Issue No. 39
September 2008

IGACtivities Newsletter

of the International Global Atmospheric Chemistry Project

In this Issue:

Science Features

A Note from the IGAC Co-chairs: Phil Rasch and Kathy Law

We write this note only a week after the conclusion of the 10th IGAC International Conference, held in the beautiful mountain town of Annecy, France. We would like to extend our special thanks to Paulo Laj and Claire Granier who, along with Kathy, were the lead organizers for this year's conference, and to Paul Monks and Mary Barth, who were the chairs of the conference program committee. They all, along with the full local organizing committee and the session chairs put in a great deal of effort behind the scenes to make the week the success that it was. The community really embraced the "Bridging the Scales" theme of the conference, making for many thought-provoking talks and posters. An exciting new aspect of this years' conference was live web-casting of all the plenary talks. These talks are now archived and can be viewed at any time: http://webcast.in2p3.ft/IGAC2008/. We thank France's CNRS for providing this excellent service. We have already received a number of positive comments about the webcasting and hope it will become an increasingly important part of the meeting.

In this issue of IGACtivities we have three articles related to activities which IGAC is jointly pursuing with other projects. First, Roland von Glasow presents an overview of the role of halogens in the troposphere, an emerging area of science that is being covered in an IGAC Task ("HitT") that is co-endorsed by IGAC and SOLAS (IGBP's Surface Ocean Lower Atmosphere Study). It appears that halogens may play an important role not only in stratospheric chemistry but also in the chemistry of the troposphere, most clearly in the polar regions but also possibly more broadly, such as in the marine boundary layer both near land and in the open ocean.

The second and third articles – on the importance of understanding boundary-layer processes for quantifying surface-atmosphere fluxes and on aerosol, cloud, precipitation and climate interactions ("ACPC") – are both subjects of joint interest to IGAC and IGBP's Integrated Land-Atmosphere Ecosystem Processes Study (iLEAPS). Ganzeveld et al. make a compelling argument for needing both to better understand small-scale processes in the boundary layer and to do a better job of incorporating existing knowledge into models. The third article by Stevens describes the science behind a new joint iLEAPS, IGAC, and WCRP-GEWEX (Global Energy and Water Experiment) activity on ACPC. A series of planning meetings are in progress to define the ACPC activity, using as a starting point the recently-published IAPSAG (WMO/IUGG International Aerosol Precipitation Science Assessment Group) report.

Finally, we'd like to note that the first phase of the IGAC AICI Task has concluded with the publication of five articles comprising a special issue of Atmospheric Chemistry and Physics: http://www.atmos-chem-phys.net/special_issue80.html. AICI has entered its second phase with a refocused set of goals and with tight connections to HitT. We congratulate the AICI Task team for their excellent work and look forward to more exciting results.

A Core Project of the Internations Geosphere-Biosphere Programme

In Cooperation with IAMAS Commission on Atmospheric Chemistry and Global Pollution

Recent developments in Tropospheric Halogen Chemistry

Contributed by **Roland von Glasow** *University of East Anglia, School of Environmental Sciences, Norwich, NR4 7TJ, UK* (R.von-Glasow@uea.ac.uk)

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.

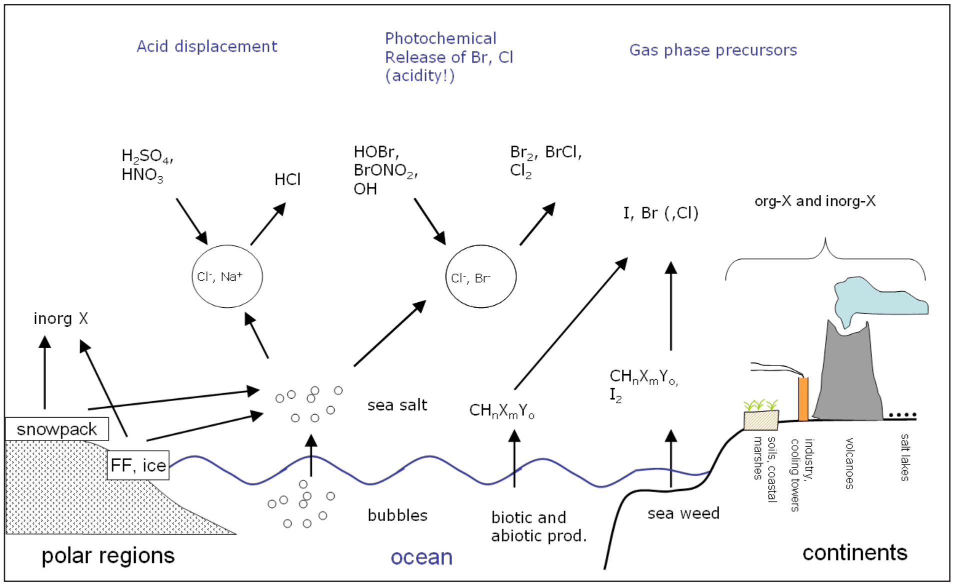


Figure 1. Schematic depiction of the main release mechanisms for reactive halogens in the troposphere (including some not mentioned in the text).

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 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:

$$
\begin{array}{lll}
 & HOBr & \rightarrow HOBr_{aq} \\
 & HOBr_{aq} + Br^- + H^+ & \rightarrow Br_{2,aq} + H_2O \\
 & Br_{2,aq} & \rightarrow Br_2 \\
 & Br_2 + h\nu & \rightarrow 2\,Br \\
 & Br + O_3 & \rightarrow BrO + O_2 \\
 & BrO + HO_2 & \rightarrow HOBr + O_2 \\
\text{net:} & H^+ + Br^- + HO_2 + O_3 & \rightarrow Br + H_2O + 2O_2
\end{array}
$$

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

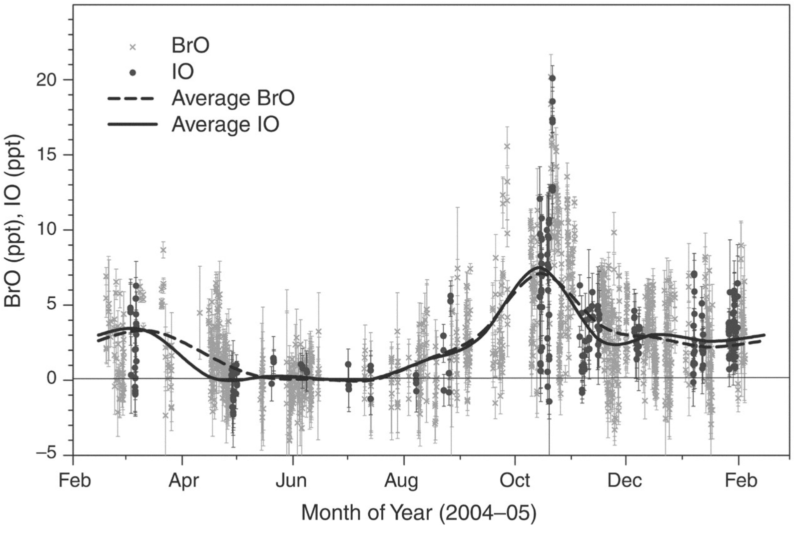


Figure 2. Annual variation of the halogen oxides measured at Halley Station by Saiz-Lopez et al. (2007b). The 10-day moving averages of BrO and IO are indicated by a dashed line and a solid line, respectively. The maximum IO and BrO mixing ratios occurred in spring (October), whereas during winter (May 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).

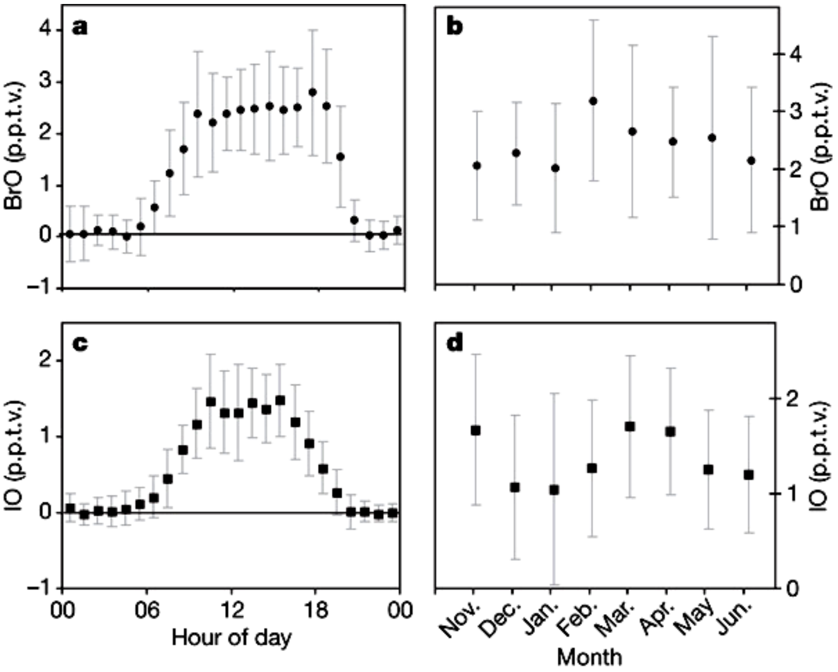


Figure 3. Average diurnal profiles for (a) BrO and (c) IO for the measurements by Read et al. (2008b) on the Cape Verde islands. Errors (1 σ) are indicated as grey lines. The points show average concentrations seen from 09:00 to 17:00 UT. (b) and (d) demonstrate seasonal variation in BrO and IO respectively.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

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 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).

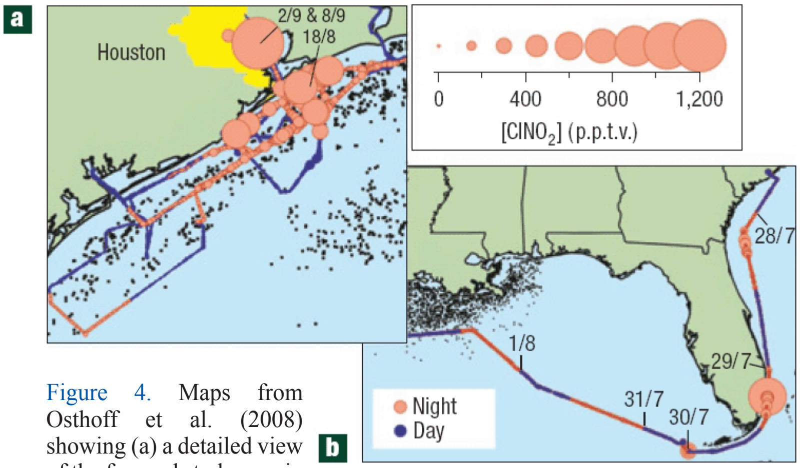


Figure 4. Maps from Osthoff et al. (2008) showing (a) a detailed view of the focused study area in the vicinity of Houston, Texas (shown in yellow); and (b) the ship track along the United States southeast coastline and across the Gulf of Mexico. Measured $ClNO_2$ mixing ratios (5 min average) are plotted along the track scaled by size. The colour coding differentiates night time (red) from daytime (blue).

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_2O_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_2O_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_2O_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_2O_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_2O_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 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

References

Alicke, B., K. Hebestreit, J. Stutz, and U. Platt. Iodine oxide in the marine boundary layer. *Nature*, **397**, 572-573, 1999.

Allan, B. J., G. McFiggans, J. M. C. Plane, and H. Coe. Observation of Iodine Oxide in the Remote Marine Boundary Layer. *J. Geophys. Res.*, **105**, 14,363-14,370, 2000.

Atkinson, R., D. L. Baulch, R. A. Cox, J. N. Crowley, R. F. Hampson, R. G. Hynes, M. E. Jenkin, M. J. Rossi, and J. Troe. Evaluated kinetic and photochemical data for atmospheric chemistry: Volume III - gas phase reactions of inorganic halogens. *Atmos. Chem. Phys.*, **7**, 981-1191, 2007.

Avallone, L. M., D. W. Toohey, T. J. Fortin, K. A. McKinney, and J. D. Fuentes. In situ measurements of bromine oxide at two high-latitude boundary layer sites: Implications of variability. *J. Geophys. Res.*, **108**, 4089, doi: 10.1029/2002JD002 843, 2003.

Baker, A. Inorganic Iodine Speciation in Tropical Atlantic Aerosol. *Geophys. Res. Lett.*, **31**, L23S02, doi:10.1029/2004GL020 144, 2004.

Baker, A. Marine Aerosol Iodine Chemistry: The Importance of Soluble Organic Iodine. *Env. Chem.*, **2**, 295-298, 2005.

Barrie, L. A., J. W. Bottenheim, R. C. Schnell, P. J. Crutzen, and R. A. Rasmussen. Ozone destruction and photochemical reactions at polar sunrise in the lower Arctic atmosphere. *Nature*, **334**, 138-141, 1988.

Bobrowski, N., G. Hönninger, B. Galle, and U. Platt. Detection of bromine monoxide in a volcanic plume. *Nature*, **423**, 273-276, 2003.

Bobrowski, N. and U. Platt. SO2/BrO ratios studied in five volcanic plumes. *J. Volc. and Geotherm. Res.*, **166**, 147-160, 2007.

Bobrowski, N., R. von Glasow, A. Aiuppa, S. Inguaggiato, I. Louban, O. W. Ibrahim, and U. Platt. Reactive halogen chemistry in volcanic plumes. *J. Geophys. Res.*, **112**, D06 311, doi:10.1029/2006JD007 206, 2007.

Bottenheim, J. W. and E. Chan. A trajectory study into the origin of spring time Arctic boundary layer ozone depletion. *J. Geophys. Res.*, **111**, D19 301, doi:10.1029/2006JD007 055, 2006.

Burkholder, J. B., J. Curtius, A. R. Ravishankara, and E. R.

Lovejoy. Laboratory studies of the homogeneous nucleation of iodine oxides. *Atmos. Chem. Phys.*, **4**, 19-34, 2004.

Carpenter, L. J. Iodine in the marine boundary layer. *Chem. Rev.*, **103**, 4953-4962, 2003.

Duce, R. A., J. W. Winchester, and T. W. van Nahl. Iodine, bromine, and chlorine in the Hawaiian marine atmosphere. *J. Geophys. Res.*, **70**, 1775-1799, 1965.

Fietkau, S., T. Medeke, A. Richter, N. Sheode, B.-M. Sinnhuber, F. Wittrock, N. Theys, M. van Roozendael, and J. P. Burrows. Ground-based measurements of tropospheric and stratospheric Bromine Monoxide above Nairobi (1°S, 36°E). *Atmos. Chem. Phys. Discuss.*, **7**, 6527-6555, 2007.

Finlayson-Pitts, B. J. The tropospheric chemistry of sea salt: A molecular-level view of the chemistry of NaCl and NaBr. *Chem. Rev.*, **103**, 4801-4822, 2003.

Finlayson-Pitts, B. J., M. J. Ezell, and J. N. Pitts, Jr. Formation of chemically active chlorine compounds by reactions of atmospheric NaCl particles with gaseous N_2O_5 and $ClONO_2$. *Nature*, **337**, 241-244, 1989.

Foster, K. L., R. A. Plastridge, J. W. Bottenheim, P. B. Shepson, B. J. Finlayson-Pitts, and C. W. Spicer. The Role of Br_2 and BrCl in Surface Ozone Destruction at Polar Sunrise. *Science*, **291**, 471-474, 2001.

Frieß, U., T. Wagner, I. Pundt, K. Pfeilsticker, and U. Platt. Spectroscopic Measurements of Tropospheric Iodine Oxide at Neumayer Station, Antarctica. *Geophys. Res. Lett.*, 28, 1941-1944, 2001.

Galbally, I. E., S. T. Bentley, and C. P. M. Meyer. Mid-latitude marine boundary layer ozone destruction at visible sunrise observed at Cape Grim, Tasmania, 41°S. *Geophys. Res. Lett.*, **27**, 3841-3844, 2000.

Gerlach, T. M. Volcanic sources of tropospheric ozone-depleting trace gases. *Geochem. Geophys. Geosyst.*, **5**, Q09 007, doi: 10.1029/2004GC000 747, 2004.

Gilfedder, B., S. Lai, M. Petri, H. Biester, and T. Hoffmann. Iodine speciation in rain, snow and aerosols and possible transfer of organically bound iodine species from aerosol to droplet phases. *Atmos. Chem. Phys. Discuss.*, **8**, 7977-8008, 2008.

Grannas, A. M., A. E. Jones, J. Dibb, M. Ammann, C. Anastasio, H. J. Beine, M. Bergin, J. Bottenheim, C. S. Boxe, G. Carver, G. Chen, J. H. Crawford, F. Dominé, M. M. Frey, M. I. Guzm´an, D. E. Heard, D. Helmig, M. R. Hoffmann, R. E. Honrath, L. G. Huey, M. Hutterli, H. W. Jacobi, P. Kl´an, B. Lefer, J. Mc- Connell, J. Plane, R. Sander, J. Savarino, P. B. Shepson, W. R. Simpson, J. R. Sodeau, R. von Glasow, R. Weller, E. W. Wolff, and T. Zhu. An overview of snow photochemistry: evidence, mechanisms and impacts. *Atmos. Chem. Phys.*, **7**, 4329-4373, 2007.

Hausmann, M. and U. Platt. Spectroscopic measurement of bromine oxide and ozone in the high Arctic during Polar Sunrise Experiment 1992. *J. Geophys. Res.*, **99**, 25,399-25,413, 1994.

Hebestreit, K., J. Stutz, D. Rosen, V. Matveiv, M. Peleg, M. Luria, and U. Platt. DOAS Measurements of Tropospheric Bromine Oxide in Mid-Latitudes. *Science*, **283**, 55-57, 1999.

Hendrick, F., M. V. Roozendael, M. P. Chipperfield, M. Dorf, F. Goutail, X. Yang, C. Fayt, C. Hermans, K. Pfeilsticker, J.-P. Pommereau, J. A. Pyle, N. Theys, and M. D. Mazière. Retrieval of stratospheric and tropospheric BrO profiles and columns using ground-based zenith-sky DOAS observations at Harestua, 60°N. *Atmos. Chem. Phys.*, **7**, 4869-4885, 2007.

Hönninger, G. Halogen Oxide Studies in the Boundary Layer by Multi Axis Differential Optical Absorption Spectroscopy and Active Longpath-DOAS. Ph.D. thesis, Universität Heidelberg, Germany, http: www.ub.uni-heidelberg.de/archiv/1940, 2002.

Hönninger, G., N. Bobrowski, E. R. Palenque, R. Torrez, and U. Platt. Reactive bromine and sulfur emissions at Salar de Uyuni, Bolivia. *Geophys. Res. Lett.*, **31**, L04 101, doi: 10.1029/2003GL018 818, 2004.

Jimenez, J. L., D. R. Cocker, R. Bahreini, H. Zhuang, V. Varutbangkul, R. C. Flagan, J. H. Seinfeld, C. O'Dowd, and T. Hoffmann. New Particle Formation from Photooxidation of Diiodomethane (CH_2I_2). *J. Geophys. Res.*, **108**, 4318, 10.1029/2002JD002 452, 2003.

Kaleschke, L., A. Richter, J. Burrows, O. Afe, G. Heygster, J. Notholt, A. M. Rankin, H. K. Roscoe, J. Hollwedel, T. Wagner, and H.-W. Jacobi. Frost flowers on sea ice as a source of sea salt and their influence on tropospheric halogen chemistry. *Geophys. Res. Lett.*, **31**, L16 114, doi: 10.1029/2004GL020 655, 2004.

Kaltsoyannis, N. and J. M. C. Plane. Quantum chemical calculations on a selection of iodine-containing species (IO, OIO, INO_3, $(IO)_2$, I_2O_3, I_2O_4 and I_2O_5) of importance in the atmosphere. *Phys. Chem. Chem. Phys.*, **10**, 1723-1733, 2008.

Keene, W. C., J. Stutz, A. A. P. Pszenny, J. R. Maben, E. V. Fisher, A. M. Smith, R. von Glasow, S. Pechtl, B. C. Sive, and R. K. Varner. Inorganic chlorine and bromine in coastal New England air during summer. *J. Geophys. Res.*, **112**, D10S12, doi:10.1029/2006JD007 689, 2007.

Knipping, E. M. and D. Dabdub. Impact of chlorine emissions from sea-salt aerosol on coastal urban ozone. *Environ. Sci. Technol.*, **37**, 275-284, 2003.

Lee, C., Y. J. Kim, H. Tanimoto, N. Bobrowski, U. Platt, T. Mori, K. Yamamoto, and C. S. Hong. High ClO and ozone depletion observed in the plume of Sakurajima volcano, *Japan. Geophys. Res. Lett.*, **32**, 21 809, doi:10.1029/2005GL023 785, 2005.

Leser, H., G. Hönninger, and U. Platt. MAX-DOAS Measurements of BrO and NO_2 in the Marine Boundary Layer. *Geophys. Res. Lett.*, **30**, 1537, doi:10.1029/2002GL015 811, 2003.

Lowe, D. C., W. Allan, M. R. Manning, T. Bromley, G. Brailsford, D. Ferretti, A. Gomez, R. Knobben, R. Martin, Z. Mei, R. Moss, K. Koshy, and M. Maata. Shipboard determinations of the distribution of 13C in atmospheric methane in the Pacific. *J. Geophys. Res.*, **104**, 26,125-26,135, 1999.

Matveev, V., M. Peleg, D. Rosen, D. S. Tov-Alper, K. Hebestreit, J. Stutz, U. Platt, D. Blake, and M. Luria. Bromine Oxide - Ozone interaction over the Dead Sea. *J. Geophys. Res.*, **106**, 10,375-10,387, 2001.

McFiggans, G., H. Coe, R. Burgess, J. Allan, M. Cubison, M. R. Alfarra, R. Saunders, A. Saiz-Lopez, J. M. C. Plane, D. Wevill, L. Carpenter, A. R. Rickard, and P. S. Monks. Direct evidence for coastal iodine particles from Laminaria macroalgae -linkage to emissions of molecular iodine. *Atmos. Chem. Phys.*, **4**, 701-713, 2004.

Morin, S., G. M. Marion, R. von Glasow, D. Voisin, J. Bouchez, and J. Savarino. Precipitation of salts in freezing seawater and ozone depletion events: a status report. *Atmos. Chem. Phys. Discuss.*, **8**, 9035-9060, 2008.

Nagao, I., K. Matsumoto, and H. Tanaka. Sunrise ozone destruction found in the sub-tropical marine boundary layer. *Geophys. Res. Lett.*, **26**, 3377-3380, 1999.

O'Dowd, C. D. Biogenic coastal aerosol production and its influence on aerosol radiative properties. *J. Geophys. Res.*, **106**, 1545-1549, 2001.

O'Dowd, C. D., M. Geever, M. K. Hill, M. H. Smith, and S. G. Jennings. New particle formation: Nucleation rates and spatial scales in the clean marine coastal environment. *Geophys. Res. Lett.*, **25**, 1661-1664, 1998.

O'Dowd, C. D., J. L. Jimenez, R. Bahreini, R. C. Flagan, J. H. Seinfeld, K. Hämeri, L. Pirjola, M. Kulmala, S. G. Jennings, and T. Hoffmann. Marine particle formation by biogenic iodine emissions. *Nature*, **417**, 632-636, 2002.

O'Dowd, C. D., Y. J. Yoon, W. Junkerman, P. Aalto, M. Kulmala, H. Lihavainen, and Y. Viisanen. Airborne measurements of nucleation mode particles I: coastal nucleation and growth rates. *Atmos. Chem. Phys.*, **7**, 1491-1501, 2007.

Oltmans, S. J. and W. Komhyr. Surface ozone distributions and variations from 1973 - 1984 measurements at the NOAA Geophysical Monitoring for Climate Change Baseline observatories. *J. Geophys. Res.*, **91**, 5229-5236, 1986.

Oppenheimer, C., V. I. Tsanev, C. F. Braban, R. A. Cox, J. W. Adams, A. Aiuppa, N. Bobrowski, P. Delmelle, J. Barclay, and A. J. McGonigle. BrO formation in volcanic plumes. *Geochim. Cosmochim. Acta*, **70**, 2935-2941, 2006.

Osthoff, H. D., J. M. Roberts, A. R. Ravishankara, E. J. Williams, B. M. Lerner, R. Sommariva, T. S. Bates, D. Coffmann, P. K. Quinn, H. Stark, J. B. Burkholder, R. K. Talukdar, J. Meagher, F. C. Fehsenfeld, and S. S. Brown. Unexpectedly High $ClNO_2$ Mixing Ratios in the Polluted Subtropical Marine Boundary Layer. *Nature Geosc.*, **1**, 324-328, 2008.

Pechtl, S., E. R. Lovejoy, J. B. Burkholder, and R. von Glasow. Modeling the possible role of iodine oxides in atmospheric new particle formation. *Atmos. Chem. Phys.*, **6**, 503-523, 2006.

Pechtl, S., G. Schmitz, and R. von Glasow. Modeling iodide iodate speciation in atmospheric aerosol. *Atmos. Chem. Phys.*, **7**, 1381-1393, 2007.

Pechtl, S. and R. von Glasow. Reactive chlorine in the marine boundary layer in the outflow of polluted continental air: A model study. *Geophys. Res. Lett.*, **34**, L11 813, doi:10.1029/2007GL029 761, 2007.

Peters, C., S. Pechtl, J. Stutz, K. Hebestreit, G. Hönninger, K. G. Heumann, A. Schwarz, J. Winterlik, and U. Platt. Reactive and organic halogen species in three different European coastal environments. *Atmos. Chem. Phys.*, **5**, 3357-3375, 2005.

Piot, M. and R. von Glasow. The potential importance of frost flowers, recycling on snow, and open leads for Ozone Depletion Events. *Atmos. Chem. Phys.*, **8**, 2437-2467, 2008.

Platt, U., W. Allan, and D. Lowe. Hemispheric average Cl atom concentration from $^{13}C/^{12}C$ ratios in atmospheric methane. *Atmos. Chem. Phys.*, **4**, 2393-2399, 2004.

Platt, U. and G. Hönninger. The role of halogen species in the troposphere. *Chemosphere*, **52**, 325-338, 2003.

Platt, U. and C. Janssen. Observation and Role of the Free Radicals NO_3, ClO, BrO and IO in the Troposphere. *Faraday Discuss.*, **100**, 175-198, 1995.

Read, K. A., A. C. Lewis, S. Bauguitte, A. M. Rankin, R. A. Salmon, E. W. Wolff, A. Saiz-Lopez, W. J. Bloss, D. E. Heard, J. D. Lee, and J. M. C. Plane. DMS and MSA measurements in the Antarctic boundary layer: impact of BrO on MSA production. *Atmos. Chem. Phys.*, **8**, 2985-2997, 2008a.

Read, K. A., A. S. Mahajan, L. J. Carpenter, M. J. Evans, B. V. E. Faria, D. E. Heard, J. R. Hopkins, J. D. Lee, S. J. Moller, A. C. Lewis, L. Mendes, J. B. McQuaid, H. Oetjen, A. Saiz-Lopez, M. J. Pilling, and J. M. C. Plane. Extensive halogenmediated ozone destruction over the tropical Atlantic Ocean. *Nature*, **453**, 1232-1235, 2008b.

Roberts, J. M., H. D. Osthoff, S. S. Brown, and A. R. Ravishankara. N_2O_5 Oxidizes Chloride to Cl_2 in Acidic Atmospheric Aerosol. *Science*, page 10.1126/science. 1158777, 2008.

Saiz-Lopez, A. and C. S. Boxe. A mechanism for biologically-induced iodine emissions from sea-ice. *Atmos. Chem. Phys. Discuss.*, **8**, 2953-2976, 2008.

Saiz-Lopez, A., K. Chance, X. Liu, T. P. Kurosu, and S. P. Sander. First observations of iodine oxide from space. *Geophys. Res. Lett.*, **34**, L12 812, doi:10.1029/2007GL030 111, 2007a.

Saiz-Lopez, A., A. S. Mahajan, R. A. Salmon, S. J.-B. Bauguitte, A. E. Jones, H. K. Roscoe, and J. M. C. Plane. Boundary layer halogens in coastal Antarctica. *Science*, **317**, 348-351, 2007b.

Saiz-Lopez, A. and J. M. C. Plane. Novel iodine chemistry in the marine boundary layer. *Geophys. Res. Lett.*, **31**, L04 112, doi: 10.1029/2003GL019 215, 2004.

Saiz-Lopez, A., J. A. Shillito, H. Coe, and J. M. C. Plane. Measurements and modelling of I2, IO, OIO, BrO and NO_3 in the mid-latitude marine boundary layer. *Atmos. Chem. Phys.*, **6**, 1513-1528, 2006a.

Saiz-Lopez, A. J. M. C. P., G. McFiggans, P. I. Williams, S. M. Ball, M. Bitter, R. L. Jones, C. Hongwei, and T. Hoffmann. Modelling molecular iodine emissions in a coastal marine environment: the link to new particle formation. *Atmos. Chem. Phys.*, **6**, 883-895, 2006b.

Sander, R., J. Burrows, and L. Kaleschke. Carbonate precipitation in brine - the trigger for tropospheric ozone depletion events. *Atmos. Chem. Phys.*, **6**, 4653-4658, 2006.

Sander, R. and P. J. Crutzen. Model study indicating halogen activation and ozone destruction in polluted air masses transported to the sea. *J. Geophys. Res.*, **101**, 9121-9138, 1996.

Sander, R., W. C. Keene, A. A. P. Pszenny, R. Arimoto, G. P. Ayers, E. Baboukas, J. M. Cainey, P. J. Crutzen, R. A. Duce, G. Hönninger, B. J. Huebert, W. Maenhaut, N. Mihalopoulos, V. C. Turekian, and R. V. Dingenen. Inorganic bromine compounds in the marine boundary layer: A critical review. *Atmos. Chem. Phys.*, **3**, 1301-1336, 2003.

Saunders, R. W. and J. M. C. Plane. Formation Pathways and Composition of Iodine Oxide Ultra-Fine Particles. *Env. Chem.*, **2**, 299-303, 2005.

Schönhardt, A., A. Richter, F. Wittrock, H. Kirk, H. Oetjen, H. K. Roscoe, and J. P. Burrows. Observations of iodine monooxide (IO) columns from satellite. *Atmos. Chem. Phys.*, **8**, 637-653, 2008.

Schroeder, W. H., K. G. Anlauf, L. A. Barrie, J. Y. Lu, A. Steffen, D. R. Schneeberger, and T. Berg. Arctic springtime depletion of mercury. *Nature*, **394**, 331-332, 1998.

Simpson, W. R., R. von Glasow, K. Riedel, P. Anderson, P. Ariya, J. Bottenheim, J. Burrows, L. Carpenter, U. Frie, M. E. Goodsite, D. Heard, M. Hutterli, H.-W. Jacobi, L. Kaleschke, B. Neff, J. Plane, U. Platt, A. Richter, H. Roscoe, R. Sander, P. Shepson, J. Sodeau, A. Steffen, T. Wagner, and E. Wolff. Halogens and their role in polar boundary-layer ozone depletion. *Atmos. Chem. Phys.*, **7**, 4375-4418, 2007.

Smoydzin, L. Modelling Gas Phase and Aerosol Phase Chemistry in the Atmospheric Boundary Layer. Ph.D. thesis, Universität Heidelberg, Germany, http: www.ub.uni-heidelberg.de/archiv/8501, 2008.

Spicer, C. W., E. G. Chapman, B. J. Finlayson-Pitts, R. A. Plastridge, J. M. Hubbe, J. D. Fast, and C. M. Berkowitz. Unexpectedly high concentrations of molecular chlorine in coastal air. *Nature*, **394**, 353-356, 1998.

Steffen, A., T. Douglas, M. Amyot, P. Ariya, K. Aspmo, T. Berg, J. Bottenheim, S. Brooks, F. Cobbett, A. Dastoor, A. Dommergue, R. Ebinghaus, C. Ferrari, K. Gardfeldt, M. E. Goodsite, D. Lean, A. J. Poulain, C. Scherz, H. Skov, J. Sommar, and C. Temme. A synthesis of atmospheric mercury depletion event chemistry in the atmosphere and snow. *Atmos. Chem. Phys.*, **8**, 1445-1482, 2008.

Strong, C., J. D. Fuentes, R. E. Davis, and J. W. Bottenheim. Thermodynamic attributes of Arctic boundary layer ozone depletion. *Atmos. Environ.*, **36**, 2641-2652, 2002.

Stutz, J., R. Ackermann, J. D. Fast, and L. Barrie. Atmospheric Reactive Chlorine and Bromine at the Great Salt Lake, Utah. *Geophys. Res. Lett.*, **29**, 1380, doi: 10.1029/2002GL014 812, 2002.

Stutz, J., O. Pikelnaya, S. C. Hurlock, S. Trick, S. Pechtl, and R. von Glasow. Daytime OIO in the Gulf of Maine. *Geophys. Res. Lett.*, **34**, L22 816, doi:10.1029/2007GL031 332, 2007.

Tanaka, P. L., S. Oldfield, J. D. Neece, C. B. Mullins, and D. T. Allen. Anthropogenic Sources of Chlorine Formation in Urban Atmospheres. *Environ. Sci. Technol.*, **34**, 4470-4473, 2000.

Tanaka, P. L., D. D. Riemer, S. Chang, G. Yarwood, E. C. McDonald-Buller, E. C. Apel, J. J. Orlando, P. J. Silva, J. L. Jimenez, M. R. Canagaratna, J. D. Neece, C. B. Mullins, and D. T. Allen. Direct Evidence for Chlorine-Enhanced Urban Ozone Formation in Houston, TX. *Atmos. Environ.*, **37**, 1393-1400, 2003.

Theys, N., M. V. Roozendael, F. Hendrick, C. Fayt, C. Hermans, J.-L. Baray, F. Goutail, J.-P. Pommereau, and M. D. Maziè°re. Retrieval of stratospheric and tropospheric BrO columns from multi-axis DOAS measurements at Reunion Island (21° S, 56° E). *Atmos. Chem. Phys.*, **7**, 4733-4749, 2007.

Van Roozendael, M., T. Wagner, A. Richter, I. Pundt, D. W. Arlander, J. P. Burrows, M. Chipperfield, C. Fayt, P. V. Johnston, J.-C. Lambert, K. Kreher, K. Pfeilsticker, U. Platt, J.-P. Pommereau, B.-M. Sinnhuber, K. K. Tørnkvist, and F. Wittrock. Intercomparison of BrO measurements from ERS-2 GOME, ground-based and balloon platforms. *Adv. Space Res.*, **29**, 1661-1666, 2002.

Vogt, R., P. J. Crutzen, and R. Sander. A mechanism for halogen release from sea-salt aerosol in the remote marine boundary layer. *Nature*, **383**, 327-330, 1996.

Vogt, R., R. Sander, R. von Glasow, and P. Crutzen. Iodine Chemistry and its Role in Halogen Activation and Ozone Loss in the Marine Boundary Layer: A Model Study. *J. Atmos. Chem.*, **32**, 375-395, 1999.

von Glasow, R. and P. J. Crutzen. Model study of multiphase DMS oxidation with a focus on halogens. *Atmos. Chem. Phys.*, **4**, 589-608, 2004.

von Glasow, R. and P. J. Crutzen. Tropospheric halogen chemistry. In Treatise on Geochemistry Update 1, vol.4.02 (eds. H. D. Holland and K. K. Turekian), pages 1-67. Elsevier-Pergamon, Oxford, 2007.

von Glasow, R., R. Sander, A. Bott, and P. J. Crutzen. Modeling halogen chemistry in the marine boundary layer. 1. Cloud-free MBL. *J. Geophys. Res.*, **107**, 4341, doi: 10.1029/2001JD000 942, 2002a.

von Glasow, R., R. Sander, A. Bott, and P. J. Crutzen. Modeling halogen chemistry in the marine boundary layer. 2. Interactions with sulfur and cloud-covered MBL. *J. Geophys. Res.*, **107**, 4323, doi: 10.1029/2001JD000 943, 2002b.

von Glasow, R., R. von Kuhlmann, M. G. Lawrence, U. Platt, and P. J. Crutzen. Impact of reactive bromine chemistry in the troposphere. *Atmos. Chem. Phys.*, **4**, 2481-2497, 2004.

Wagner, T., C. Leue, M. Wenig, K. Pfeilsticker, and U. Platt. Spatial and temporal distribution of enhanced boundary layer BrO concentrations measured by the GOME instrument aboard ERS-2. *J. Geophys. Res.*, **106**, 24,225-24,235, 2001.

Wagner, T. and U. Platt. Satellite mapping of enhanced BrO concentrations in the troposphere. *Nature*, **395**, 486-490, 1998.

Watanabe, A., Y. Nojiria, and S. Kariyab. Measurement on a commercial vessel of the ozone concentration in the marine boundary layer over the northern North Pacific Ocean. *J. Geophys. Res.*, **110**, D11 310, doi:10.1029/2004JD005 514, 2005.

Wingenter, O. W., D. R. Blake, N. J. Blake, B. C. Sive, F. S. Rowland, E. Atlas, and F. Flocke. Tropospheric hydroxyl and atomic chlorine concentrations, and mixing timescales determined from hydrocarbon and halocarbon measurements made over the Southern Ocean. *J. Geophys. Res.*, **104**, 21,819-21,828, 1999.

Wingenter, O. W., M. K. Kubo, N. J. Blake, T. W. Smith, Jr., D. R. Blake, and F. S. Rowland. Hydrocarbon and halocarbon measurements as photochemical and dynamical indicators of atmospheric hydroxyl, atomic chlorine, and vertical mixing obtained during Lagrangian flights. *J. Geophys. Res.*, **101**, 4331-4340, 1996.

Yang, X., R. A. Cox, N. J. Warwick, J. A. Pyle, G. D. Carver, F. M. O'Connor, and N. H. Savage. Tropospheric bromine chemistry and its impacts on ozone. *J. Geophys. Res.*, **110**, D23 311, doi:10.1029/2005JD006 244, 2005.

Zingler, J. and U. Platt. Iodine oxide in the Dead Sea Valley: Evidence for inorganic sources of boundary layer IO. *J. Geophys. Res.*, **110**, D07 307, doi:10.1029/2004JD004 993, 2005.

* * *

Expert Workshop

On the relevance of surface and boundary layer processes for the exchanges of reactive- and greenhouse gases

Wageningen, Netherlands, 9-12th October, 2007

Contributed by **Laurens Ganzeveld** *Environmental Sciences Group, Chair group Earth System Sciences, Wageningen University and Research Centre (WUR), Netherlands & Max Planck Institute for Chemistry, Germany* (Laurens.Ganzeveld@wur.nl) **Jordi Vilà-Guerau de Arellano**, *Environmental Sciences Group, Chair group Meteorology and Air Quality, WUR, Wageningen, Netherlands,* **Cor Jacobs** *Environmental Sciences Group, Alterra, WUR, Wageningen, Netherlands,* ***et al.****

*front row, left to right: Jordi Vilà-Guerau de Arellano, Jose Fuentes, Chiara Di Marco, Leonor Tarrason, Daniela Famulari; 2nd row: Douglas Martins, Herbert ter Maat, Mary Barth, Arnoud Frumau, Mary-Anne Carroll, Laurens Ganzeveld, Mike Sanderson, Janne Rinne, Stefano Galmarini, Petra Kroon, Monica Gorska, Maarten Krol, Elise Hendriks, Lars Nieradzik, Veronica Wolff; back row: Harm Jonker, Ned Patton, Cor Jacobs, Jielun Sun, Don Lenschow, Bert Holtslag, Sarah Cornell, Dennis Baldocchi, Rainer Steinbrecher, Anton Beljaars, Alex Gunther, Delphine Farmer, David Simpson, Chiel van Heerwaarden, Franz Meixner, Jens Mayer; participants missing from photo: David Fowler, Thomas Karl, Maria Rosa Soler, Otávio Acevedo and Pau Casso

Demanding air quality policies and the established role of greenhouse gases, reactive trace gases and aerosols in climate and global change have challenged us to assess the reliability of our understanding of the physical and chemical processes influencing the distribution of these atmospheric compounds. In particular, the surface and atmospheric boundary layer play a key role in the distribution and evolution of atmospheric compounds since the majority of sources and sinks are located at or near the Earth's surface, yet many critical boundary layer processes are still poorly understood and/or are not well represented in models.

About 40 experts gathered 9-12 October, 2007 in Wageningen, The Netherlands, to present and discuss current issues around surface and boundary layer exchanges of reactive- and greenhouse gases. The workshop aimed to review the current knowledge of the relationship between physical and chemical processes in the boundary layer and their impact on the larger spatial and temporal scale distribution of atmospheric compounds. Three main themes were discussed: 1) Atmosphere-land interaction: sources and sinks of atmospheric compounds 2) Boundary layer processes: mixing, dispersion and exchange with free troposphere 3) Implementation of surface and boundary layer models in air quality and atmospheric chemistry-transport models.

Recent development of new measurement and data analysis techniques as well as the possibility of using finer scale models allows us to tackle new questions regarding the role of small scale processes in trace gas exchanges. Consequently, one important goal of the workshop was to determine whether these new observational, data analysis and modelling techniques are suited to address the key questions in surface and boundary layer greenhouse and reactive trace gas exchange. Another objective of the workshop was to discuss the need for and optimal design of future experimental campaigns to provide balanced information on the role of physical and chemical surface and boundary layer processes in atmospheric chemistry. Therefore, the workshop also aimed to establish a close interaction between modellers and experimentalists and to promote interaction between the atmospheric physics and chemistry communities.

In previous meetings of the Scientific Steering Committee (SSC) of iLEAPS (integrated Land-Ecosystem Atmosphere Processes Study, http://www.ileaps.org/) and IGAC and also in a GABLS (GEWEX Atmospheric Boundary Layer Study) meeting, June 2007, we received very positive feedback on presentations in which we addressed the need for a renewed focus on this topic. In addition, we, as organizers, had numerous discussions on the subject. Based on the received feedback and these discussions we concluded that organization of such a focussed meeting was timely and would be well-received by the community.

In this letter, we present a brief description of the main topics and highlights of the discussions relevant to the atmospheric chemistry community. Our intention is to use the workshop outcome as a roadmap of the topics that require further investigation in the near future. These are:

1) the current status and deployment of measurement technology to conduct trace gas flux measurements;
2) uncertainties in fluxes inferred from observed tracer concentrations in the boundary layer;
3) reactive trace gas exchanges under nocturnal conditions;
4) the impact of turbulence and non-uniform emissions on chemical reactivity; and
5) the dependence of modelled tracer concentration on the representation of the planetary boundary layer (day-time and night-time conditions).

These issues were addressed at the workshop in presentations by Dennis Baldocchi, David Fowler, Franz Meixner, Alex Guenther, Laurens Ganzeveld, Thomas Karl, Jordi Vilà-Guerau de Arellano, Stefano Galmarini, Jose Fuentes, Harm Jonker, David Simpson, Mary Barth, Anton Beljaars and Mike Sanderson.

Flux measurements

The direct measurement of reactive trace gas fluxes is particularly relevant to improve our understanding of reactive trace gas exchanges since concentration measurements are often not sufficient to infer sources and sinks (emissions, deposition and chemistry) due to the role of fast chemical transformations. These chemical transformations can result in a flux-divergence, which implies that measurements at a particular height do not necessarily reflect the actual surface sources or sinks. A further implication is that the "big leaf" approach (including the canopy as a bulk entity without considering the vertical gradients in radiation, turbulence, etc.) to representing atmosphere-biosphere exchanges in models such as atmospheric chemistry and transport models (ACTMs), is not valid. As such, the development and application of flux measurement technology is particularly important for improving our understanding of reactive trace gas exchanges.

Presentations at the workshop included thorough reviews of techniques for flux measurements of trace gases. Topics ranged from the comparison of gradient- and Relaxed Eddy Accumulation (REA) ammonia flux measurements, the application of the Eddy-Covariance (EC) technique over urban areas, airborne trace gas flux observations and the use of remote sensing techniques to infer trace gas emissions. New measurement technologies, e.g., ozone chemiluminescence sensors, protonated mass spectrometers (PTR-MS) and laser spectrometers, now allows us to observe the concentrations of many trace gases, including reactive components and even radicals. However, the requirement to measure concentrations at frequencies > 1 Hz poses the main limitation to the direct measurement of the flux of many reactive compounds based on EC systems. Therefore, more indirect alternatives are often deployed, including the gradient, REA and Disjunct Eddy Covariance techniques.

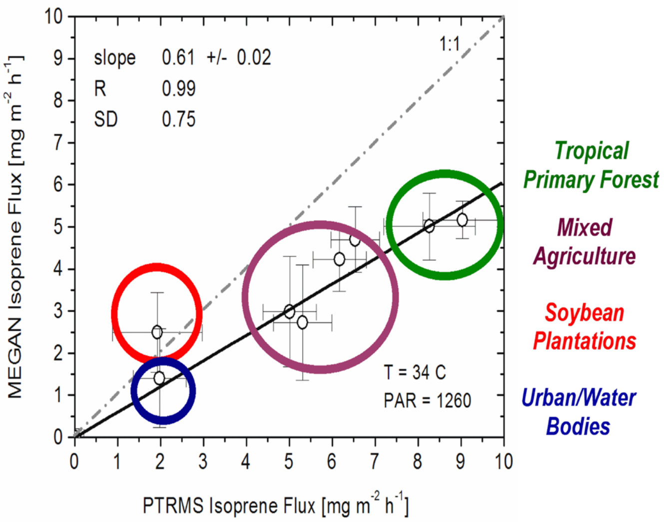


Figure 1. Comparison of airborne observed (x-axis) and simulated (y-axis) isoprene emission flux for different tropical landscapes indicating differences between a state-of-the-art emission model and the observations as well as the range and spatial variability in source strengths (Karl *et al.*, 2007)

At present, there is a lack of long-term (> ~1 month) observations of reactive trace gas fluxes. Such observations are needed to address important scientific questions associated with seasonal and inter-annual variations in reactive trace gases exchanges in response to climate change and ecological disturbances. Long-term monitoring of reactive trace gas fluxes should be co-located at the carbon and water flux sites (FLUXNET, Baldocchi et al., 2001) in order to assure that the complementary information on meteorological and biological drivers of reactive trace gas exchanges such as turbulent transport, photosynthesis, and soil moisture, are available. At present, interpretation of results from atmospheric chemistry campaigns are quite often hampered by missing information on these drivers.

New measurement technology also allows us to assess the impact of fast chemical transformations on the exchange of reactive compounds, including NO_x, O_3 and biogenic volatile organic compounds (BVOCs). There is quite substantial evidence from, e.g., missing OH reactivity and missing sources of secondary aerosols, that a large fraction of the BVOCs, emitted inside the canopy is not adequately sampled using EC instruments, since these BVOCs do not escape the canopy due to fast chemical transformations. Canopy scale ozone fluxes measurements are extremely useful to indicate the presence of "missing compounds" that are highly reactive towards ozone. This underlines the need of multi-specie flux and concentration measurements, in this particular case of BVOC and O_3.

One remaining challenge regarding flux measurements of trace gases is the development of instruments with sufficiently low detection limits, fast response and high precision. In addition, there is the need for the development of EC systems for a wider selection of volatile organic compounds (e.g., sesquiterpenes), semi-volatile organic compounds (important for Secondary Organic Aerosol production), chemically speciated aerosols, nitrogen and halogen compounds. The development of such instruments could benefit from newly emerging technologies such as chemical ionization mass spectrometry instruments and optical techniques. Another challenge is the further development and application of airborne and remote sensing measurement technology, which is extremely useful to assess the magnitude of as well as spatial variability in reactive trace gas exchanges at multiple scales ranging from the mesoscale (> BL depth, ~1km) up to the grid size of atmospheric chemical transport models (ACTMs, > 50km). One particular example that illustrates such an application of airborne flux technology to assess multi-scale surface fluxes is given in Figure 1, which shows an assessment of the spatial variability in BVOC emissions and a comparison with a state-of-the-art emission inventory (MEGAN; Guenther et al., 2006). Another example is the current development of remote sensing techniques to observe the boundary layer (BL) depth, which will ultimately provide the most optimal data to validate the BL depth in large scale models such as the ACTMs.

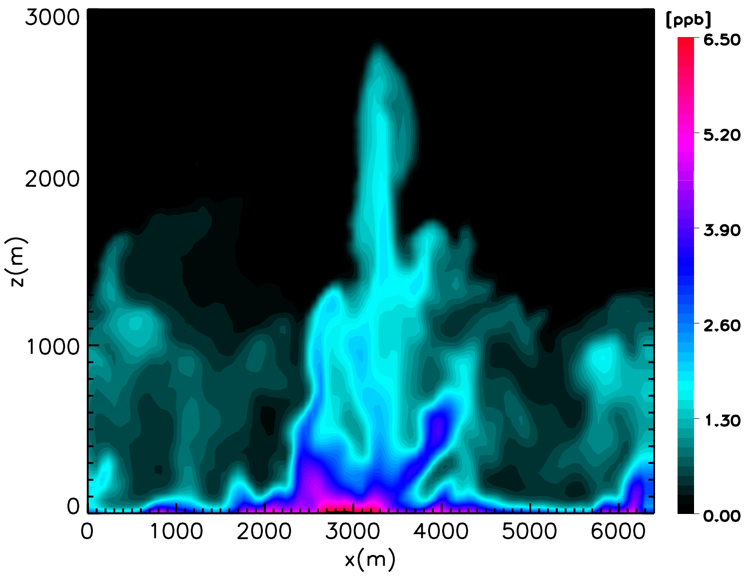


Figure 2. Simulated mixing ratio of a generic reactive hydrocarbon compound as a function of altitude within the 6km domain of a Large Eddy Simulation (LES) model, showing the enhanced upward transport through the presence of shallow cumulus clouds on top of the BL (Vilà-Guerau de Arellano and van den Dries, 2008).

Limitations on boundary layer mass budget methods

One of the topics discussed at length during the workshop was the limitations of the application of boundary layer mass budget methods. Despite recent development in flux observation techniques there is still a large number of reactive compounds for which surface fluxes can only be inferred from concentration measurements – e.g., from the surface layer gradient or from the observed BL concentration evolution and an assumed mixing volume. Application of the surface layer gradient method is hampered by the potential importance of counter-gradient transport and different footprints of the observations at different heights. Limitations on the applicability of the boundary layer mass budget method were discussed in some detail during the workshop, including in the context of the significance of the exchange between the BL and the overlaying free troposphere (FT), the so-called entrainment or detrainment fluxes, and the role of enhanced mixing due to the presence of clouds.

Entrainment (the mixing of FT air into the BL) or detrainment (ventilation out of the BL) is quite often ignored because it is assumed that these fluxes are relatively small compared to surface fluxes and other BL source and sink terms. However, for any compound with FT concentrations not that different from or substantially higher than those in the BL (e.g, for BVOC oxidation products formed in the nocturnal residual layer, see also next section) mass budget calculations to infer surface fluxes should consider the extra source through entrainment of FT air masses.

In the BL mass budget method the boundary layer height is assumed to reflect the mixing volume and the method is extremely sensitive to a proper characterization of the BL height. The BL depth may change rapidly and varies between some 100m for a nocturnal inversion to a fully developed BL with a depth ranging from 500m (over wet surface for relative cool conditions), to 1500m over tropical forests, to up to 3000m over hot deserts. The BL depth can be diagnosed from the potential temperature (θ) and moisture profiles. However, the method is highly complicated by the presence of clouds due to their effect on the profiles and the mixing conditions. This is illustrated in Figure 2 which shows the mixing ratios of a generic reactive hydrocarbon compound as a function of altitude as simulated with an Large Eddy Simulation (LES) model that includes the role of shallow cumulus convection (Vilà-Guerau de Arellano and van de Dries, 2008). The presence of the clouds can be clearly identified from the enhanced mixing ratios (> 1ppbv) in the updraft up to an altitude of 2800m. Shallow cumulus clouds may result in a decrease in the average mixing ratio of up to 50% as compared to the clear sky situation, depending on the lifetime of the tracer under consideration. Thus the uncertainty in inferring surface fluxes from concentrations in the BL is strongly increased in the presence of clouds. This fact stresses the point that using the BL budget methodology to infer emissions requires a critical assessment of the role of this enhanced mixing mechanism through careful diagnosis of the vertical profiles of physical properties and, preferably, of tracers with different lifetimes.

Nocturnal trace gas exchanges

The previous discussion on the limitations of the application of the BL budget method is not restricted to the role of daytime processes. For example, daytime entrainment and detrainment fluxes also depend on the nocturnal evolution of the residual layer (remnant of the daytime boundary layer) from which air masses are being entrained into the growing BL after sunrise.

There are a number of challenges involved in understanding and quantifying nocturnal trace gas exchanges. One is that suppressed turbulence during the night complicates proper measurements of the nocturnal fluxes. Moreover, during nocturnal suppressed turbulence conditions chemical interactions may occur at timescales shorter than the turbulent timescale resulting in large flux divergences (Galmarini et al., 1997) and fluxes measured above the canopy do not represent the actual surface emission or deposition flux.

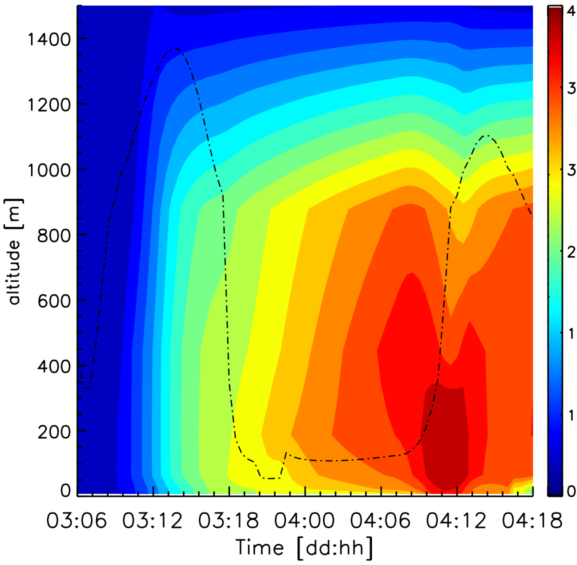


Figure 3. HCHO mixing ratios (ppbv) for 2 days (3-4 October) up to 1500m over the Guyana's tropical forest, as simulated with a single column chemistry and climate model. The black dashed line denotes the diagnostic PBL height (Ganzeveld *et al.*, 2008).

Another important and interesting topic discussed during the workshop is the role of the composition of and chemical processes in the nocturnal residual layer. Figure 3 shows formaldehyde (HCHO) mixing ratios for two days up to 1500m altitude as simulated by a single-column chemistry and climate model (along with the diagnostic BL depth) over a tropical forest. These results indicate that HCHO, accumulating in the residual layer at night, provides an additional source of HCHO and sink for oxidants, e.g., hydroxyl, in the early morning through the entrainment of these air masses into the growing BL. Unfortunately, these simulations could not be validated due to the lack of observations in the nocturnal residual layer, a feature which consequently should be included in future campaigns (Ganzeveld et al., 2008).

Finally, observed and surprisingly high surface removal rates of a number of volatile organic compounds (Karl et al., 2004) were discussed. One postulated explanation for these high removal rates is enhanced uptake due to the presence of dew. This makes sense for soluble compounds, e.g., methanol, but does not seem a feasible explanation for the observed efficient removal of insoluble compounds like isoprene. These results indicate that the theory on dry deposition processes – used to develop dry deposition algorithms implemented in ACTMs – needs to be revisited. Since turbulent transport to the surface becomes a limiting term for the observed efficient surface removal rates, such a future revision would also rely on the progress made by the GABLS (http://www.gewex.org/gabls.htm) community on the representation of the stable boundary layer (SBL) in meteorological and climate models.

Influence of turbulence and emission variability on the reactivity

The "intensity of segregation" (I_s; the ratio of the covariance between reactants normalized by the ensemble horizontal mixing ratio average) expresses the change in the reaction efficiency due to non-homogenous mixing conditions. The significance of the intensity of segregation has been intensively studied in the past (Petersen and Holtslag, Krol et al., 2000, Patton et al., 2001) using analytical as well as numerical analyses, which indicate a maximum decrease in the efficiency of the reaction between isoprene and OH on the order of 10-20%. However, those analyses generally applied rather idealized and simple chemistry representations. Present computing facilities now allow the inclusion of more detailed chemical reaction schemes in, for example, large eddy simulation (LES) models. Recent numerical and observational studies have also addressed the role of shallow cumulus convection in chemistry and in transport interactions, indicating a significant impact of clouds on I_s but these results need further corroboration (Karl et al., 2007; Vilà-Guerau de Arellano and van de Dries, 2008). A recent study by Butler et al. (2008) of isoprene oxidation over Guyana's tropical forest suggested an I_s of 50% is needed for the OH-C_5H_8 reaction in order to reconcile simulated and observed OH and C_5H_8 concentrations. This estimate is substantially larger than the maximum simulated $I_{sC_5H_8\text{-}OH}$ shown in Figure 4, which shows the

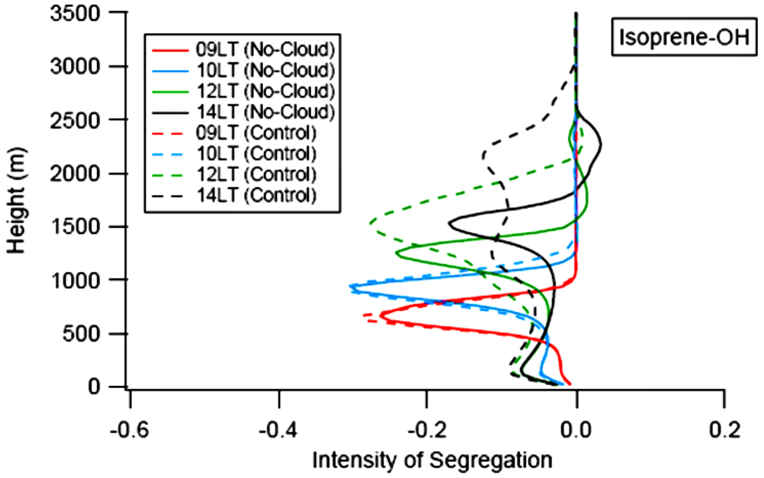


Figure 4. Simulated evolution in the 9:00-14:00 local time (LT) vertical profiles of the intensity of segregation, Is, between isoprene and OH for a clear-sky (solid lines) and cloudy (dashed lines) cases (Kim *et al.*, 2004).

evolution of the vertical dependence of $I_{sC_5H_8\text{-}OH}$ for a clear-sky and a cloud case. These results indicate that in the clear sky case the maximum intensity of segregation of 30% peaks at the top of boundary layer whereas in cloudy case there is a segregation of about 10% throughout the cloud layer (Kim et al., 2004).

During the workshop it was concluded that the intensity of segregation does have a significant impact at the local and short time scales on the efficiency of reactions which occur on a timescale comparable to that of the turbulent and convective transport. However, this area still requires further research using new observational and modeling tools, to assess its relevance at larger (e.g., ACTMs grid scale) and longer time- (> days) scales. The main challenges here appear to be assessing the relevance of the intensity of segregation, preferably through high temporal resolution measurement of the I_s, for those chemical species which react at timescales comparable to the turbulent timescale. This should not be limited to the BL turbulence regime but should also include the mixing conditions inside the canopy and in the lower free troposphere with clouds present.

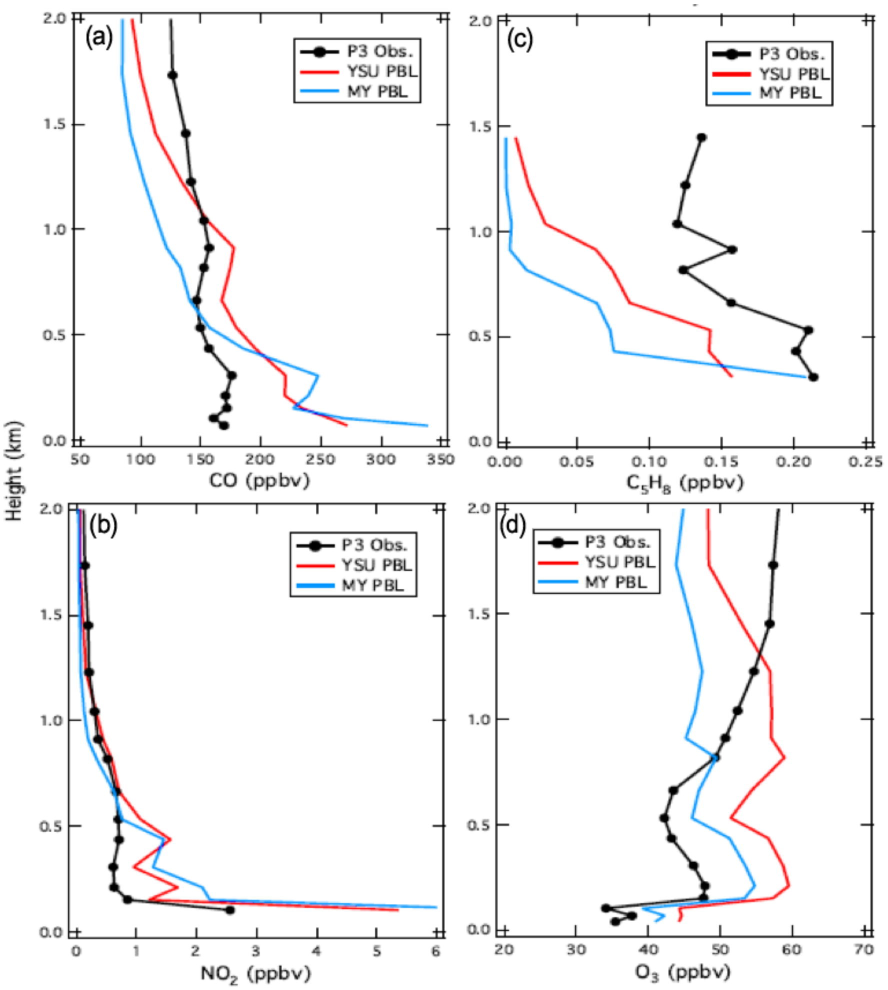


Figure 5. Comparison of observed (black solid-dotted line) and simulated mixing ratios for the YSU (red) and Mellor-Yamada (blue) boundary layer schemes for (a) CO, (b) NO_2, (c) C_5H_8, and (d) O_3 (Kim *et al.*, 2006).

Sensitivity in tracer concentrations to different BL models

It is often thought that the representation of temporal and spatial variability in boundary layer mixing in ACTMs is appropriate to serve the purpose of these models. However, those representations are commonly based on rather simple schemes such as the so-called first-order or K-theory schemes, which are known to suffer from severe limitations such as their inability to deal with counter-gradient transport. The meteorological boundary layer community has demonstrated that there are many limitations in these BL turbulent transport models, including in the representation of the stable boundary layer (SBL) and regarding the role of stratocumulus clouds at the top of BL, which it is known can have a strong impact on tracer transport. In addition, many campaigns have provided observations of the BL structure which reveal large discrepancies between the observed BL properties and those simulated in ACTMs. This raises the question of the implications of these discrepancies in the models' representation of simulated reactive trace gas exchanges. Figures 5a, b, c and d show the CO, NO_2, C_5H_8 and O_3 mixing ratios, respectively, simulated with two different BL schemes (Mellor-Yamada, MY, and YSU) implemented in the WRF-CHEM model (http://ruc.fsl.noaa.gov/wrf/WG11/) and a comparison with observations (Kim et al., 2006). For CO, NO_2 and O_3 both BL schemes result in a serious overestimation of the mixing ratios below 500m when compared to the observations. However, there is an underestimation above the BL for the longer-lived CO, with a vertical profile that reflects surface emission, and for O_3, with the typical deposition profile, which suggests a misrepresentation of the exchange between the BL and FT. Overall the analysis showed significant differences between the simulated summertime BL average mixing ratios of these compounds over the U.S. for the two different BL schemes. This appears to be the first comprehensive assessment of the sensitivity of atmospheric chemistry simulations to boundary turbulent transport schemes. As such, these results indicate the uncertainty that one can expect in the ACTMs' simulated BL reactive trace gas mixing ratios associated with the current representation of BL turbulent transport.

Conclusions

It was concluded at the workshop that the atmospheric chemistry community would benefit from a coordinated activity that focuses on improving our understanding and quantification of the role of surface and boundary layer processes in atmospheric chemistry. In addition, a balanced analysis of the relevance of chemical versus non-chemical processes is needed for the interpretation of observed surface and boundary layer concentrations and fluxes of reactive compounds as well as for evaluating ACTM simulations, through comparison with surface and BL observations. This is particularly relevant for compounds with a lifetime comparable to the surface and boundary layer turbulent transport timescales since the temporal and spatial variability in their concentrations and fluxes reflects to a large extent the variability in non-chemical surface and boundary layer processes. Such a coordinated activity should aim to increase the awareness among the atmospheric chemistry community about the relevance of these non-chemical surface and boundary layer processes. It should also provide guidance on the optimal planning of observations with balanced representation of chemical versus non-chemical measurements and, finally, it should provide the tools, e.g., improved models of nocturnal and daytime boundary layer tracer transport, for implementation in ACTMs.

Acknowledgments

We highly appreciate the financial endorsement for this expert workshop by ACCENT's (Atmospheric Composition Change, the European Network of Excellence) T&TP (Transport and Transformation Processes) and QUEST (Quantifying and Understanding the Earth System). The workshop has been scientifically endorsed by iLEAPS. We also highly appreciate the help by Kees van den Dries and Ria Cuperus in the organization of the workshop and want to thank Si-Wan Kim, Mary Barth and Thomas Karl for providing some of the figures.

References

Galmarini, S., Vilà-Guerau de Arellano, J., and Duynkerke, P. G., Scaling the turbulent transport of chemical compounds in the surface layer under neutral and stratified conditions, *Q. J. R. Meteorol. Soc.,* **123***,* 223-242, 1997.

Ganzeveld, L., Eerdekens, G., Feig, G., Fischer, H., Harder, H., Königstedt, R., Kubistin, D., Martinez, M., Meixner, F. X., Scheeren, B., Sinha, V., Taraborrelli, D., Williams, J., Vilà-Guerau de Arellano, J., and Lelieveld, J., Surface and Boundary Layer Exchanges of Volatile Organic Compounds, Nitrogen Oxides and Ozone during the GABRIEL Campaign, *Atmos. Chem. Phys. Discus.,* 2008.

Guenther, A., et al., Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature), *Atmos. Chem. Phys.,* **6**, 3181–3210, 2006.

Karl, T., Potosnak, M, Guenther, A, et al., Exchange processes of volatile organic compounds above a tropical rain forest: Implications for modeling tropospheric chemistry above dense vegetation, *J. Geophys. Res.,* **109**, D18306, doi:10.1029/2004JD004738, 2004.

Karl, T., Guenther, A., Yokelson, R.J., Greenberg, J., Potosnak, M., Blake, D.R., and Artaxo, P., The tropical forest and fire emissions experiment: Emission, chemistry, and transport of biogenic volatile organic compounds in the lower atmosphere over Amazonia, *J. Geophys. Res.,* **112**, doi:10.129/2007JD008539, 2007.

Kim, S.-W., M. C. Barth, C.-H. Moeng, The effect of shallow cumulus convection on the segregation of chemical reactants, in Proceedings of the 16th Symposium on Boundary Layers and Turbulence, August 9-13, 2004.

Kim, S.-W. et al., The influence of PBL parameterizations on the distributions of chemical species in a mesoscale chemical transport model, WRF-Chem, in Proceedings of the 17th Symposium on Boundary Layers and Turbulence, 2006.

Krol, M. C., Molemaker, J. M., and Vilà Guerau de Arellano, J., Effects of turbulence and heterogeneous emissions on photochemically active species in the convective boundary layer, *J. Geophys. Res.,* **105***,* 6871-6884, 2000.

Patton, E. G., Davis, K. J., Barth, M. C., and Sullivan, P. S., Decaying scalars emitted by a forest canopy: A numerical study, *Boundary Layer Meteorol.*, **100**, 91-129, 2001.

Petersen, A. C., and Holtslag, A. M., A first-order closure for covariances and fluxes of reactive species in the convective boundary layer, *J. of Applied Meteorolog.,* 1758–1776, 1999.

Vilà-Guerau de Arellano, J. and van den Dries, K., Atmospheric turbulent reacting flows influenced by shallow cumulus: a large-eddy simulation study, ERCOTFAC (European Research Community on Flow, Turbulence and Combustion) research letters, September 2008.

* * *

Aerosols, Clouds, Precipitation, Climate (ACPC): Outline for a new joint IGBP/WCRP initiative

Bjorn Stevens *Dept. of Atmospheric and Ocean Sciences, University of Lost Angeles, California, USA* (bstevens@atmos.ucla.edu), *the* **ACPC Planning Team** *and* **Participants of the ACPC workshop***, 8-10 October 2007, Boulder, Colorado, USA*.

Background

Environmental hazards in the form of air pollution, floods and droughts affect a large portion of the world's population. Increases in atmospheric aerosol associated with industrialization have caused health-related problems associated with worsening air quality, while floods and droughts result in major losses in lives and property, displacing millions from their homes every year. Recent studies suggest that increased aerosol loading may have changed the energy balance in the atmosphere and at the Earth's surface (Denman et al., 2007) and altered the global water cycle in ways that make the climate system more prone to precipitation extremes.

As yet, we do not fully understand how aerosols affects the development of precipitation, nor the extent to which it affects the cycles of water and radiant energy in the climate system as a whole. Hence, achieving a better understanding of how aerosols affects clouds and precipitation, and consequently large-scale circulations, is not only a major scientific challenge but is also important to policy makers and stakeholders for making decisions on mitigation strategies.

Over the past decades new measurements from satellite-based remote sensors have revealed conspicuous associations amongst aerosols, clouds and precipitation (Lin et al., 2006; Rosenfeld, 1999). In accord with expectations based on *in situ* measurements, clouds forming in a polluted environment appear to have smaller droplets, which, in the absence of other effects, may suppress the formation of rain by shallow clouds (Andreae et al., 2004).

Correlations between aerosol and cloud fraction and cloud liquid-water (both positive and negative) have been demonstrated (Myhre et al., 2007 and ref therein), with commensurate effects on the amount of solar radiation reflected back to space.

In deep clouds the low-level suppression of warm rain appears to be associated with modified microphysical pathways, enhanced ice precipitation aloft, and invigoration of the convection.

It appears that both the radiative and cloud-mediated aerosol effects induce large changes in precipitation patterns, which in turn may change not only regional water resources, but also the horizontal and vertical distribution of diabatic heating that propels the regional and global circulation systems that constitute the Earth's climate.

This has been the impetus for large observational, modeling, and theoretical efforts which have focused mainly on the radiative components of these aerosol-cloud interactions and their impact on the climate system (e.g., Ramanathan et al., 2005). While this has led to a much deeper understanding of the interactions between aerosols, radiation, and precipitation, much still remains to be learned about these radiative effects.

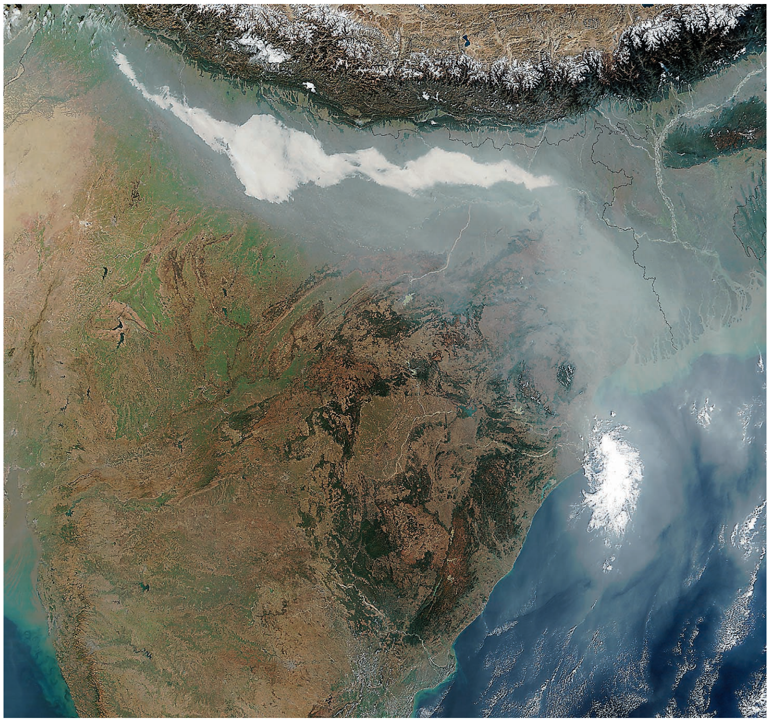
On the other hand, there has not yet been a comparable research effort concerning the microphysical effects of aerosols on clouds and precipitation, and the consequences for the water cycle and large scale circulation. Scientific understanding in this realm therefore remains very incomplete, hampering our ability to make projections of future climate change and to propose mitigating actions.

The SMOCC92 campaign in the Amazon Basin—M O Andreae and D Rosenfeld with the research aircraft at Cruzeiro do Sul airport. In the back a deforestation fire with a pyrocumulus cloud building above it.

Much of the energy that drives the climate system is infused into the troposphere by deep convective rain clouds. However there are no quantitative measurements of the impact of the aerosol on deep convective clouds, their propensity to precipitate, the vertical distribution of heating, and the subsequent modulation of circulation systems and rainfall distribution.

For this reason, and because the effects of the aerosol on shallow cloud systems is a topic of much existing effort, it makes sense to initially focus any proposal for a new program on questions that affect deep, precipitating convection. Such a program, which we call the Aerosols, Clouds, Precipitation and Climate (ACPC) program, is outlined below. ACPC is being undertaken as a joint effort of IGBP-iLEAPS (Integrated Land Ecosystem-Atmosphere Process Study; www.ileaps.org), the WCRP GEWEX project (Global Energy and Water Cycle Experiment; www.gewex.org) and IGAC.

A first step towards this program was taken with a previous article in the iLEAPS newsletter (iLEAPS Newsletter No. 4, 2007). The present paper outlines the scientific justification, fundamental questions, and general implementation concepts for ACPC. A detailed science and implementation plan is under development by the ACPC planning team and will be presented in the near future.



MODIS image of mixture of smoke, haze, fog and bright clouds trapped by the topography of the Indo-Gangetic Plain.

Scientific Issues

Many of the important questions can be cast in broad categorical terms:

- What is the relationship between surface rain and cloud microstructure, i.e., the number of activated cloud droplets or nucleated ice crystals? To the extent that they exist, are such relationships modulated by meteorological conditions?
- Looking toward smaller scales, what is the relationship between cloud microstructure and the ambient aerosol? How will aerosol dynamics together with atmospheric chemistry affect cloud microphysics?
- If changes in the development of precipitation can be attributed to perturbations to the aerosol, how do changes in the vertical structure of latent heating affect the subsequent development of circulations systems on scales ranging from that of the cloud or cloud-system to the regional and beyond?
- Likewise, to what extent do radiative perturbations (including those mediated by the surface) which are attributable to the varying physicochemical and optical properties of the aerosol impact circulation systems across these many scales?
- In closing the loop, to what extent do changes in clouds, precipitation, and circulation systems regulate the distribution of the aerosol itself?
- Ultimately, how well can (or do) we represent existing understanding of the above respects in our theories and models of the climate system?

It has proven difficult to extract a harmonized view of the relationships of the type articulated above for a variety or reasons (IAPSAG Report, 2007). Foremost, in many situations we simply have not been listening, which is to say that significant gaps in the observational record are apparent.

But even when we have been paying attention, it has been difficult to extract a signal, with confounding factors being: the background roar of the ambient meteorology; a narrow focus on individual clouds for which the noise of circumstance is often loudest; consonance between the background aerosol and the meteorological conditions making it difficult, and often impossible, to isolate one from the other; and dissonance amongst myriad processes embodied by any categorical relationship.

As an example of this dissonance we note that the relationship between cloud microstructure and rain may depend on many factors, ranging from microscale processes such as the local intensity of turbulence in the cloud, to larger-scale processes such as the efficacy of cold-pool development, distribution of cloud-top heights, or the relative humidity of the cloud environment.

Likewise, the various ice-nucleation processes and the myriad microphysical pathways via which rain forms in mixed-phase clouds have thwarted attempts to quantitatively relate the character of the aerosol to the microphysical properties of glaciated clouds, and surface rainfall.

Given the history of attempts to draw demonstrable links of the type we seek, it seems natural to ask, what is new? To some extent we are more knowledgeable. In part, because the maturation of Earth System science has increased the discourse amongst diverse intellectual communities, questions such as ours are no longer the domain of scientists drawn from a single discipline, but are now being embraced by a diverse community.

This discourse has been facilitated and accelerated by the relatively recent realization that climate change, and associated effects on the hydrological cycle, are a problem of immense importance. In the present context these include experts in land-surface processes, aerosol and cloud physics, chemistry, radiative transfer and remote sensing, fluid simulation, and large-scale modeling, among others.

Such intermingling is giving birth to new experimental designs. In particular our understanding of the aerosol, and its relationship to the microstructure of warm-phase clouds has advanced significantly (Andreae and Rosenfeld, 2008; McFiggans et al., 2006) over the past decade, both as a result of advances in aerosol instrumentation, but also as a product of the deployment of such instruments in a series of field studies spanning the globe. Some of these experiments have also helped expand our imagination in terms of where to look for relationships between aerosols, clouds and precipitation.

Deliberate burnings in near tropical regions such as the South African Savannah, rain forests of the Amazon, or the sugar cane fields on subtropical islands provide opportunities for exploring these questions; these are natural laboratories in which one can hope, for the first time, to separate the effects of meteorology and the aerosol on large scales.

The empirical and conceptual progress in our understanding parallels other advancements in measurement science. Tremendous advances in remote sensing, using both space- and surface-based sensors, means that characterization of cloud microphysical and optical properties from space-borne active and passive sensors, together with surface networks of multi-parameter and multi-wavelength radars, lidars and microwave radiometers, now provide an unprecedented opportunity to quantify cloud structure, water content, and surface rain rates at a range of scales.

Such opportunities are amplified by a number of other developments: the emergence of new classes of autonomous vehicles (unmanned aerial vehicles, UAVs); new radar-scanning technologies, such as phased arrays; a satellite observing system in the form of the A-Train (the satellite constellation; e.g., CALIOP/CALIPSO and CPR/CloudSat), providing data of unprecedented quality, whose capabilities are unlikely to be improved upon in the coming decade; a new fleet of modern aircraft capable of deploying large payloads with great endurance and at tremendous altitude; and modeling simulation/assimilation systems capable of synthesizing diverse and rich data streams on the one hand, and parsing the conceptual landscape on the other.

These developments lead to new opportunities. For instance the emergence of strategies for untangling aerosol perturbations from meteorological ones, e.g., by focusing on areas well downwind of deliberately set fires.

The articulation of questions, such as: how do clouds and precipitation modify the size and composition of aerosol? Can changes in profiles in the convective heating/drying, long measured by sounding arrays, be related to aerosol effects? How does aerosol modification of the surface heat budget affect convection and precipitation?

Likewise, advancements in measurement science offer the possibility to statistically characterize differences in the life-cycle of convective complexes as a function of the aerosol, or to begin thinking about parsimonious descriptions of the joint distribution of aerosol properties and cloud microphysical structure.

Strategy

To realize these opportunities and make progress in understanding physical relationships among aerosols, clouds and precipitation we propose a coordinated international effort encompassing a strategy that embodies the following elements:

(i) isolation of, and focus on systems where there are strong indications of aerosol effects on deep convection;

(ii) an emphasis on statistical characterizations of aerosol-cloud-precipitation interactions;

(iii) the development of approaches that leverage past and ongoing activities;

(iv) thorough integration of modeling and observational activities; and

(v) a hierarchical approach to both modeling and data collection/analysis.

Passage of a line of low-level cumulus clouds on the Mont Hombori, in the morning of 16 August 2005. These clouds are the last remnants of an MCS which propaged throughout the previous night. Photo by Francoise Guichard and Laurent Kergoat. Copyright CNRM-GAME & CESBIO (CNRS)

Systems with strong indications of aerosol effects on deep convection

Item (i) above focuses attention on tropical or monsoonal regions over the Amazon, Africa, South and East Asia and the Maritime Continent. These regions are known for very high anthropogenic aerosol loading from mega-cities and industrial complexes, and/or biomass burning aerosols, and dust, which in the case of the latter can sometimes also be traced to land-use practices.

Regions of biomass burning, particularly within a season, are a particularly attractive target for more intensive study; because, to the extent fires reflect seasonal (rather than day-to-day) variations in the meteorology, one stands a chance of de-correlating the biomass burning aerosol and the meteorology.

In this respect the Amazon is particularly attractive as past experience (The Large Scale Biosphere-Atmosphere Experiment in Amazonia, LBA field study) suggests that meteorology and aerosol loading may indeed de-correlate on sub-seasonal timescales (Andreae et al., 2004).

Already-planned activities in South and East Asia such as JAMEX (Joint Aerosol-Monsoon Experiment; Lau et al, 208) as part of the planned Asia Monsoon Year (AMY 2008-2012), and the recent AMMA2006 (African Monsoon Multidisciplinary Analyses; Redesperger at al., 2006) program over West Africa also provide unique opportunities that should be further developed prior to renewed commitment of resources elsewhere.

While AMMA concentrated mainly on the radiative and dynamic aspects and SMOCC (Andreae et al., 2004) on the microphysical impacts of the aerosols, an integrated approach is needed to make further progress.

Statistical characterizations of aerosol-cloud-precipitation interactions

The second element of the strategy, which emphasizes the development of statistical relationships, can be implemented through studies that consider extended ranges in space and/or time, such as remote sensing studies at basin scales and long term measurements at potentially sensitive locations worldwide.

Statistical relationships are most likely to arise from large samples in homogeneous conditions, thus favoring observational regions that maximize the observational area while minimizing the heterogeneity in both the underlying surface and the expected composition of the aerosol.

Of the monsoon and tropical regions discussed above, the Amazon and Equatorial Africa satisfy this constraint better, both because of more homogeneous land-surface features, but also because of the perception that they are more locally forced, i.e., large-scale factors associated with the reorganization of monsoonal circulations are still poorly understood (Bell et al., 2008).

Also, past experience suggests that it is important to first evaluate the likelihood of observations being able to test a particular statistical hypothesis. Such an evaluation is critical to both the framing of the hypotheses and the design of the observational network intended to test them. Hence initial work incorporating simulation studies of cases from past, and ongoing, field work should focus on such an evaluation.

Preparatory work of this type may usefully be performed in the context of the GEWEX Cloud Systems Studies (GCSS) working group activities, although it could also be carried out by individual groups.

Development of approaches that leverage past and ongoing activities

The importance of leveraging past and ongoing work is essential to both the observational and the simulation components of the ACPC program.

In terms of simulations, GCSS has a rich history of using observations to evaluate models and, in cases where existing observations have been insufficient, designing entire field campaigns (for instance the phase two of the Dynamics and Chemistry of Marine Stratocumulus, DYCOMS-II and Rain in Cumulus over the Ocean, RICO) centered on specific questions that emerge from the modeling.

In terms of ongoing and past field work, AMMA2006 provides a unique opportunity to explore how enhancements to the observational network better constrain tropical clouds.

Likewise, AMY2008-2012 provides new chances to test components of an emerging experimental strategy, and perhaps, through modest augmentation of the already-planned resource deployment, begin developing the basis for better exploring the affects of the aerosol on deep convection in the context of the Asian Monsoon (Lau et al, 2006).

Apart from the deployment of additional instruments during the AMY2008-2012, one idea that addresses many aspects of the above would be to use GCSS to develop case studies from the AMMA2006 or AMY2008-2012 field data, with an eye toward better framing the issues for a possible future Amazon field study. So doing would ensure the thorough integration of simulations and observations, thereby addressing both the third and fourth elements of the strategy outlined above.

Thorough integration of modeling and observational activities

The integration of models and measurements also places demands on the models. The physics of current models, particularly general circulation models (GCM), inadequately (if at all) represent relevant processes for aerosol effects on precipitation.

Traditionally, cloud microphysical processes are only included in GCM parameterizations of stratiform clouds but not in convective clouds (Lohmann and Feichter, 2005). Also, most GCMs only allow one convective cloud type per grid cell instead of the whole spectrum of convective clouds.

Options to be exploited include the development and implementation of different (more detailed) representations of parameterized convective clouds, the multi-scale model framework (MMF), and global (or very large-scale) cloud resolving models.

In terms of the latter, the emphasis on AMMA2006 by the Cascade project (at the University of Reading), provides a unique opportunity to explore issues pertaining to aerosols, clouds, and precipitation in the context of very large-scale cloud resolving modeling studies.

Hierarchical approach to both modeling and data collection/analysis

Finally, the development of a systematically multi-tiered, or hierarchical approach is of paramount importance.

In terms of the modeling this involves the careful design of test cases that link the full range of relevant models: (1) detailed physicochemical models of aerosol-cloud interactions (perhaps in parcel models); (2) microphysical models of the precipitation formation process; (3) fine-scale models that explore cloud and boundary layer-scale interactions associated with the effects of a changing aerosol on cloud radiative or microphysical properties; (4) cloud-system resolving models that can explore the effects of aerosol mediated changes to the radiative forcings and/or precipitation on the scale of cloud systems; and (5) regional or global scale models capable of both feeling the global constraints that may restrict the effects of perturbations seen on smaller scales, and extending the effects of such perturbations remotely (through teleconnections).

In terms of observations, a multi-tiered approach means that the observational strategy must be refined through the exploration of existing data sets, particularly from a whole range of satellite sensors and consolidated meteorological data sets (e.g., AMMA2006), strategic partnerships in ongoing or planned experiments (e.g., JAMEX/AMY, but ongoing plans for a 'year of tropical convection' provide another opportunity), and the development of base-line, longer-term measurements in an area targeted for more intensive study.

Additionally, periods of more intensive study should be repeated in two or more seasons and in ways that afford the best opportunity to extrapolate local findings to regional and even global scales using the current generation of earth observing satellites.

Smallish late-summer cumulonimbus as seen from Viikki, Helsinki, Finland, 30 August 2007. Photo by Timo Nousiainen.

In this context advanced data assimilation techniques are essential, which in practice means active collaboration with the European Center for Medium Range Weather Forecasting (ECMRF), whose state-of-the-art data assimilation system is essential to integrated assessment activities spanning a wide range of scales.

Summary

We encourage the development of a new initiative focused on quantifying aerosol-cloud-precipitation interactions in regions of deep tropical convection.

Such an initiative should build on ongoing and past activities, and include long-term monitoring in strategic locations (perhaps the Amazon), the enhancement of observational networks for already planned field studies, further analysis of existing and emerging data sets, coordinated modeling studies that span a range of scales (perhaps in the context of GCSS), building toward a period of more intensive field work spanning one or more seasons. Preliminary work suggests that the Amazon has many features that would lend itself well to such a study.

At the very least, such a study stands to significantly advance our understanding of deep, precipitating, convective systems, long a meteorological enigma. There is also reason to believe that such an effort could provide bounds on the susceptibility of such systems to changes in the atmospheric aerosol; both would be a great leap forward.

The transfer of knowledge gained from such an effort to regional weather forecasting centers to improve weather and climate prediction will be of substantial benefit to society.

This article first appeared in the iLEAPS Newsletter No. 5 (www.ileaps.org) and was accompanied by a series of articles on the topic of aerosols, clouds, precipitation and climate.

References

Andreae, M.O. and D. Rosenfeld, Aerosol-cloud-precipitation interactions. Part 1. The nature and sources of cloud-active aerosols, *Earth Sci. Rev.*, **89**, 2008.

Andreae, M.O., D. Rosenfeld, P. Artaxo, A.A. Costa, G.P. Frank, L.M. Longo and M.A.F. Silva-Dias, Smoking rain clouds over the Amazon, *Science,* **303**, 1337– 1342, 2004.

Bell, T.L., D. Rosenfeld, K.-M. Kim, J.M. Yoo, M.I. Lee and M. Hahnenberger, Midweek increase in US summer rain and storm heights suggests air pollution invigorates rainstorms. J. Geophys. Res., **107**, D20, 8072, doi: 10.1029/2001JD000225, 2008.

Denman, K.L., G. Brasseur, A. Chidthaisong, P. Ciais, P.M. Cox, R.E. Dickinson, D. Hauglustaine, C. Heinze, E. Holland, D. Jacob, U. Lohmann, S. Ramachandran, P.L. da Silva Dias, S.C. Wofsy and Zhang, "Couplings between changes in the climate system and biogeochemistry:" In Climate

Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Solomon S, Qin D, Manning M, Chen Z, Marquis M, Averyt KB, Tignor M and Miller HL (eds.). Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 2007.

IAPSAG 2007, WMO/IUGG International Aerosol Precipitation Science Assessment Group (IAPSAG) Report: *Aerosol Pollution Impact on Precipitation: A Scientific Review*. World Meteorological Organization, 482 pp.iLEAPS-IGAC-GEWEX joint white paper on Aerosols, Clouds, Precipitation and Climate Initiative (ACPC), 2007: iLEAPS Newsletter No. 4, 52–53. (http://www.ileaps.org/index.php?option=com_docman&Itemid=186)

Lau, K.M., V. Ramanathan, G.-X. Wu, Z. Li, S.-C. Tsay, C. Hsu, R. Sikka, B. Holben, D. Lu, G. Tartari, M. Chin, P. Koudelova, H. Chen, Y. Ma, J. Huang, K. Taniguchi and R. Zhang, The Joint Aerosol-Monsoon Experiment (JAMEX): a new challenge for monsoon climate research. *Bull. Amer. Met. Soc*., **89**, 2008.

Lau, K.M. and K.M. Kim, Observational relationships between aerosol and Asian monsoon rainfall, and circulation. *Geophys Res Let.*, **33**, L21810, doi: 10.1029/2006GL027546, 2006.

Lin, J.C., T. Matsui, R.A. Pielke Sr and C. Kummerow, Effects of biomass burning-derived aerosols on precipitation and clouds in the Amazon basin: a satellite-based empirical study. *J. Geophys. Res*., **111**, D19204, doi: 10.1029/2005JD006884, 2006.

Lohmann, U. and J. Feichter, Global indirect aerosol effects: a review. Atmos. Chem. Phys., **5**, 715–737, 2005.

McFiggans, G., P. Artaxo, U. Baltensperger, H. Coe, M.C. Facchini, G. Feingold, S. Fuzzi, M. Gysel, A. Laaksonen, U. Lohmann, T.F. Mentel, D.M. Murphy, C.D. O'Dowd, J.R. Snider and E. Weingartner, The effect of physical and chemical aerosol properties on warm cloud droplet activation. *Atmos. Chem. Phys*., **6**, 2593–2649, 2006.

Myhre. G., F. Stordal, M. Johnsrud, Y.J. Kaufman, D. Rosenfeld, T. Storelvmo, J.E. Kristjansson, T.K. Berntsen, A. Myhre and I.S.A. Isaksen, Aerosol-cloud interaction inferred from MODIS satellite data and global aerosol models. *Atmos. Chem. Phys*., **7**, 3081–3101, 2007.

Ramanathan, V., C. Chung, D. Kim, T. Bettge, L. Buja, J.T. Kiehl, W.M. Washington, Q. Fu, D.R. Sikka and M. Wild, Atmospheric brown clouds: Impacts on South Asian climate and hydrological cycle. *Proc. Nat. Acad. Sci. USA*, **102**, 5326–5333, 2005.

Redelsperger, J.-L., C.D. Thorncroft, A. Diedhiou, T. Lebel, D.J. Parker and J. Polcher, African Monsoon Multidisciplinary Analysis: An International Research Project and Field Campaign. *Bull. Amer. Met. Soc*., **12**, 1739–1746, doi: 10.1175/BAMS-87–12–1739, 2006.

Rosenfeld, D. TRMM observed first direct evidence of smoke from forest fires inhibiting rainfall, *Geophys. Res. Lett*., **26**, 3105–3108, 1999.

Announcements

Congratulations to the Young Scientist Poster Winners

1. Susannah Burrows - Max Planck Institute, Germany

"Modelling the transport of bacteria as aerosol in the chemistry climate model ECHAM5/MESSy"

2. Timothy Bertram - Univ. of Washington, USA

"Towards in-situ observations of N_2O_5 reactivity"

3. Aldona Wiacek - ETH Zürich, Switzerland

"Observational constraints on upper tropospheric mineral dust aerosol"

4. Ariela Dangiola - Atomic Energy National Commission of Argentina

"Development of new on-road transport emission inventories for the Metropolitan Area of Buenos Aires, Argentina and its spatial disaggregation"

5. Michelle Cain - Univ. of Reading, UK

"Transport and ozone photochemistry in the West African Monsoon region"

Annecy
bridging the scales
2008

**10th Biennial
IGAC Conference
7-12 September 2008, Annecy, France:**

Honorable Mentions go to:

Sachin Ghude, India

Samuel Illingworth, U.K.

Kate Furneauz, U.K.

Rachel Pike, U.K.

Gaelle Clain, Reunion, France

Delphine Farmer, Colorado, USA

Apostolos Voulgarakis, U.K.

Yu Xia, Switzerland

Gunter Eerdekens, Germany

Save the Date!

Joint CACGP / IGAC Conference

July 6-10 2010
Halifax, Canada

Please help us keep our mailing list up to date by sending your revised contact information:

IGAC Core Project Office
NOAA-PMEL
7600 Sand Point Way
Seattle, WA 98115-6349 USA

email: igac.seattle@noaa.gov

IGACtivities Newsletter

Editor: Sarah Doherty
Production manager: Ho Ching Lee
Newsletter formatting: Beth Tully
IGAC logo: Linda Kubrick

Published by IGAC Core Project Office
RESEARCH CENTER FOR ENVIRONMENTAL CHANGE
ACADEMIA SINICA
128 Academia Rd. Sec. 2
P.O. Box 1-55 NanKang
Taipei, 11529 Taiwan

臺灣郵政台北誌字第137號執照登記為雜誌交寄
發行人：劉紹臣
發行所：中央研究院環境變遷研究中心
發行地址：台北市115南港區研究院路二段128號1-55號信箱

IGAC was initiated by the Commission on Atmospheric Chemistry and Global Pollution (CACGP) and is a Core Project of the International Geosphere-Biosphere Programme (IGBP). The IGAC Seattle Core Project Office is currently supported by the National Science Foundation (NSF), National Aeronautics and Space Administration (NASA), and National Oceanic and Atmospheric Administration (NOAA). The IGAC Taipei Core Project Office is funded by Academia Sinica, Taipei. The Rome Core Project Office is supported by the Italian National Research Council and by the European Commission Network of Excellence ACCENT.

IGACtivities
Newsletter

Taipei TAIWAN
R.O.C.
POSTAGE PAID
NEWSLETTER
LICENCE NO.N285

國　　內
郵資已付

台北郵局許可證
台北字第 285 號

IGAC Core Project Office
RESEARCH CENTER FOR ENVIRONMENTAL CHANGE
ACADEMIA SINICA
128 Academia Rd. Sect. 2
P.O. Box 1-55 NanKang
Taipei, 11529 Taiwan

Printed on Recycled Paper
Please Recycle after Use!