HitT – Climate impact of seasalt-derived Cl atoms

Background information was circulated before in a document called HitT_Cl_workshop_Aug2012.pdf. Here we just want to repeat a few guiding questions for this workshop:

Motivating questions of workshop ("top level" questions)

1) *Is tropospheric Cl chemistry a significant aspect of atmospheric reactivity, and to what extent is this a natural vs anthropogenic effect?*

2) *Do we have to include chlorine chemistry in future climate models to improve the calculation of the radiative forcing and if so, what level of process understanding is required?*

Main specific questions

- Efficiency of multiphase cycling of chlorine in the MBL and resulting speciation of gas phase chlorine
- Relevance of bromine for the release of chlorine (via BrCl) from sea salt
- Global inventory of gaseous chlorine, especially chlorine atom concentrations
- Regional and global relevance of chlorine chemistry for ozone, mercury and methane budget

Goals of the workshop

- Summarise current knowledge and most important gaps
- Assess the current state and potential for new advances in atmospheric detection, laboratory studies, and modelling
- Design observational strategies to improve understanding of photochemical processes and assess the impact of chlorine chemistry on the marine boundary layer. Ideally start to plan a field campaign to address (some of) the open questions.
- If appropriate: Brief review/synthesis paper for peer-reviewed journal

Agenda

17 Dec 2012 **Focus on: Current knowledge**

12:00 Arrival, lunch
13:00-18:00 Current knowledge (science talks by participants)
15:30 – 16:00 Coffee
19:00 Dinner

13:00 – 13:10 Welcome, logistics (Eric Saltzman, Roland von Glasow, SOLAS officers)
13:10 – 13:20 Scientific introduction, goals of the workshop (Eric Saltzman, Roland von Glasow)
13:20 – 13:30 Introduction of attendees (all)

13:30 – 14:30
A Previous field campaigns

Bill Keene, Alex Pszenny: Survey of existing HCl measurements
Eric Saltzman: Measurements of Cl_x in the MBL, esp. at Cape Verde
Joel Thornton: $ClNO_2$ as a direct and indirect Cl-atom source: observational constraints and some dangerous speculations.
John Crowley: Measurements of $ClNO_2$ in Germany

14:30 – 16:30 *[incl coffee break]*
B Model studies

Roberto Sommariva/Roland von Glasow: MBL, 1D model
Linda Smoydzin: $ClNO_2$ over Germany - can marine sources of particle Cl^- alone explain measurements?
Peter Bräuer: Model results from a new comprehensive halogen multiphase mechanism - The CAPRAM Halogen Module 2.0
Martin Chipperfield: Technical possibilities regarding global tropospheric Cl modelling and lessons learnt from stratospheric chlorine modelling."
Xin Yang: global model?

16:30 – 17:00
C Laboratory experiments

Joelle Buxmann: Chlorine Explosion in a simulated atmosphere
Sumi Wren: Photochemical chlorine activation from artificial saline snow

17:00 – 17:30

D Instrument development

Fred Stroh: Potential of ground-based CCRF measurements of Cl and Br atoms, ClO and BrO
Denis Pöhler "Examples of DOAS measurements of ClO and OClO and potentials for improvements"

17:30 – 18:00
Discussion of science issues

18 Dec 2012 **Focus on: Main open questions and ways to answer them**

09:00 start
10:30 – 11:00 coffee
12:30 – 13:30 lunch
15:30 – 16:00 coffee
18:30 end

09:00 – 12:00 Discussion of key science issues *[incl coffee break]*
Brief discussion in plenum then break-out groups by topic

- What are the problems keeping us from a quantitative assessment of the climate relevance of chlorine?
    - Uncertainties in the kinetics i.e. reaction mechanism? If so: what is most limiting: gas phase, uptake or condensed phase reactions?
    - Uncertainty of chlorine source?
    - Uncertainty in dynamics, e.g. exchange between marine boundary layer and free troposphere?
    - Too little field observations?
    - What are the main regions: marine boundary layer, snow-covered areas, continents...?
    - Goal: List of topics with ranking by priority and quantification of uncertainty.

12:00 – 12:30 Reports from break-out groups

13:30 – 17:30 Discussion of way forward *[incl coffee break]*
Brief discussion in plenum then break-out groups by topic

- What can we do to move forward?
    - Specific suggestions for
        - Lab work
        - Field work
        - Modelling
- At SOLAS conference in Suncadia (May, 2012) we agreed on the need for a field campaign, likely in the west North Atlantic.
    - Which question can we answer this way, which won't we be able to address?
    - Will it be best to have a small, exploratory campaign possibly followed by a larger campaign or one big campaign?
    - Details of field campaign:
        - Location
        - Time frame
        - Essential instrumentation
        - Supporting modelling

17:30 – 18:30 Reports from break-out groups, general discussion

19 Dec 2012 **Focus on: Specific way forward**

09:00 start
10:30 – 11:00 coffee
12:30 – 13:30 lunch, departure

Discussion (plenum)

- Finalise discussion from previous day
- Any amendments to discussion from yesterday
- Action items for groups and individuals
- Funding:
    - How can individual projects be funded?
    - How can a larger campaign be funded?

For background reading we recommend the following papers (sorry for any omissions!):

Saiz-Lopez and von Glasow (2012) is the latest review on tropospheric halogens.

Reviews:

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., Halogens in the Troposphere, Analytical Chemistry, 82, 770 – 776, 2012

Rossi, M. J., Heterogeneous reactions on salts, Chem. Rev., 103, 4823 – 4882, 2003

Saiz-Lopez, A., R. von Glasow, Reactive halogen chemistry in the troposphere, Chem. Soc. Rev., 41, 6448-6472, 2012; http://pubs.rsc.org/en/content/articlelanding/2012/cs/c2cs35208g

von Glasow, R. and P. J. Crutzen, Tropospheric Halogen Chemistry, Holland H. D. and Turekian K. K. (eds), Treatise on Geochemistry Update1, vol. 4.02, pp 1 - 67, 2007; http://dx.doi.org/10.1016/B0-08-043751-6/04141-4

Recent papers:

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:10.1029/2006JD007689, 2007; http://dx.doi.org/10.1029/2006JD007689

Lawler, M. J., B. D.Finley, W. C. Keene, A. A. P. Pszenny, K. A. Read, R. von Glasow, and E. S. Saltzman, Pollution-enhanced reactive chlorine chemistry in the eastern tropical Atlantic boundary layer, Geophys. Res. Lett., 36, L08810, doi:10.1029/2008GL036666, 2009; http://dx.doi.org/10.1029/2008GL036666

Lawler, M. J., R. Sander, L. J. Carpenter, J. D. Lee, R. von Glasow, R. Sommariva, and E. S. Saltzman. HOCl and Cl2 observations in marine air. Atmos. Chem. Phys., 11, 7617-7628, 2011; http://www.atmos-chem-phys.net/11/7617/2011/acp-11-7617-2011.html

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 Geoscience, 1, 324 – 328, 2008

Phillips, G. J., M. J. Tang, J. Thieser, B. Brickwedde, G. Schuster, B. Bohn, J. Lelieveld and J. N. Crowley. Significant concentrations of nitryl chloride observed in rural continental Europe associated with the influence of sea salt chloride and anthropogenic emissions, Geophys. Res. Lett., 39, L10811, doi:10.1029/2012GL051912, 2012

Pszenny, A. A. P. and J. Moldanova and W. C. Keene and R. Sander and J. R. Maben and M. Martinez and P. J. Crutzen and D. Perner and R. G. Prinn. Halogen cycling and aerosol pH in the Hawaiian marine boundary layer. Atmos. Chem. Phys., 4, 147 – 168, 2004

Riedel, Theran P., Timothy H. Bertram, Timia A. Crisp, Eric J. Williams, Brian M. Lerner, Alexander Vlasenko, Shao-Meng Li, Jessica Gilman, Joost de Gouw, Daniel M. Bon, Nicholas L. Wagner, Steven S. Brown, and Joel A. Thornton. N itryl Chloride and Molecular Chlorine in the Coastal Marine Boundary Layer. Env. Sci. Tech., 46, 10463 – 10470, 2012. http://pubs.acs.org/doi/abs/10.1021/es204632r

Sommariva, R. and R. von Glasow. Multi-phase halogen chemistry in the tropical Atlantic Ocean. Env. Sci. Tech., 46, 10429-10437, 2012; http://pubs.acs.org/doi/abs/10.1021/es300209f

Thornton, J. A., J. P. Kercher, T. P. Riedel, N. L. Wagner, J. Cozic, J. S. Holloway, W. P. Dube, G. M. Wolfe, P. K. Quinn, A. N. Middlebrook, B. Alexander and S. S. Brown. A large atomic chlorine source inferred from mid-continental reactive nitrogen chemistry. Nature, 464, 271 – 274, 2010