

SOLAS/IGAC HitT Cl Workshop
GEOMAR - Kiel, Germany
17th-19th December 2012
Minutes written by Hannah Mantle, Univ Leeds

Day One (17th December)

13:00 – Welcome and Introductions

- Introduction to SOLAS (Eric Saltzman)
- Introduction to the workshop “Climate Impact of Sea Salt-Derived Cl Atoms” (Roland von Glasow)
 - Effects to be considered:
 - Oxidation of CH₄
 - Destruction of O₃
 - Sulphur cycle
- Big questions:
 - Is tropospheric Cl chemistry a significant aspect of atmospheric reactivity? If so, to what extent is this natural vs anthropogenic?
 - Do we need to include Cl chemistry in future climate models to improve the calculation of the associated radiative forcing, and if so, what level of process understanding is required?
- Introduction of participants
- Participant talks A – Previous Fieldwork
 - Survey of Existing HCl Measurements – Alex Pszenny (Bill Keene) (Uni of New Hampshire)
 - Reactive Chlorine in Marine Air at Cape Verde – Eric Saltzman (Uni of California, Irvine)
 - ClNO₂ as a Direct and Indirect Cl-Atom Source – Joel Thornton (Uni of Washington, Seattle)
 - ClNO₂ at the Kleiner Feldberg, Germany –John Crowley (Max-Planck-Institute)
- Participant talks B – Modelling
 - MBL, 1-D Model - Roland von Glasow (Uni of East Anglia)
 - ClNO₂ Over Germany: Can Marine Sources of Cl- Alone Explain Measurements? – Linda Smoydzin (Max-Planck-Institut)
 - Model Results from a New Comprehensive Halogen Multiphase Mechanism: The CAPRAM Halogen Module 2.0 – Peter Bräuer (Leibniz-Institut)
 - Global Tropospheric Cl Modelling: Lessons from BR/I/stratospheric Cl – Martyn Chipperfield (Uni of Leeds)
 - Preliminary Global Modelling Studies of the Impact of ClNO₂ on CH₄ and $\delta^{13}\text{C}_{\text{CH}_4}$ – Xiang Yang (Nicola Warwick) (Uni of Cambridge)
- Participant talks C – Experiments

- Chlorine Explosion in a Simulated Atmosphere - Joelle Buxmann (Uni of Heidelberg)
 - Photochemical Chlorine Activation from Artificial Saline Snowpacks – Sumi Wren (Uni of Toronto)
 - Participant Talks D – Instrument Development
 - Tropospheric In-Situ Measurements of Cl and Br Atoms, ClO and BrO - Fred Stroh (Institute for Energy and Climate Research, JULICH)
 - DOAS Measurements of ClO and OCIO and Potential for Improvements – Denis Pöhler and AG Ulrich Platt (Uni of Heidelberg)
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Day Two (18th December)

09:00 – Introduction to today and recap of yesterday

Main discussion points for Day Two:

- Chemistry
- Modelling – how to make best approximations in order to allow modelling work to progress without knowing the intricacies of physical chemistry processes completely?
- Experimental – smog chambers? Must work with high concentrations where we are at the far end of a highly non-linear system. Must bear in mind requirement to scale back to the more moderate conditions experienced in MBL and FT
- Field campaign?

12:15 - Group Breakout Reports

Group 1

- Uncertainties in Kinetics, Mechanisms and Models
 - Gas-phase OK
 - Heterogeneous processes: effect of organics
 - Sea salt in MBL
 - SOA in continental – no data to allow modelling
- Condensed phase chemistry
 - BrCl not observed in field but is present in models and lab experiments
 - Cl oxidation via organics
 - Model treatment of particle chemistry
- Model development
 - Resolution improvement
 - Chemical schemes
 - Emissions inventories
 - Deposition
 - Comparison with observations
- Chlorine Source Uncertainty

- Measurement of ClO (low NO_x)
- Measurement of ClNO₂ (high NO_x)
- Source strength and distribution of particle chloride
- HCl measurements needed
- Total Cl and total sink of Cl atoms (new technique to be developed?)
- Uncertainty in Dynamics
 - MBL effects of clouds
 - Advection uncertainty
- Lack of field campaigns and therefore ...
- Lack of comprehensive suite of chemical species measured by existing field campaigns
- Not enough attention to Cl. Can now make use of new instruments with increased temporal resolution and sensitivity
- Airborne (Lagrangian) measurements necessary, particularly altitude dependence for models
- Seasonal dependence of halogen chemistry
- MBL. Areas of natural acidification (equatorial upwelling) and outflow of pollutants to ocean
- Continental. Is there a marine influence?
- Snow-covered is less important for climate effect of Cl.
- GOALS:
 - Cl chemistry in high NO_x regime
 - Sources of continental Cl⁻ and total active Cl
 - Rate of Cl release
 - High NO_x in polluted outflow and other halogen nitrates
 - Spatial extent
 - Cl chemistry in low to medium NO_x regime (MBL)
 - BrCl formation
 - More observations required

Group 2

- Uncertainty: BrCl and Unknown Release Processes
 - Why is BrCl present in models but not in the field? Is this an instrument problem?
 - CIMS inter-comparison in smog chamber may be useful.
 - First step: simple system with known injection of Br₂, Cl₂, O₃
 - Second step: Use artificial and real sea spray aerosols
- Scientific Question
 - Is it aqueous chemistry?
 - Temperature dependence?
 - Inter-comparison with DOAS, BrO, N₂O₅?
- Mechanistic Evaluation by Model Studies
- Proposal for inter-comparison campaign
- Uncertainty: Continental ClNO₂
 - Anthropogenic source? Field campaign at Kleiner Feldberg?
 - Can we detect ClNO₂ at other continental regions?

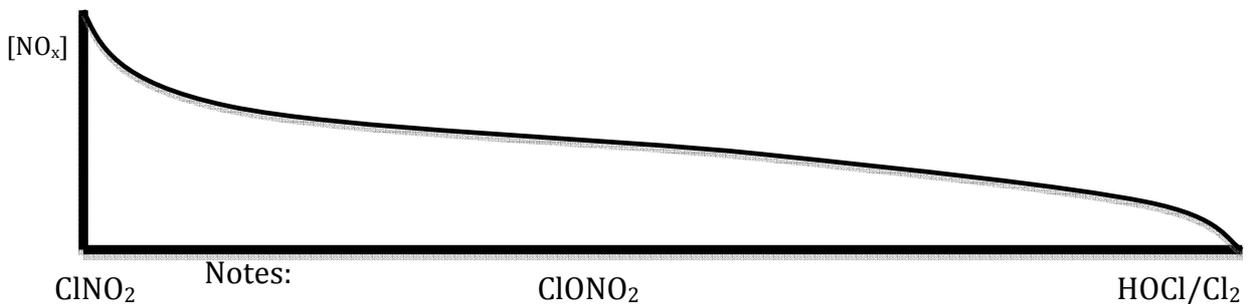
- Role of Volcanic Plumes?

Group 3

- Process-level Modelling
 - Create a list of reactions that should be revisited in the lab
 - Make a priority list identifying key processes
 - Uncertainties in insolubility, alpha-coefficients for nitrates, Cl, Br. Respective temperature dependence
 - Possible influence of different SS compositions on efficiency of recycling
 - Top-down approach. Identify atmospheric problem and corner the key reactions used in process-level models. Approach lab groups
 - Field measurements. Which species are more useful to constrain budget? Would ClO help the cause? More than ClNO₂?
 - Possible location for field campaign? Bermuda?
 - Interactions with NO_x discussed but not with sulphur (Important to consider!)
 - Upper-scale modelling. Determine range of limits at which Cl may have an atmospheric relevance in terms of CH₄ oxidation

13:45 – PM Session

- Three regimes: high NO_x, low NO_x, and intermediate regime



- Non-linear
- NO₃/N₂O₅
- Cl_x source
- BrCl

Discussion:

- Ship Campaign. How is it best approached?
 - Stationary measurements? Aged ship plume?
 - Require location with very good chances of different regimes
 - Ship campaign would render DOAS unusable
 - May do an OClO cavity – limited technical problems
 - Do we need to probe all three regimes or is it enough to go to each end only?

- What can be achieved in the next 2/3 years? Individual group funding?
- High NO_x regime campaign. East Europe, far from oceans e.g. Ukraine/Poland. Non-mountainous region
- Global model work – UEA and Leeds. Lead time = approx. 1 year
- Smog chamber experiments – effect of organics. SAPPHIRE large chamber in order to simulate real world conditions (lifetime longer than deposition rate achieved by a large chamber size)
 - Organic aerosol
 - Small vs large chamber
 - Expertise in lab kinetics has been somewhat lost. Leibniz is a possibility – enquire re: current workload/time available/manpower. Alternatively publish a review and seek out inorganic chemists (not necessarily with atmospheric expertise) who may be able to work on the project
 - Sensitivity tests – BrCl
 - More lab experiments involving real SS aerosol required. How difficult to suspend organic aerosol? Would need CIMS to measure Br, Cl, BrCl, and DOAS for a full-suite of measurements

Way forward:

- Process and global modelling is relatively straightforward and already UEA-Leeds connections have implemented first steps
- Funding for other areas is an issue, particularly for a field campaign and necessary required instrumentation. CIMS, ClO instruments (2), mist chamber. Is it realistic (finance and time) to get instruments required to a field site? 1 year lead time required for CIMS instruments (Eric)
- Field campaign: Unrealistic to get anything in next nine months. Max-Planck-Institute available for continental campaign late 2013/2014 but will need lead time required by USA groups for a collaborative effort
- Important to note that a lot of activities may be completed by individual groups and could be completed before a mass field campaign is conducted
- Sommariva and Monks have submitted a field campaign proposal to measure ClNO₂ in the UK
- Some global models have Cl species and sea salt in (as well as Br and I) and will be investigated in order to produce maps
- Sufficiently low pH, NO_x, N₂O₅ would be useful to provide maps for a field campaign proposal. Distributions of Cl precursors would be more beneficial than product species

TO DO:

- Modellers to provide Cl precursor maps in order to advise re: field campaign
- More lab work to investigate kinetics and BrCl issue etc
- Find group to work on lab kinetics
- Critical list of molecules produced in case of outside expertise previously missed

16:00 – Modelling Breakout

- Use of existing model output to guide field campaign proposals
 - Eric - most useful to see underlying variables that drive halogen chemistry. Parameters like NO_x , NO_y , N_2O_5 , aerosol acidity, sea-salt levels, O_3 , DMS. The type of things you would use to drive a box model calculation but not necessarily on a global scale
- Leeds have gas phase species implemented. Possibility to run CTM at a higher resolution (1x1 deg) in order to avoid smearing of particular grid boxes and avoid necessity of moving one box further away from points such as Bermuda and Cape Verde in order to avoid high NO_x
- Compare sea salt mass with observations. Compare model performance necessary? Individual model performance should have been validated already (has it?)
- Needed to try to identify different regimes in order to plan field campaigns
- Determine a classification in terms of NO_x , Cl, O_3 , to see how these vary with climatology. Inter-annual variability may be asking too much?
- How do modellers implement recycling in order to deliver this? Is this necessary? What level of detail is required?
- Alfonso: CAM-Chem results show Cl atoms in mid-upper troposphere from breakdown of halocarbons (5 species) (organics and photolysis) is greater than from sea salt at surface. Depends on loading of chlorobromo's and lifetime, also location (e.g. convection). 10^5 Cl maintained even though there are very fast loss processes at work. Methane oxidation efficiency (an order of magnitude quicker) will come from these photolysed Cl atoms. Interesting to calculate Cl atom production flux per second. Chlorine production on the order of 1ppt hr⁻¹ so therefore methane oxidation at same rate. Crudely scaled-up results in 1-3% methane oxidation globally

Lab Work Discussion

- Issue: Why do we see BrCl in the chamber (Thornton CIMS) and in the model but not in the field (Salzmann), but we do also see it in the polar region (Spicer)?
 - Margerum report Keq. Fickert et al. report BrCl formation.
 - Assume field experiment is sensitive to BrCl
 - Are the chamber experiments biased by incorrect temperature or by lack of organics? Is the field work biased by organics?
 - Solutions:
 1. New chamber experiments with organics.
 2. New chamber experiments with different T
 3. HOBr experiments (no light)
 - Chamber instruments:

HO_x , dihalogens	CIMS
BrO, ClO, OClO	DOAS
NO, NO_2 , O_3	CLD-DOAS
O_3	UV

SMPS

ASA

Br-depletion

ICP-MS

- Effective production rate of reactive halogens dependent on O₃, light, T, and organic components
- Organics: Start with real seawater and compare with synthetic seawater and use bubble generator. Analyse for total organic matter
- This sort of chamber experiment may give you a chance of looking at organics and photosensitized halogen oxidation
- Alternative solution:
 - Do some real aqueous phase kinetics with in-situ detection of BrCl etc. T dependence
- Issue: What is the uptake coefficient and ClNO₂ generation efficiency for N₂O₅ on organic sea-salt?
 - Experiments: Aerosol flow tube with N₂O₅ and ClNO₂ detection (and Cl₂)
 - Detect: ASA, AMS, N₂O₅, ClNO₂
 - Parameters: organics, aerosol type, T, RH
- Issue: HOCl uptake to acidified sea salt
 - Literature: None (IUPAC recommend an upper limit)
 - Method: Aerosol flow tube (with CIMS)
 - Chamber with supply of HOCl
 - CIMS detection of HOCl, Cl₂, BrCl
- Issue: HOCl photochemistry?

Day Three (19th December)

09:00 – Field Campaign Discussion Continuation

- Previous work in Boulder 1500 km from ocean
- Can sea salt travel as far as Boulder from the Pacific?
- About ¾ of sodium and chloride particles were larger than 1 µm
 - Sea salt generation algorithm in FLEXPART shows that currently it can be said that it is plausible that sea salt has been detected in Boulder, however composition data does not. More work is needed (and is currently being conducted)
 - Therefore field campaign in a different location is a viable proposal
- Zeppelin possibility. Owned by a company in S Germany, may be possible to hire. Campaign to fly over N Germany and Finland planned. Three packages: aerosol nucleation, photochemistry, clouds. Should be possible to put forward a proposal to use it (although not in the next year)

- Better for Ulrich to approach, as has previous experience with the company
 - NOAA group flew CIMS to measure ClNO₂, some indication that they measured aloft. No strong vertical gradient measured, unlike N₂O₅, however number of data points was small.
 - Need to look at column to assess tropospheric impact
 - Question of whether it is worthwhile returning to Kleiner Feldberg
 - Predominant wind directions need to be looked into
 - Require a continuous period of Easterly winds
 - Estimated 6/7 groups that have CIMS capability
 - Calibration necessary.
 - Do we know of anyone focusing on marine influence with existing funding?
 - No one who is currently working on it but there are a few people who may be interested in doing it. Would require encouragement/support to tackle the issue as it is complex.
 - Down to individual groups to secure funding and use SOLAS as a link to other knowledge and expertise.
- Discussion about possibility of returning to a marine site
 - Are Cape Verde measurements isolated or can they be found elsewhere?
 - Linda to provide model output to inform of suitable sites (see yesterdays Modelling Discussion).
 - Bermuda is still a good candidate for a campaign
 - Algal beds just upwind of the site. Need to make sure they are not iodine-generating
 - Challenging as tower is on hillside
 - Similar set of instruments required as in Cape Verde. Chlorine specific instruments. ClO measurements, Cl reactivity instrument (John), VOCs?
 - Bring a limited suite of instruments, detect Cl signal, bring a bigger package of instruments needed to characterise signal
 - Is this something an individual group can do?
 - Not the full project. Eric's group could go and detect Cl signal but cannot bring the fuller suite of instruments to characterise
 - Funding required
 - If global model output indicates that Bermuda is a suitable site, Eric to write proposal
 - Possible field campaign locations: Bermuda, Azores (closer to outflow/ship input inc), Iceland, Korea, Indian Ocean
- If a study was proposed, how much of the process understanding would be improved?
 - Two suggestions of ClO instruments; all require money, work and time to develop
 - Discussions to begin to investigate how quickly this can be done

- Should this group meet regularly?
 - Format? Dedicated workshop? EGU/AGU/SOLAS add-on? Latter may be more appropriate; not everyone will be able to attend but may be enough to update community on developments
- Role of chlorine chemistry in future climate
 - Natural vs anthropogenic. Addition of acidity to the atmosphere which leads to increased release of Cl from natural reservoirs. NO_x and NO₂ emissions have developed in the last decade. Industrialisation has led to a simultaneous increase (developing countries) and decrease (developed countries). Increase in coal burning in China and India is greater than all of Russia - worth looking into. SO₂ easier to reduce than CO₂. Future effect is strongly linked to this kind of development but near end of century input of anthropogenic acids into the atmosphere would decrease.
 - Do we know enough to do a projection?
 - Assume a certain economic development in terms of energy consumption, technology development = reduced emissions
 - In terms of consequences however, is Cl chemistry known well enough to provide a reliable prediction? Not yet. But it is a future goal and should be worked towards.
 - Current understanding is qualitative. Need to improve quantitative understanding in order to provide a realistic projection
 - Can be assessed in a global model
 - CCMI developed scenarios for stratosphere and troposphere. Describe tropospheric emission scenarios.
 - Covers previous runs used for IPCC
 - Can use tropospheric chemistry
 - Runs will be set up soon (document describing the emission scenarios distributed last week)
- Global inventory of gaseous chlorine, especially chlorine atom concentrations
 - 3-D models being developed and improved will hopefully be able to provide this soon.
- Brief meeting report in EOS to communicate to the wider community and raise awareness of this topic (Eric and Roland)
- Brief pieces in SOLAS and IGAC newsletters
- **Reminder: EGU abstract deadline on 9th January 2013**