of satellite observations with observation from various other platforms.
- Split samples of size-resolved aerosols and analyze by both ion chromatography and neutron activation to quantify the contribution of ionic bromide to total particulate bromine.
- Combine *in-situ* with integrative measurements or tomographic remote sensing instruments to get information spatial heterogeneity i.e. try to achieve synergy from different measurement techniques.

- Try to capture small scale variations especially in coastal regions (see previous bullet).
- Snow pack/sea ice/frostflower composition: do we need new instruments for this? (AICI overlap), ice-robot?
- Develop techniques for "non-contact" measurements (salt lakes, ice fields, algae).
- Use the ratio of DMS to DMSO as indirect evidence for BrO chemistry.
- Coastal iodine studies: Continue using DOAS (I_2, IO, OIO) parallel to in situ instruments like CRDS, denuder-ICPMS, mass specs (X_2), and the chemical conversion/resonance fluorescence instrument (XO).

3.4) Numerical modeling

Current state of the art

Computer models have been written to simulate halogen chemistry in polar regions [*e.g. Tang and McConnell, 1996, Sander et al, 1997, Michalowski et al., 2000, Evans et al, 2003, Lehrer et al., 2004*], in the marine boundary layer [*e.g. Sander and Crutzen, 1996, Vogt et al, 1996, 1999, Stutz et al. 1999, McFiggans et al 2000, Moldanová and Ljungström, 2001 Toyota et al., 2001, Shon and Kim, 2002, von Glasow et al, 2002a,b, Knipping and Dabdub, 2003, Pszenny et al., 2004, von Glasow and Crutzen, 2004*], over salt lakes [*Stutz et al. 1999*], and in the free troposphere [*von Glasow et al., 2004, Lary, 2005, Yang et al., 2005*]. From a meteorological point of view, most of these models are simple box or column (both lagrangian and eulerian) models. So far the main focus has been on chemistry, trying to understand the complex halogen reaction mechanism but first results with CTMs have been published [*von Glasow et al., 2004, Yang et al., 2005*] and other global models including halogen chemistry are being developed [*Kerkweg, 2005*]. The results of these model studies have been mentioned in the respective sections above.

Future requirements and applications

i) Model studies can play a vital role in answering the open questions and can help locate measurement sites, where, according to current knowledge as implemented in the models, promising situations should be present. More specifically: Where and when should we plan field campaigns? Under what meteorological and chemical conditions can we expect high concentrations of reactive halogens?

ii) Models can be crucial tools to help interpret measurement results, esp. when information about the airmass history is available ("satellite" stations around a "supersite").

iii) Models should be used to follow the temporal evolution of halogen chemistry in plumes (e.g. volcanoes, biomass burning, and dust plumes)

where reactive surfaces or the composition of the plume can lead to drastic effects compared to background air outside the plume.

iv) Test how well the usually very shallow polar boundary layer is represented in current meteorological models of varying complexity.

v) Further aspects that should be covered in model development and application include:

- Aerosols are an important source and recycling site for reactive halogens, their effect depends on their age and their size. Size resolved aerosol models must be coupled to halogen chemistry. We need to find parameterizations that are suitable for inclusion in global models.
- Small scale variability, e.g. at the coast line or in the snow pack, has to be taken into account in models
- Apply models to salt lake conditions to test if known halogen activation mechanisms are sufficient to explain the observations of if additional processes have to be considered.
- Find a suitable and computationally feasible way to consider activity coefficients in aqueous-phase chemistry.
- Finally, future models should abstain as far as possible from constraining the halogen chemistry. If this leads to disagreement between models and observations, it must be seen as an opportunity to find missing processes, not as a reason to constrain the model.

Initiatives that would improve current understanding:

- Couple the current box models to global 3-dimensional chemical transport or global circulation models.
- Eliminate unnecessary complexity when implementing halogen chemistry into global models; use sensitivity studies to simplify and parameterize both the chemical mechanism and physical processes.
- Use models to help plan future field campaigns by identifying areas that might be suitable and of interest for the research question.
- Use model-field data comparisons to test if our current understanding as implemented in the model is sufficient to explain the observations.
- Assess future changes in halogen sources (e.g. increase in the fraction of annually re-formed sea ice in the Arctic).
- Test the regional and global significance of processes that have been investigated with locally focused campaigns and/or process modeling.

4) Implementation strategy and working plan

Key to extending our knowledge are field campaigns and long-term observations, which will be accompanied by and closely coordinated with laboratory and modeling studies. In the following we outline HitT activities for the next 9 years, divided into three 3-year periods. A more detailed compilation will be composed at an implementation workshop.

4.1) Field campaigns: large campaigns and pilot studies

Results from previous field studies, global and regional **models**, as well as **satellite** observations should be used to identify interesting locations where reactive halogen chemistry might be more active or more easily studied than elsewhere.

Several main **field campaigns** are planned during each phase to comprehensively characterize the situation. Suited for large campaigns are areas (i.e. domains) where we know that RHCs are present. These campaigns should be comprehensive studies with the goal to address the research qeustions from all perspectives, e.g., by measuring *all* properties known to be relevant simultaneously ("closure" approach) in a way that useful comparison with models is achievable.

Domains where large field campaigns would be feasible include:
- polar regions (International Polar Year 2007/2008)
- salt lakes (esp. Dead Sea with its special topography)
- Mace Head, Brittany, Bay of Maine, or other coastal regions with the presence of large amounts of macroalgae; the EU-funded MAP project started in October 2005
- open ocean (requires suited islands or better ship time etc); see below

In each phase several **pilot studies** should be made at promising spots where no halogen measurements were made before in order to identify locations where a large campaign can be done. If possible they should be designed as "add-ons" to other field campaigns so that other measurements are available which can be helpful for a better understanding of the underlying processes.

- coastal regions other than Mace Head and Appledore Island to investigate how widespread coastal halogen chemistry is;
- Megacities (both coastal and non-coastal);
- free troposphere (airborne)
- open ocean; see below

Note on **open oceans:** A large (ship based) open ocean campaign might only be feasible with instrumentation that is more sensitive than the currently available; maybe do pilot studies as "guests" on other cruises as soon as such

instruments are available to test them and identify possible "hot spots" for a large field campaign later in this program.

Phase 1 should include one main field campaign in the polar regions because of the upcoming International Polar Year 2007/2008. Pilot studies for this phase could be (coastal) cities and the free troposphere.

The possibility to use airships and/or several coordinated ground stations will be explored, esp. to study small but highly heterogeneous regimes like volcanic or biomass burning plumes or "hot spots" in coastal regions.

4.2) Long term observatories

Background observatories should not be impacted by local pollution or meteorological effects. Sites that are influenced by different wind regimes (polluted, semi-polluted, clean MBL) would also be very useful. At some sites halogen measurements are already made, other sites could be supplemented by a suite of RHC measurements. The Global Atmospheric Watch (GAW) network provides potentially good sites with time series that sometimes exist already for decades and which are supposed to be maintained for long periods. The Atmospheric Brown Cloud project (ABC) is building a network of new/improved measurement sites around Asia that might also be suited to host RHC instruments.

Data from satellites provide the potential of global coverage and should always be used in addition to the sites listed here. They have already been used very successfully for studies of polar BrO clouds but with the availability of data from the instruments SCIAMACHY and OMI this can be extended to other regions in the future.

Free troposphere:

Possible sites to study the occurrence and transformations of RHC in the free troposphere could be observatories on high mountains, like the Zugspitze (DOAS measurements have already started) or the Jungfraujoch, both in the Alps. On island stations like Hawaii or Tenerife passive DOAS instruments could be deployed at the base of mountain and at the summit to be able to differentiate between halogen oxides in the boundary layer and the free troposphere.

Passenger aircraft platforms like CARIBIC II, IAGOS (="MOZAIC IV"), even though they are no real "observatories" will provide over time the same measurements from similar flight tracks and are therefore very valuable to establish longer time series as well.

Marine boundary layer:

Large parts of the northern hemisphere oceans are downwind of continental plumes with anthropogenic, biomass burning, and/or dust emissions and are

affected by heavy ship traffic whereas large parts of the southern hemisphere are very clean with very little ship traffic and with biomass burning plumes being the only significant sources of pollution. Existing measurement stations that can be supplemented by measurements should have priority in this region because of logistical constraints and to be able to identify possible correlations of RHC with other compounds so that the existing time series could be extended back in time with the help of these proxies.

Present volcanic surveillance networks should be augmented to measure RHCs (see EU-project NOVAC).

Possible sites for observatories in the marine boundary include:

- Mace Head (however strong local effects)
- Bermuda (also BATS oceanographic station)
- Hawaii (also HOT oceanographic station)
- Cape Grim (aerosol halide time series existing)
- remote Pacific Island (New Zealand?)
- Trinidad Head (AGAGE site)
- Barbados (long term record of aerosol composition – AEROCE and related projects)
- Cape Verde (new time-series record initiated)
- Christmas Islands

Polar regions:

Several ground stations have records from various intensive field campaigns and several have already started to collect time series of halogen oxides or are planning to do so. In the Arctic these sites include Alert (Canada), Barrow (Alaska), Spitsbergen, and the Hudson Bay and in the Antarctic Neumayer (Germany), Scott Base (New Zealand), and Halley (UK).

4.3) Collaborations and links to international initiatives:

The key research questions of HitT are also fundamental topics addressed in the sponsoring research activities IGAC and SOLAS. Close collaboration is envisioned with the tasks AICI and OASIS and to a somewhat smaller extent with iLEAPS. Ongoing and planned national as well as international research projects that fall into the scope of HitT include Marine Aerosol Production MAP, Network for Observation of Volcanic and Atmospheric Change (NOVAC), Marine Multi-Phase Halogen Chemistry and its Coupling to Nitrogen and Sulfur Cycles MAPHiNS, Chemistry of the Antarctic Boundary Layer and the Interface with Snow (CHABLIS). Polar halogen chemistry is one of the foci of the International Polar Year (IPY).

4.4) Publicity:

The task has already been presented at several international conferences (IGAC 2004, Christchurch, SOLAS 2004, Halifax, EGU 2005, Vienna). The main ideas have been published in the SOLAS Newsletter (Spring 2006) and we plan similar articles in periodicals such as the IGACtivities, EOS, EGGS, etc. We have received endorsement from the SOLAS scientific steering committee and have formally asked for endorsement from the IGAC scientific steering committee.

Appendix

This White Paper is the product of an expert workshop held in Heidelberg, Germany in May 2004 and has undergone a phase of open discussion in the scientific community. The following scientists participated at the Heidelberg workshop in May 2004:

Lucy Carpenter, University of York, UK
John Crowley, MPI Mainz, Germany
Paul Crutzen, MPI Mainz, Germany, Scripps, USA
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Additional text, comments, and ideas were contributed by Parisa Ariya, McGill Univ., Canada; John Burrows, Univ. Bremen, Germany; Barbara Finlayson-Pitts, UC Irvine, USA; Juan Carlos Gómez Martín, Univ. Bremen, Germany; Pavel Jungwirth, Academy of Sciences, Czech Republic; Kelly Redeker, Queens Univ. Belfast, UK; Gabriela Sousa Santos, MPI Hamburg, Germany; Robyn Schofield, NOAA, USA; Darin Toohey, Univ. Colorado, USA; Eric Wolff, British Antarctic Survey, UK.

The paper was compiled and edited by Roland von Glasow. Thanks to the International SOLAS Office for editorial help.

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