

**Marine Aerosol-Cloud Interaction (MaCloud Inc. 2.5)****Denis Pöhler****Observations of Halogens with different DOAS techniques****Introduction and motivation**

The Earth's atmosphere represents a complex chemical and dynamical system. Its behavior is governed by various feedback mechanisms and interactions with other subsystems of the Earth – such as ocean, biosphere and cryosphere – that frequently cause non-linear responses of the atmosphere to external perturbations, often with harmful consequences for the environment. It is therefore of great importance to quantify the key processes controlling the chemical, dynamical and radiative properties of our atmosphere as a whole.

During recent years it became increasingly clear that halogen chemistry - beyond its well known influence on stratospheric ozone - plays an important role in the chemical and physical processes of the troposphere [e.g. Barrie and Platt 1997, Platt 2000, Platt and Hönninger 2003, von Glasow and Crutzen 2007, Pöhler et al. 2010]. This is particularly evident within the marine boundary layer [e.g. Sander and Crutzen 1996, von Glasow et al. 2002a, b, Read et al. 2008], but chemical processes related to reactive halogen species (RHS) i.e. halogen atoms, molecular halogens and oxidised halogen species may affect the entire troposphere [e.g. Platt and Hönninger 2003, von Glasow et al. 2004]. Also it turned out that liberation and the recycling of RHS is largely promoted by multi-phase processes [e.g. Vogt et al. 1996, Tuckermann et al. 1997, Platt and Lehrer 1997]. To date significant involvement of reactive halogen species has been identified in a large number of processes, many of them connected to the atmospheric oxidation capacity and the nitrogen and sulfur cycling between the atmosphere and the ocean. These include:

- Modification of the tropospheric oxidation capacity
- Formation of new particles through nucleation of iodine oxides
- Change in the DMS degradation mechanism leading to reduced formation of sulfur particles
- Ozone destruction and reduction of ozone formation
- Enhancement of the OH/HO<sub>2</sub> ratio
- Enhancement of the NO/NO<sub>2</sub> ratio (Leighton ratio)

In summary it is now very likely that halogen chemistry has a significant influence on – at least - the marine atmospheric chemistry and physics on a global scale. However, many underlying mechanisms are presently not understood. Also the spatial emission and extent of the areas where halogen chemistry is of importance needs to be much better quantified. The most likely source of reactive iodine is the photolysis of molecular iodine and organohalogens emitted by macro algae at coastal sites if they set under “stress”. O’Dowd et al. [2002] and Mäkelä et al. [2002] indicate that reactive iodine plays a key role in the formation of new particles in coastal areas which could also be shown by our group [e.g. Seitz et al. 2010]. If those particles grow to become cloud condensation nuclei (CCN), they could influence cloud properties and therefore have an impact on climate.

However the emission strength variability and influence on aerosol formation are not well quantified. In addition to coastal iodine-driven nucleation and growth events, it has been recently established that open ocean particle production and growth is quite frequent over the NE Atlantic and appears to be driven by organics.

To quantify both formation processes the measurements of particles in combination with RHS are required. However RHS observations are rare as their low concentration and high reactivity makes the observation impossible with most measurement techniques. Many field studies on RHS were carried by applying the LP-DOAS technique at the Mace Head atmospheric research station [e.g., Alicke et al., 1999; Hebestreit, 2001; Saiz-Lopez and Plane, 2004; Saiz-Lopez et al., 2004a, 2006a,b; Peters et al., 2005; Seitz et al. 2010]. The most relevant RHS at such coastal sites is Iodine oxide (IO) which is studied in this project. IO emissions seem to be highest at high solar radiation, and thus in summer, with coincidental low tide, when the coastal macro algae are set under “stress”.

Model calculations from Burkholder et al. [2004] state that the concentrations of iodine species (the most relevant RHS in these coastal areas) derived so far (at different locations including Mace Head) with the LP-DOAS measurements are too low to account for the large aerosol production observed. They suggested a

possible reason for the disagreement between model calculations and field observations which is an inhomogeneous location of iodine sources, with much above average IO mixing ratios, so called “hot-spots”. This would have significant influence on the RHS chemistry and particle formation processes and thus the total impact of RHS on a global scale. Such strong local variations are possible as emitted RHS can have a very low lifetime and/ or chemical processes directly occur after emission.

Recently our group from Heidelberg could support this theory by observations at the MRI, where concentrations of IO were very different on the scale of few 100m observed with two averaging LP-DOAS light paths [Seitz et al. 2010]. To prove the theory of inhomogeneous iodine sources and chemistry several authors [e.g. Seitz et al., 2010; Furneaux, 2010] recommend further in-situ measurements with new mobile I<sub>2</sub> or IO instruments that measure these trace gases directly inside the macroalgae beds and thus allow to determine reliable emission factors for different macro algae and seaweed species in their natural environment. Furthermore this would also allow to quantify the local distribution of reactive iodine with a high spatial resolution, a key information for the validation of chemical models which is important to improve our understanding of tropospheric halogen chemistry.

## Scientific objectives

MaCloud Inc. (Marine Aerosol –Cloud Interactions) was aimed to build on recent advances in marine aerosol formation processes, both in terms of secondary and primary formation processes. Different measurement techniques were applied to better characterize these coastal and open ocean events. Therefore different aerosol mass spectrometry observations are used to quantify marine aerosol organic characteristics with effective cloud nucleating properties. The project was aimed to characterize the growth factor and CCN activity of varying organic matter enrichments in sea-spray aerosol in combination with a series of gaseous characterization. In particular, the project was applying for the aerosol observation:

- (1) use a range of on-line aerosol mass spectrometric techniques and off-line HNMR techniques for aerosol chemical characterisation (e.g. AMS, ATOFMS, MOVI-CIMMS, TD-CIMMS);
- (2) use a range of aerosol physics instrumentation for physical characterisation (NAIS/AIS, PH-CPC, nano SMPS, SMPS) with a focus on cluster formation as a function of I<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub>;
- (3) use a range of mass spectrometer and spectroscopic techniques for gaseous characterisation (IO, O<sub>3</sub>, VOC, OH, H<sub>2</sub>SO<sub>4</sub>, MSA, I<sub>2</sub>, BrO, AMSs API-TOF, PSM, and PTR-MS)
- (4) use a range of hygroscopic uptake and CCN instruments both for air and laboratory studies into secondary and primary organic aerosol. (HTDMA, VHTDMA, CCN, Bubble tanks).

With the aim:

- (1) to source apportion marine aerosol
- (2) quantify formation and evolution characteristics
- (3) quantify hygroscopic and CCN properties
- (4) quantify of marine aerosol impacts on cloud microphysics.

The 2011 campaign was characterising the high biological activity period impacts on aerosol formation and aerosol-cloud interactions and follows the winter 2010 low biological activity period of measurements in 2010 which was part supported by EUSAAR.

Our part was to quantify the contribution of coastal halogen emissions on aerosol formation by measurements of RHS. To derive the spatial variability of the RHS and thus the possible very local influence on aerosol formation, we applied a new in-situ technique (CE-DOAS for IO) in combination with the well established LP-DOAS (IO, BrO, O<sub>3</sub>) technique.

## Reason for choosing station

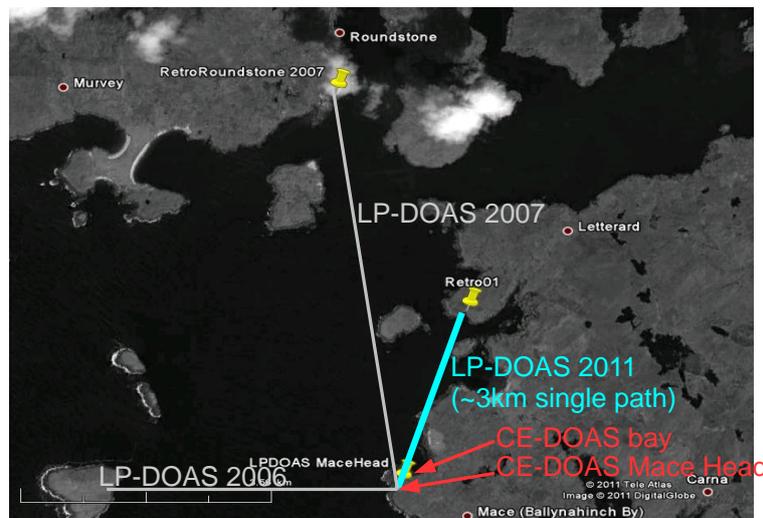
The West coast of Ireland is famous for large amounts of different macro algae and the remote site Mace Head is perfect for the investigation of naturally emitted RHS from coastal macro algae and the formation of particles. In this area interferences with human pollution are low. Most of former investigations of RHS are made at Mace Head, thus new techniques and measurements can be compared to these observations. Only 6km south-east from Mace Head the Martin Ryan Institute (MRI) is located where the Marine Science is investigated including macro algae. Our cooperation with the MRI helps us to quantify the different algae types and thus their influence on RHS. The permanent measurement of aerosols at MaceHead, and the additional aerosol characterisation during MaCloud, gives the possibility to put the RHS observation in context to aerosol formation.

## Method and experimental set-up

The DOAS technique, investigated by Prof. U. Platt (University of Heidelberg, Platt et al. 1979), allows the direct observation of many RHS in the atmosphere. The basic principle is based on the absorption spectroscopy of the molecules. To separate between different molecules and the aerosols, DOAS use the spectrally narrow and characteristic structures of the molecules in the UV and visible spectral range. Therefore active Long Path (LP-) DOAS instruments emit a broad spectrum in the desired spectral range (typically UV and visible) which passes the atmosphere few 100m to 10km. The received spectrum can then be analysed and gives the concentration of the trace gas averaged along the light path. Most RHS are measured using LP-DOAS at ppt level with several kilometer light paths. One has to keep in mind that possible inhomogeneous distributions of RHS cannot be resolved along the path.

We developed in Heidelberg two new measurement instruments also based on the DOAS technique to quantify the spatial variability of IO which is part of current research.

First, a new LP-DOAS instrument was developed and applied for the first time during the MaCloud campaign. The new instrument allows now to setup LP-DOAS measurements of RHS within few hours at different locations and thus to quantify the concentrations at different coastal sites. The lower power consumption allows a battery power supply. The LP-DOAS was setup at Mace Head with a light path of 3km crossing three bays with potential RHS emissions (Fig. 1).



*Fig 1: Set-up of LP-DOAS and CE-DOAS at Mace Head. LP-DOAS was set-up this time to cross 3 bays with high macro algae amount and thus be more correlated to coastal affects that for the measurements in 2007. The CE-DOAS was located first directly at Mace Head, and later about 200m from the station directly at the water line (bay).*



*Fig 2 Set-up of the new CE-DOAS instrument at the Mace Head research station for observations of IO.*

Second, we applied the very new Cavity Enhanced (CE) – DOAS technique [Platt et al. 2009, Meinen et al. 2010], to the observation of IO in the ppt range. CE-DOAS uses passive optical resonators to provide long light paths (> 1km), in a relatively compact setup with resonator lengths in the order of 1m (see Fig 2). Thus a CE-DOAS instrument achieves the same sensitivity like a LP-DOAS but measures the air mass just at the

instrument location. We focused on the development of a mobile CE-DOAS instrument for the observation of IO down to 1ppt, which is the first instrument of this kind. Our final setup has a weight of about 25 kg and can be placed on two tripods at any location. Thus it can observe so called “hot spots” with locally very high concentration. In combination with the compact LP-DOAS instrument it can answer the question of spatial iodine variations at coastal sites and their influence on aerosol formation and tropospheric ozone destruction. The instruments are complemented by an Ozone monitor.

Continuous measurements were done at Mace Head (incl. installation) between 14<sup>th</sup> to 30<sup>th</sup> may 2011. Thereby the CE-DOAS instrument was varied between two locations, one directly at the measurement station, and a second about 200m away directly at the waterline in the bay where significant algae are present. Afterwards measurements were performed at other coastal sites outside Mace Head. The research station was still used as base for repair of instruments and calibration. Measurements were performed for several days at the Martin Ryan Institute (MRI), Carna, one day at Meenish Island, one day at an Belly Conelly and one day at a seaweed factory. The Days at Mace Head research station were as follows:

Date	Access days	Persons	Done work at Mace Head
14/05-30/05	16.5	3	Installation and continuous measurements at Mace Head, Calibrations
31/05	1	3	Calibration
04/05	1	3	Calibrations
06/06	0.5	3	Repair instrument
08/06	1	3	Calibration
09/06	1	3	Packing equipment
Total	21	*3	= 63

### Preliminary results and conclusions

Measurements with the two applied instruments could be realised at Mace Head during several days. However weather conditions were very bad for this time of year and thus unfavourable for emissions of RHS. Most of the days were rainy or cloudy with wind speeds above 10m/s. Thus solar radiation was too low for RHS emissions. If emissions arise the strong wind resulted in a very fast dilution so that RHS concentrations are typically below detection limit. During days with stormy weather (23<sup>rd</sup> and 26<sup>th</sup> of May), with wind speeds above 20m/s, the instruments had to be dismantled to avoid larger damages. At these metrological conditions the observed concentrations are most of the time below the detection limits of the instruments (LP-DOAS 1.5ppt; CE-DOAS 2ppt), as expected. Only during two days the LP-DOAS observed concentrations of up to 2ppt (Fig 3), with max. concentration of up to 2ppt. Concentration peak correlates well with high solar radiation and low tide as expected. However the level is much lower than typically observed for this time of year. Thus particle formation due to RHS is less important during the MaCloud measurement campaign than it is the typical case for Mace Head. The CE-DOAS instrument could not observe IO on the same days, but for a short sunny period on the 30<sup>th</sup> of May with levels of up to 22ppt when it was not measured with the LP-DOAS. The differences in both instruments, which actually observe the IO concentration from different air masses, indicate that emissions are very inhomogeneous. The CE-DOAS could see very shortly a very high concentration as it was located only few m from the algae. However the LP-DOAS averages over a large area, but may also see emissions further away due to different algae types.

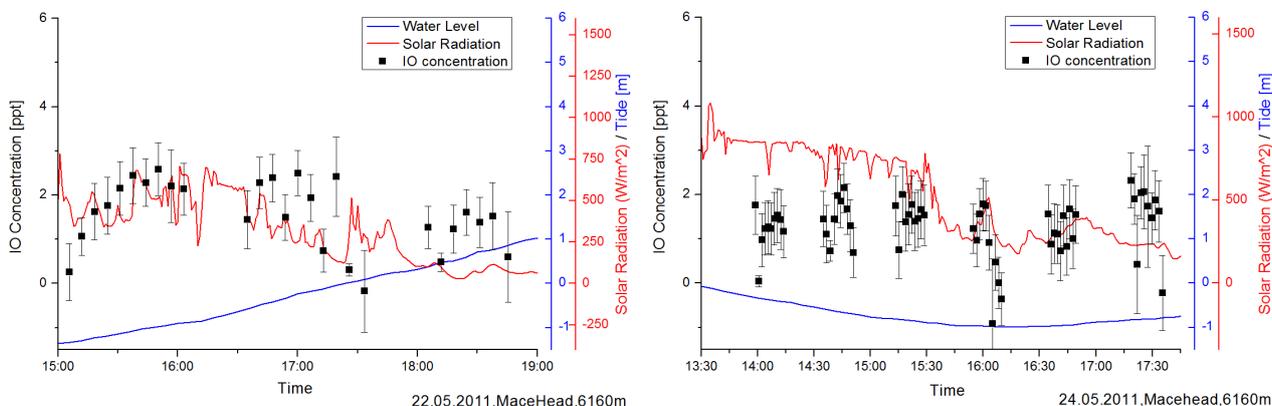


Fig 3 Observed IO up to 2ppt at Mace Head with the LP-DOAS. Concentration peak correlates well with high solar radiation and low tide. However the concentration is very low for this time of year and location.

In June measurements were performed at other coastal sites outside from Mace Head. These were typically locations where large areas with macro algae were exposed to the air during low tide. Even if metrological conditions were better as for the measurements at Mace Head, the observed concentrations were one order of magnitude higher than at Mace Head (Fig 4). Also very strong local variability could be observed. For example on the 2<sup>nd</sup> of June when the LP-DOAS measured up to 30ppt averaged over 1012m, the CE-DOAS could observe even 100ppt in the algae field itself (Fig. 4). On other days when the CE-DOAS could still observe significant IO levels of much more than 10ppt in the algae field the LP-DOAS just saw a few ppt (<10ppt) (Fig 4). These observations prove the spatial inhomogeneous emission of iodine and distribution of IO.

Similar observations could also be made at the Coast of Meanish Island. We also saw very strong variability between the locations. Thus much more observations are required to do any assumptions about total emissions and impact of iodine for the whole coastline.

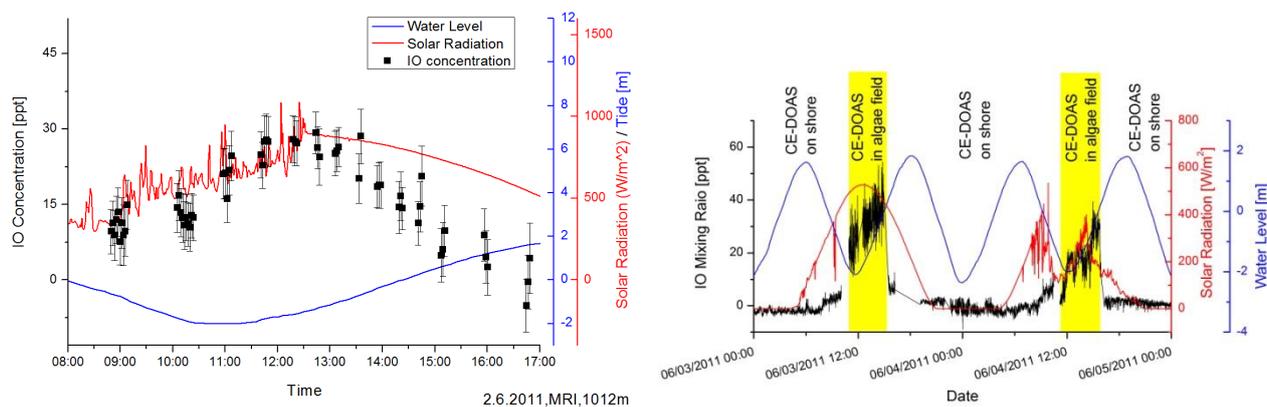


Fig 4 Observed IO up to 30ppt at the MRI with the LP-DOAS (left). Concentration peak correlates well with high solar radiation and low tide. The CE-DOAS observed at the same time up to 100ppt. Also CE-DOAS observed IO up to 50ppt at days when the LP-DOAS just observed levels around few ppt (right).

### Outcome and future studies

We conclude that the RHS concentrations are very low at Mace Head during cloudy and windy weather situations. RHS are not significantly involved in aerosol formation and ozone depletion during MaCloud. Different concentrations observed with the two instruments indicate very different sources with strong spatial variability. A general conclusion with any RHS measurement cannot be made for aerosol formation as their concentration may be spatially very variable. Further improvements to the instruments are necessary to be more resistant to the strong winds permanently arising at Mace Head.

Future observations at Mace Head and surrounding should be performed over a longer period to perform measurements at various metrological situations and thus have the possibility to conclude on the variability of RHS levels for different conditions.

At other locations close to Mace Head, with much higher macro algae abundance, much higher IO concentrations are observed. Thus indicating that halogen emissions are maybe much more important at the West coast of Ireland than so far expected from measurements at Mace Head. Further measurements of RHS are necessary especially at various coastal sites to investigate the local importance and difference from coast to coast. However many of these measurements are necessary as the metrological conditions have a very strong influence on the actual emissions.

We could prove that local IO concentrations are several times higher in these algae field than so far observed with the LP-DOAS averaging over a few 100m. Thus concentrations are actually above the algae field sufficient high to initiate particle nucleation as described above.

Additional measurements of IO with the improved instruments are planned for summer 2012 at Mace Head and along the Irish West coast. The results from the measurements 2010 are planned to be publish.

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