Recent developments in Tropospheric Halogen Chemistry

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The relevance of halogen chemistry for the stratosphere – especially ozone destruction – is very well known, but reactive halogens play a role in tropospheric chemistry as well. The sources for reactive halogens in the troposphere are largely natural, to a large extent connected to the presence of halogens in ocean water (see Figure 1 for an overview). Recently a number of exciting measurements of reactive halogen compounds have been reported from a wide range of environmental conditions, such as the finding of very high concentrations of iodine oxide, IO, in the Antarctic with a surprising correlation to bromine oxide, BrO (Saiz-Lopez et al., 2007b); the first detection of IO from space (Saiz-Lopez et al, 2007a); the first detection of nitryl chloride ($ClNO_2$) in the boundary layer at mixing ratios of up to 1 nmol mol^{-1} in polluted air off North America (Osthoff et al., 2008); and the discovery of the year-round presence of BrO and IO at the Cape Verde islands (Read et al., 2008b). I discuss details of these studies below. Workshops, especially on polar regions, as well as tropospheric halogen chemistry sessions at EGU and AGU meetings have highlighted an increasing interest in this topic, which is also reflected in a number of review articles that have been published in the last few years. Platt and Hönninger (2003) and von Glasow and Crutzen (2007) give a general overview of halogens in the troposphere. Sander et al. (2003) compiled a very large number of gas and particulate phase measurements from the marine boundary layer, whereas Simpson et al. (2007) concentrate on recent developments in polar regions. Carpenter (2003) focused on iodine chemistry, Finlayson-Pitts (2003) on relevant laboratory experiments and Atkinson et al. (2007) on a compilation of relevant kinetic data to name just a few.

In the following few sections I will first very briefly discuss the key features of the five main domains in which halogens play a role in the troposphere – polar regions, the marine boundary layer, salt lakes, volcanic plumes and the free troposphere. For each domain I will list recent developments, covering mainly the last five years, and will add a number of open questions that need to be addressed in future research.

Polar regions

The first time the consequences of reactive halogen chemistry were observed in the troposphere was in the Arctic where, during studies of Arctic Haze, sudden and drastic ozone depletion events (ODEs) were observed (e.g. Oltmans and Komhyr, 1986). Soon these ODEs were linked to the presence of bromine compounds (Barrie et al. 1988) and Hausmann and Platt (1994) identified a key radical, bromine oxide (BrO), using
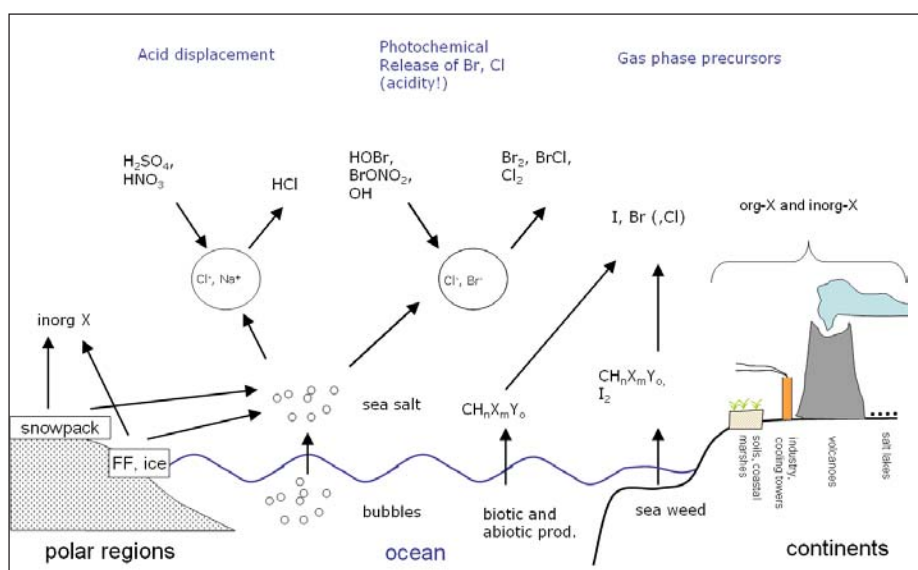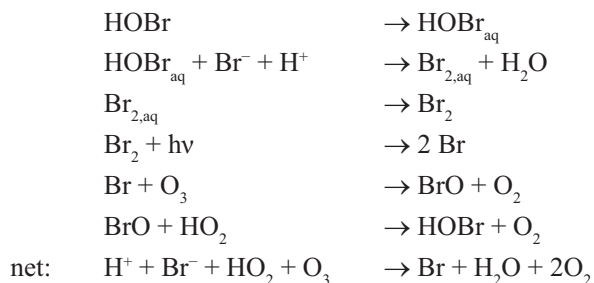

Figure 1. Schematic depiction of the main release mechanisms for reactive halogens in the troposphere (including some not mentioned in the text).

Differential Optical Absorption Spectroscopy (DOAS). The chemical reaction cycle behind the activation of bromide to bromine involves reactions in the gas phase as well as uptake to aerosol particles or snow, reactions in the condensed phase and release of photolysable bromine to the gas phase:

$$HOBr \rightarrow HOBr_{aq}$$
$$HOBr_{aq} + Br^- + H^+ \rightarrow Br_{2,aq} + H_2O$$
$$Br_{2,aq} \rightarrow Br_2$$
$$Br_2 + h\nu \rightarrow 2\,Br$$
$$Br + O_3 \rightarrow BrO + O_2$$
$$BrO + HO_2 \rightarrow HOBr + O_2$$

net:
$$H^+ + Br^- + HO_2 + O_3 \rightarrow Br + H_2O + 2O_2$$

Each bromine atom that is taken up by the condensed phase as HOBr and released as Br_2 (by addition of one bromine atom from bromide), leads to an exponential

increase of the number of bromine compounds in the gas phase, which is why this cycle has been termed the "bromine explosion" (Platt and Janssen, 1995). Mercury depletion events in the Arctic were also related to bromine chemistry (Schroeder et al., 1998). These events are relevant for Arctic life as the largely inert gaseous elemental mercury is converted into bio-available mercury. The current knowledge on mercury chemistry and its links with halogens in polar regions has been reviewed by Steffen et al. (2008).

Satellite pictures (e.g. Wagner and Platt, 1999) have shown the very widespread presence of BrO in the lower atmosphere in polar spring in both hemispheres. The fact that these BrO "clouds" are strongly correlated with the occurrence of first-year sea ice has led to the suggestion that frost flowers, which are regularly related with first-year sea ice, might play a role in bromine explosion events by providing a supply of bromine (e.g. Kaleschke et al., 2004). It has still not unambiguously been shown exactly how bromine is released from the obvious source of halides, the ocean, to provide enough mass for bromine explosions (see Simpson et al., 2007, for a thorough discussion of the current state of knowledge) but there seems to be a consensus that the following processes are key in this chain: Upon freezing of sea water, the contained salts get expelled from the ice lattice which leads to an increase of salinity underneath and around the new sea ice as well as on top of it and in brine channels. This brine is highly concentrated, and thermo-dynamical processes like preferential precipitation of ions might lead to a relative enrichment of bromine and, importantly, to a decrease in alkalinity (e.g. Sander et al., 2006, Morin et al., 2008), providing better starting conditions for the acidity-dependent bromine explosion. One can speculate that the following are some of the key processes involved in starting a bromine explosion: (i) the production of very salty aerosol particles from frost flower fields; (ii) a direct release of gaseous bromine from frost flowers to the gas phase; and (iii) wind-blown snow soaking up brine, for example in frost flower fields, followed by a bromine explosion within the snow and release of gaseous bromine to the atmosphere. As the snow pack has been shown to emit Br_2 and BrCl (Foster et al., 2001) and BrO

shows a strong vertical gradient in the vicinity of snow (Avallone et al., 2003), the snow pack is very likely to play an important role in this cycle. Certain regions have been identified in the Arctic to be key areas for the "birth" of ODEs (Bottenheim and Chan, 2006). The lifetime of ODEs seems to be several hours to more than a week (Strong et al., 2002) but it is important to stress that most studies of ODEs are made at a fixed location and that very sudden onsets of ODEs are caused by advection of an already mature ODE rather than an exceedingly rapid formation of an ODE. Piot and von Glasow (2008) tried to reproduce an ODE with a one-dimensional model where salt aerosol particles from open leads were assumed to be the actual source for bromine. They managed to reproduce the development of an ODE within 2-4 days but only if they included a fairly efficient recycling of deposited bromine back from the snow pack to the gas phase to maintain high atmospheric bromine levels.

During the Chemistry of the Antarctic Boundary Layer and the Interface with Snow (CHABLIS) campaign at the British Antarctic Survey station in Halley, year-long DOAS measurements were made at this coastal site. The measurements showed BrO at mixing ratios of 5 to 20 pmol mol^{-1} basically whenever there was sunlight (Saiz-Lopez et al., 2007a), not only during spring as the satellite record suggests. Ship-based measurements showed the presence of BrO in regions of first-year sea ice in the Antarctic about a month before BrO was detected from satellite in that region (Wagner et al., 2007). According to Read et al. (2008a) the oxidation of dimethylsulphide (DMS) under coastal Antarctic conditions is dominated by the reaction of BrO with DMS. They also suggested that this leads to a significant increase in the production of methane sulphonic acid (MSA).

Another recent and very exciting discovery was the detection of tropospheric iodine oxide (IO) both from ground (Frieß et al, 2001, Saiz-Lopez et al, 2007a) and space-based measurements (Saiz-Lopez et al., 2007b, Schönhardt et al., 2008). In the year-round measurements at Halley, IO and BrO were present in similar mixing ratios and were correlated (Saiz-Lopez et al., 2007a; see Figure 2). Only one published study so far showed the
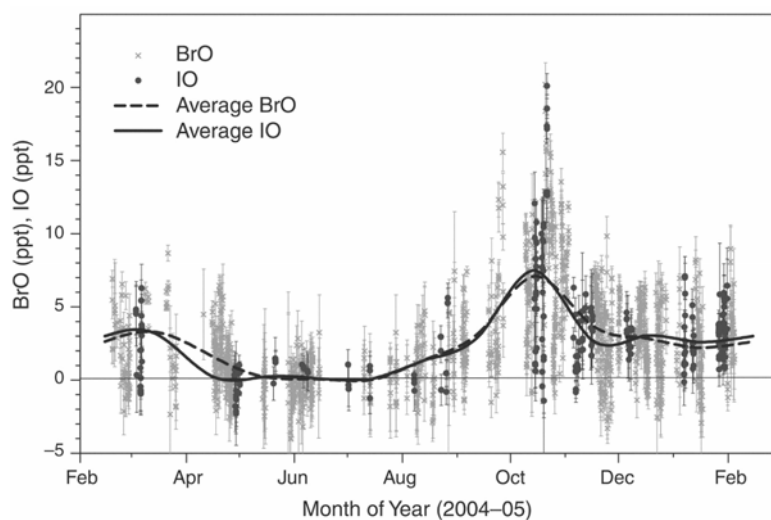

Figure 2. Annual variation of the halogen oxides measured at Halley Station by Saiz-Lopez et al. (2007b). The 10-day moving averages of BrO and IO are indicated by a dashed line and a solid line, respectively. The maximum IO and BrO mixing ratios occurred in spring (October), whereas during winter (May to August) the radicals were consistently below the detection limit. A second smaller peak in the annual halogen mixing ratio cycle may also be present during autumn (March to April). *(From Saiz-Lopez et al. (2007b). Reprinted with permission from AAAS.)*

presence of IO near the surface in the Arctic (Hönninger, 2002), whereas in other studies IO was either not investigated or was below the detection limit; all other detections of IO in polar regions have been made in the Antarctic. Possible reasons for this might include different sea ice thicknesses or different biological communities as the iodine precursors are most likely related to the enrichment of iodine from the ocean water by (ice) algae. Saiz-Lopez and Boxe (2008) suggest a model to explain the differences between the two polar regions.

As already indicated above, the main open questions in this field deal with the details of the initial release of bromine but also of iodine. An understanding of these processes is key for proper modelling of these events on a regional or global scale. Due to a lack of understanding of the underlying processes, all published model studies have so far had to make assumptions regarding important steps in the initiation of the bromine explosion.

A workshop organised by the IGAC-SOLAS task AICI (Air-Ice Chemical Interactions) in Grenoble in 2006 led to a series of review papers that were published in a special edition of *Atmospheric Chemistry and Physics* on all aspects of polar snow and ice chemistry; the most relevant for halogen chemistry are Simpson et al. (2007), Grannas et al. (2007) and Steffen et al. (2008). A number of open questions were defined at this workshop and detailed in these papers, which provided the motivation for an AICI/HitT/SPARC workshop in Cambridge in June 2008 entitled "Ices and Halogens: Laboratory Studies to Improve the Modelling of Field Data" that was organised into five sessions: 1. Surface and bulk properties of ices and clouds; 2. New experimental approaches to the study of ices and aerosols; 3. Halogen activation in the atmosphere; 4. Mercury in the cold; 5. Kinetics of the cold. Each session was introduced by a tutorial/overview presentation followed by three or four talks with sufficient time for in-depth discussions. A number of exciting new techniques were presented including glancing-angle laser-induced fluorescence probing for chemical interactions at the air-aqueous interface (Donaldson et al), 2D and 3D X-ray micro-tomography (Huthwelker, Hutterli et al), electrospray mass spectrometry (Hoffmann et al.) and X-ray diffraction studies of crystallisation (Murray et al.). The need for high quality laboratory experiments to provide quantitative data for the interpretation of field data and as input for atmospheric models was stressed. The idea of using a large "smog chamber"-like facility for a "field study in the lab" came up, in order to investigate interactions between the gas phase and ice phases (snow, quasi-liquid layer (QLL), ice crystals); realisation will require an international effort in order to equip the chamber with the relevant instrumentation.

The extent of sea ice in summer in the Arctic has been dramatically decreasing in the last few decades and it might be lost completely by the mid of this century (Simpson et al., 2007 and references therein). As the bromine release seems to be closely related to first-year sea ice, the extent and intensity of the bromine clouds can be expected to increase in the future as the ocean will continue to freeze during the winter, thereby producing an increasingly large area of first-year sea ice. Therefore the consequences for the ozone budget and mercury input into the Arctic ecosystem due to these processes will likely be more important in the future.

Marine boundary layer

For the following discussion, the marine boundary layer (MBL) will be divided into three sub-regions: the open ocean, coastal regions with extensive sea weeds and densely populated coastal regions such as megacities. In general one can say that the strongest source of bromine and chlorine in the MBL is through the production of sea salt aerosol upon bubble bursting, with a smaller fraction released from biogenic organic halogens. Iodine compounds on the other hand are largely released as organic compounds and molecular iodine from micro and macro algae that accumulate iodine from the ocean water.

Globally, sea salt aerosol is, along with dust, the strongest particle source in terms of mass. Most of this mass is associated with large particles with sizes on the order of micrometres. The lifetime of these particles is relatively short (hours to 2 days) but there are three general ways to release halogens from sea salt into the gas phase: (i) Acid displacement of HCl with H_2SO_4 or HNO_3 (this mechanism does not work for HBr or HI). (ii) Reactions on the surface of particles that lead to the release of inorganic halogens such as that of N_2O_5 which results in the release of $ClNO_2$ and $BrNO_2$ and even Cl_2. (iii) Photochemical reactions leading to the release of photolysable halogens like Br_2, BrCl and Cl_2. In clean environments only the last pathway is relevant. The iodine concentration in sea water is very small and marine aerosol acts as a sink rather than a source for iodine, as has been known for a long time (e.g. Duce et al., 1965). Recent investigations of the speciation of particulate iodine showed the presence of iodide, I^-, and iodate, IO_3^-, in varying relative importance and also the presence of organic iodine (Baker 2004, 2005). Model calculations assumed IO_3^- to be stable once formed in aerosol particles and overestimated its relative importance dramatically (Vogt et al., 1999). Baker (2005) suggested the reaction of HOI with organic matter in particles to produce I^-. Model calculations with an updated inorganic reaction mechanism and the reaction of HOI with organic material were able to reproduce measured iodine speciation when the rate coefficient of this reaction was assumed to be at least 10^5 M^{-1} s^{-1} (Pechtl et al., 2007). For further advance in this field it is imperative to measure the rate coefficients of these and related aqueous phase reactions. Measurements by Gilfedder et al. (2008) showed the presence of I^- and IO_3^- but, interestingly, also of organic iodine, in almost all of their aerosol, rain and snow samples, which span both hemispheres and many climatic zones.

Model calculations have indicated that the presence of 0.5-4 pmol mol^{-1} BrO can significantly impact the O_3 and sulphur budgets in the MBL (e.g. Sander and Crutzen, 1996, Vogt et al., 1996, von Glasow et al., 2002a,b). In aerosol particles and droplets HOBr and HOCl oxidise S(IV) to S(VI) and in the gas phase BrO adds to DMS, potentially leading to different oxidation products and the predominant growth of existing particles rather than

the production of H_2SO_4 as a precursor for new particle formation (von Glasow and Crutzen, 2004). Model calculations of iodine chemistry in the open ocean also showed strong O_3 destruction (e.g. Vogt et al., 1999).

Measurements of halogen oxides in the open ocean MBL are very difficult and very few have been published so far. IO was measured on Tenerife and at Cape Grim by Allan et al. (2000), and it is very likely that this is an open ocean signal (although coastal effects cannot entirely be excluded). The first time BrO could be measured over the ocean was with a passive DOAS instrument (i.e. using sunlight as a light source) off West Africa (Leser et al., 2003). Recently a long-path DOAS instrument was installed on the UK-SOLAS observatory on the Cape Verde islands. Even though this instrument was located on an island, local effects are thought to be minimal as, for example, no sea weed is present. Very high levels of both BrO and IO of typical daytime maxima of 2.5 and 1.4 pmol mol^{-1}, respectively, were measured (see Figure 3), which would indicate that ozone photochemistry is dominated by halogen chemistry (Read et al., 2008b). These mixing ratios are consistent with the results of the model predictions cited above. It has to be added that the O_3 budget is perturbed by halogen chemistry not only by its destruction but also by halogen induced shifts in the $OH:HO_2$ and $NO:NO_2$ ratios that lead to reduced photochemical production of O_3. If reactive halogen chemistry were indeed a widespread phenomenon, our understanding of photochemical processes in the clean MBL would have to be completely re-assessed. Indirect evidence indeed suggests a widespread role of halogen chemistry in the clean MBL as so-called sunrise ozone destruction has been observed in the West and North Pacific (Nagao et al., 1999, Galbally et al., 2000, Watanabe et al., 2005) and could be due to bromine chemistry (von Glasow et al., 2002a). Furthermore chlorine radical concentrations have been estimated to be in the range of 10^3-10^5 in the MBL (e.g. Wingenter et al. 1996, 1999, Lowe et al. 1999) with relevance mainly for the methane budget; in the southern hemisphere Cl could account for about 3.3% of CH_4 destruction (Platt et al., 2004).

Bursts of new particles that were observed at Mace Head on the west coast of Ireland (O'Dowd et al., 1998) were quickly associated with iodine chemistry due to the detection of IO (Alicke et al., 1999). In the last decade a number of studies at coasts with appreciable amounts of sea weed were performed, with Mace Head, Brittany and the Gulf of Maine being the main research locations. It now seems to be established that the exposure of sea weed at low tide leads to very strong emissions of organic iodine but especially of molecular iodine (I_2), which has a very short photolytic lifetime – on the order of 10-20 seconds. At night, I_2 mixing ratios of several tens of pmol
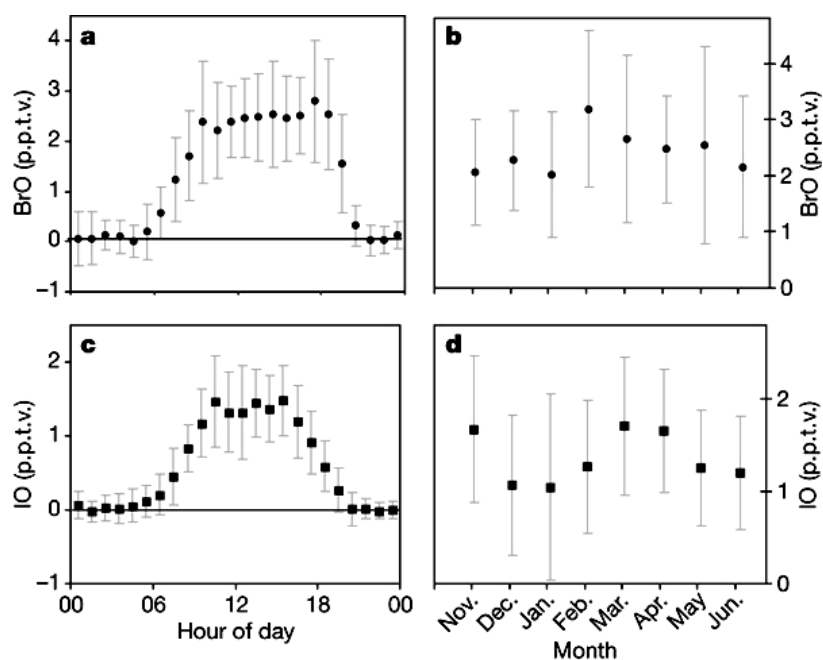

Figure 3. Average diurnal profiles for (a) BrO and (c) IO for the measurements by Read et al. (2008b) on the Cape Verde islands. Errors (1 σ) are indicated as grey lines. The points show average concentrations seen from 09:00 to 17:00 UT. (b) and (d) demonstrate seasonal variation in BrO and IO respectively. *(Reprinted by permission from Macmillan Publishers Ltd: Nature, Read et al., copyright 2008).*

mol^{-1} have been observed at various locations. Iodine radicals are produced upon I_2 photolysis and these react with O_3 to produce IO. The formation of higher iodine oxides then most likely leads to the formation of clusters which grow to nano-particles. IO concentrations are highest and particle bursts strongest when low tide and high sun coincide. This scenario is based on field studies (e.g., O'Dowd et al., 2002, Saiz-Lopez and Plane, 2004; Peters et al, 2005, Saiz-Lopez et al., 2006a), laboratory experiments (e.g., Jimenez et al., 2003, Burkholder et al., 2004, McFiggans et al. 2004, Saunders and Plane, 2005) and model results (e.g., Saiz-Lopez et al. 2006b, Pechtl et al. 2006). Even though a lot of progress has been made, many important questions remain. There are still important gaps in our knowledge of the kinetics of iodine oxides (e.g., Stutz et al., 2007), which hinder further progress in modelling, although ongoing laboratory and theoretical investigations are helping us to elucidate the mechanisms (e.g., Kaltsoyannis and Plane, 2008). The details of new particle formation from iodine oxides are also not yet resolved. In terms of ozone destruction the relevance of these fairly local events of very high iodine loadings might be limited, and although there are indications that the fine particles produced in these bursts can grow to CCN sizes (O'Dowd 2001, O'Dowd et al. 2007), more studies are needed to test on what spatial scale this might be of relevance, especially when viewed in the context of competition with other continental particle sources.

Recent measurements of chlorine compounds off the North American coast showed HCl mixing ratios exceeding 1nmol mol^{-1}. HCl was mainly displaced by HNO_3 from sea salt aerosol. Under these conditions the reaction of HCl with OH could sustain Cl-atom

concentrations on the order of 10^4 cm^{-3} (Keene et al., 2007). Model calculations for these conditions showed that multiphase cycling of chlorine compounds between sulphate and sea salt aerosol particles and the gas phase could sustain levels of more than 100 pmol mol^{-1} of reactive inorganic chlorine other than HCl for several days in continental outflow. At night Cl$_2$ levels were predicted to be between 20 and 80 pmol mol^{-1} for four nights after the air mass left the continent (Pechtl and von Glasow, 2007). The recirculation to the coast of such an air mass, which fairly rapidly acquires marine characteristics like low O$_3$ concentrations, could be an explanation for the very high Cl$_2$ mixing ratios that have been measured in on-shore winds by Spicer et al. (1998).

Osthoff et al. (2008) measured ClNO$_2$ for the first time in the atmosphere (see Figure 4). The presence of ClNO$_2$ in the polluted MBL in itself is not unexpected as laboratory experiments have shown the release of ClNO$_2$ from salt-containing particles upon reaction with N$_2$O$_5$ (e.g. Finlayson-Pitts et al., 1989). This reaction occurs on the surface of particles and is the likely explanation for the surprisingly high mixing ratios of several hundred pmol mol^{-1} and even more than 1 nmol mol^{-1} of ClNO$_2$ that were measured by Osthoff et al. (2008) when they also observed very high levels of N$_2$O$_5$. The authors could only quantitatively explain these high ClNO$_2$ mixing ratios if aerosol particles other than sea salt provide reactive surfaces for N$_2$O$_5$. These other particles would contain chlorine due to the uptake of HCl that had previously been displaced by other acids from sea salt aerosol. In recent laboratory studies, Roberts et al. (2008) found the production of Cl$_2$ from the heterogeneous reaction of N$_2$O$_5$ on chlorine-containing aerosol when the aerosol pH was less than 2, with ClNO$_2$ acting as an intermediate. At night ClNO$_2$ and Cl$_2$ are stable but they photolyse rapidly after sunrise to release Cl radicals, which in turn rapidly react with VOC thereby producing peroxy radicals which, in the presence of NO$_x$, lead to ozone production. Tanaka et al. (2000, 2003) have previously shown evidence for chlorine-mediated ozone production in Houston. Model calculations by Knipping and Dabdub (2003) showed a potential increase in O$_3$ mixing ratios by 12 ppb in the Los Angeles basin. As coastal megacities are bound to increase both in number and size in the future, chlorine-mediated ozone production might have to be addressed in future air quality strategies for coastal megacities. The release of chlorine from sea salt via the surface reactions of N$_2$O$_5$ might be very relevant in ship plumes, which cover increasingly large regions of the oceans, as they provide a "perfect" combination of pollution and sea salt.

Salt lakes

Salt lakes are an obvious region to expect halogen release from salt deposits. Very large BrO mixing ratios of 100-200 pmol mol^{-1} have indeed been observed above the Dead Sea (e.g. Hebestreit et al., 1999, Matveev et al., 2001) and smaller values above the Salar de Uyuni in
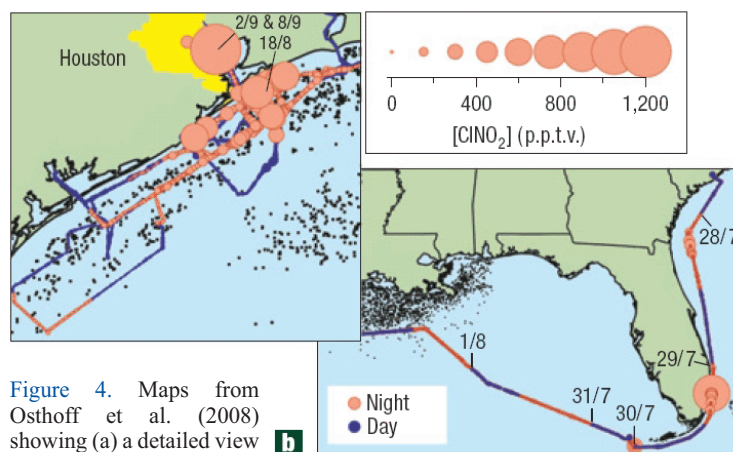
Figure 4. Maps from Osthoff et al. (2008) showing (a) a detailed view of the focused study area in the vicinity of Houston, Texas (shown in yellow); and (b) the ship track along the United States southeast coastline and across the Gulf of Mexico. Measured ClNO$_2$ mixing ratios (5 min average) are plotted along the track scaled by size. The colour coding differentiates night time (red) from daytime (blue).

Bolivia (Hönninger et al., 2004) and the Great Salt Lake in Utah (Stutz et al. 2002). Elevated BrO columns also were found from satellite above the Caspian Sea (Wagner et al., 2001). Further, Stutz et al. (2002) detected ClO over the Great Salt Lake and IO was measured at up to 10 pmol mol^{-1} over the Dead Sea by Zingler and Platt (2005). The bromine explosion mechanism discussed earlier is the likely explanation for the very high bromine levels above the Dead Sea. However, recent model calculations showed that salt aerosol alone is insufficient to release enough bromine rapidly so that either very strong fluxes of gaseous bromine from salt deposits, or somewhat smaller fluxes from the Dead Sea might be responsible for the high bromine levels (Smoydzin, 2008, Smoydzin and von Glasow, in prep.). Due to the low pH of the Dead Sea (pH=5-6), the bromine explosion mechanism could be acting in the Dead Sea water, whereas this would not be possible in the ocean (pH≈8.1).

Volcanoes

Bobrowski et al. (2003) measured the highest atmospheric BrO mixing ratios detected so far: In plumes of passively degassing volcanoes, the inferred values exceeded 1 nmol mol^{-1}. BrO was identified at a number of other volcanoes as well (e.g. Oppenheimer et al., 2006, Bobrowski and Platt, 2007), as was OClO and ClO (Lee et al., 2005, Bobrowski et al., 2007). It has been known for a long time that very large amounts of halides are emitted from volcanoes but thermodynamical modelling suggests that other inorganic halogen compounds are also emitted (Gerlach, 2004). Measurements of the BrO:SO$_2$ ratio downwind of Mt. Etna showed an increase with time of BrO concentrations and a comparison of this data with model calculations showed that the bromine explosion mechanism is sufficient to explain both the absolute amount of bromine as well as the rate of its formation (Bobrowski et al., 2007). Again, multiphase chemistry is key for these reaction cycles. As mentioned above, studies in polar regions have shown that "bromine explosion events" were correlated with the sudden

decrease in atmospheric mercury and BrO is the "prime suspect" (e.g., Steffen et al., 2008). As the BrO levels in volcanic plumes are usually much higher than those found in polar regions, I hypothesise that the net effect of volcanoes on mercury is in fact that of a "scrubber" rather than a net source, as the elevated BrO levels might lead to oxidation of not only the volcanogenic mercury but also of elemental mercury from the background atmosphere. This might lead to enhanced mercury deposition in regions near volcanoes. For island volcanoes, where the deposition of brominated mercury would be into the ocean, this might be a net sink for atmospheric mercury. Whether the deposited mercury on land is re-released to the atmosphere or remains in the ecosystem should be the subject of future field work. Quantitative model studies of this are in preparation (von Glasow, in prep).

As most volcanoes emit directly into the free troposphere, the potential for large scale effects through long-range transport and the extended lifetime of halogens through multiphase cycling is large. The expected effects include O_3 depletion and more rapid oxidation of S(IV) and, if Cl radical levels are sustained at a high enough level, enhanced oxidation of CH_4.

Free troposphere

Based on a comparison of ground-based, balloon-borne and space-based measurements, the presence of 0.5-2 pmol mol^{-1} BrO in the free troposphere was suggested (e.g. Van Roozendael et al., 2002). Recent long-term ground-based measurements are improving the fidelity of these numbers and suggest tropospheric columns of BrO of around 10^{13} molec cm^{-2}, with somewhat lower values near the equator (Fietkau et al., 2007, Hendrick et al., 2007, Theys et al., 2007). Global model studies of tropospheric bromine chemistry indicate that these levels are enough to perturb the tropospheric O_3 concentrations by 5-20% (von Glasow et al., 2004, Yang et al., 2005). The sources for bromine in the free troposphere are likely to be dominated by the breakdown of natural organic bromine gases and bromine released from sea salt (Yang et al., 2005), but bromine from volcanoes has to be considered as well.

Implications and research needs

Our knowledge about the relevance of halogen chemistry in the troposphere has increased dramatically in the last decade. The main implications of the presence of reactive halogens are a decrease of ozone in most regions but an increase in O_3 smog in densely populated coastal regions. Furthermore the activation of elemental mercury and links with the sulphur cycle are of importance. Interestingly, the large majority of reactive halogen compounds in the troposphere are of natural origin, and basically all reactive halogen compounds (RHCs) are related to the presence of halides in ocean water. This is true even for halogens in volcanic plumes as most of them originate from sea water that was, for example, included in subducted sediments.

In order to make continued progress in this field, it is imperative to keep developing new measurement techniques that provide more information about halogen speciation in the gas and aerosol phase. The detection limits of these instruments have to be very low. It is noteworthy that no instrument has so far been used in the field that can detect a key player in the bromine explosion events, namely HOBr. There are still important gaps in the kinetic information, especially for iodine reactions (gas and condensed phase). A more thorough list of research needs can be found in the White Paper of the SOLAS-IGAC task Halogens in the Troposphere (HitT). The primary objective of HitT is to determine and quantify the importance of reactive halogen compounds in tropospheric chemistry and climate forcing. Key themes are the influence of RHCs on the oxidative capacity of the atmosphere, the ozone budget, as well as on aerosol nucleation and growth. HitT tries to bring the scientific community together by organizing workshops and sessions at international conferences and to encourage projects that require international cooperation due to the interdisciplinary nature of the topic and complicated logistical effort involved in field measurements. More details on HitT and a link to the White Paper can be found on the webpage (www.HitT-task.net).

This article is based on ACCENT chapter S&I Atmospheric Composition Change: Air Quality and Health, section 3.3.1 Tropospheric Halogen Chemistry

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