

Reactive Iodine and Particle Observations (RIPO)

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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. 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]. 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/HO₂ ratio
- Enhancement of the NO/NO₂ 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 organohalogen emissions by macro algae at coastal sites if they are 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 out 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 is formed from iodine emissions and concentrations are 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 observations at the Martin Ryan Institute (Carna co. Galway, Ireland), show indications of such inhomogeneous distributions [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 I₂ or IO instruments that measure these trace gases directly inside the macro-algae 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.

Additionally our current knowledge on macro algae driven iodine emissions mainly rely on several measurements at Mace Head. Strong variations between different locations may arise due to different types and distribution of macro algae. This may have significant influence on the estimation of local and global iodine driven particle formation. Measurements from 2011 indicate that iodine concentrations are likely very different for different locations even on a scale of few km. Thus a comparison of iodine emissions of Mace Head to other coastal sites is essential to quantify the total emission of iodine and review our current understanding of the total impact on ozone depletion and particle formation.

Scientific objectives

The variability of iodine emissions between different coastal locations are poorly quantified. This project aims is to better characterize these coastal iodine emission events at the Irish west coast around Mace Head. The spatial distribution of the emissions on a small scale (~10m) close to Mace Head and on a larger scale (~5 km) are performed by combining different measurements. The first are performed to investigate locally so called « hot spots » and strongest iodine emitters and thus help to better understand the emission processes. The second are important to investigate different algae populations and better quantify the total iodine emission and impact on ozone depletion and particle formation. The measurements at Mace Head will be accompanied by aerosol physics instrumentation.

Aims and objectives:

- (1) quantify iodine emissions and its spatial variability at Mace Head
- (2) quantify formation and evolution characteristics of particle formation during these events
- (3) quantify the difference of iodine emissions from Mace Head to other location at the Irish Westcoast
- (4) test new instruments for atmospheric IO measurements

Reason for choosing station

The West coast of Ireland is famous for significant 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. Most of former investigations of RHS are made at Mace Head, and almost our whole understanding of iodine emissions from macro algae rely on these observations. Due to instrumentation limitations it was so far not possible to quantify the local emission sources and their distribution directly at the coastline in front of Mace Head. This is one main objective to quantify former observations. Additionally the variability along the coast is not quantified so far. Thus conclusion from observations of Mace Head for the whole Irish coast and globally can not be made. We perform measurements simultaneously at Mace Head and at different sites along the Irish Westcoast to quantify these variabilities. They allow to scale measurements at Mace Head to other locations and estimate a regional iodine emission.

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 derives the average concentration of the trace gas along the light path. Most RHS are measured using LP-DOAS at ppt level with several kilometre light paths. One has to keep in mind that possible inhomogeneous distributions of RHS cannot be resolved along the path.

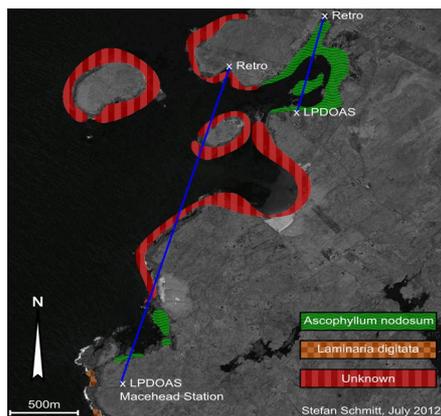


Figure 1: Map of area around Mace Head with characterised algae species and LP-DOAS light path. With the mobile LP-DOAS also measurements at a close bay were performed.

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 and applied in this project. First, two LP-DOAS instrument were applied. One was stationary at Mace Head, the second mobile and could fast (within few hours) set up at different measurement locations. The lower power consumption allows a battery power supply. The LP-DOAS at Mace Head featured a light path of 3km crossing three bays with potential RHS emissions (Figure 1).

Second, we applied the 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. 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 instrument was further improved since measurements at 2011. The instruments are complemented by an Ozone monitor, a mobile weather station and aerosol measurements at Mace Head.

Inter-comparison measurements between the different instruments and characterisation of RHS emissions at Mace Head were performed for the first part of this campaign and on the last day. During other days the one LP-DOAS was operated at Mace Head, while the other instruments were set up at other locations at the Irish west coast. We totally covered 7 measurement locations.

Preliminary results and conclusions

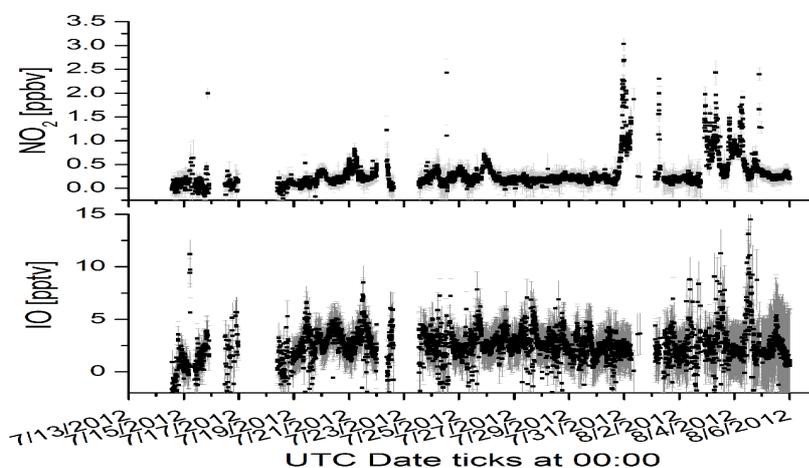


Figure 2: Preliminary results LP-DOAS Mace Head averaged over a light path of 3km along the coast to the north.

Continuous measurements of RHS compounds could be realised with a LP-DOAS at Mace Head. Weather conditions were characterised by “typical Irish” weather with temperatures of typically 15°C and regular rain and wind. We had few days with sunshine, however these days mostly did not match with days with low tide at noon, what would be preferably for RHS emissions. IO concentrations are typically below 5ppt (Figure 2). Measurement accuracy was often limited by low visibility due to fog and rain. Correlations between increased IO and tidal high for a clean air sector are identified for 3 days (19th -21st July). Highest concentrations are observed for non clean air sectors with winds from north-east with simultaneously increased NO₂ (2nd - 4th August). These RHS emissions arise from algae fields about 4km north-east of Mace Head (see Figure 1).

Measurements with the mobile LP-DOAS instruments show good agreement for the comparison at Mace Head with very low IO concentrations. Very surprisingly, measurements at all other measurement locations at the coast show much higher IO levels and thus much stronger RHS emissions compared to Mace Head (Figure 3) and even much higher concentrations at unfavourable weather conditions ever observed at Mace Head.

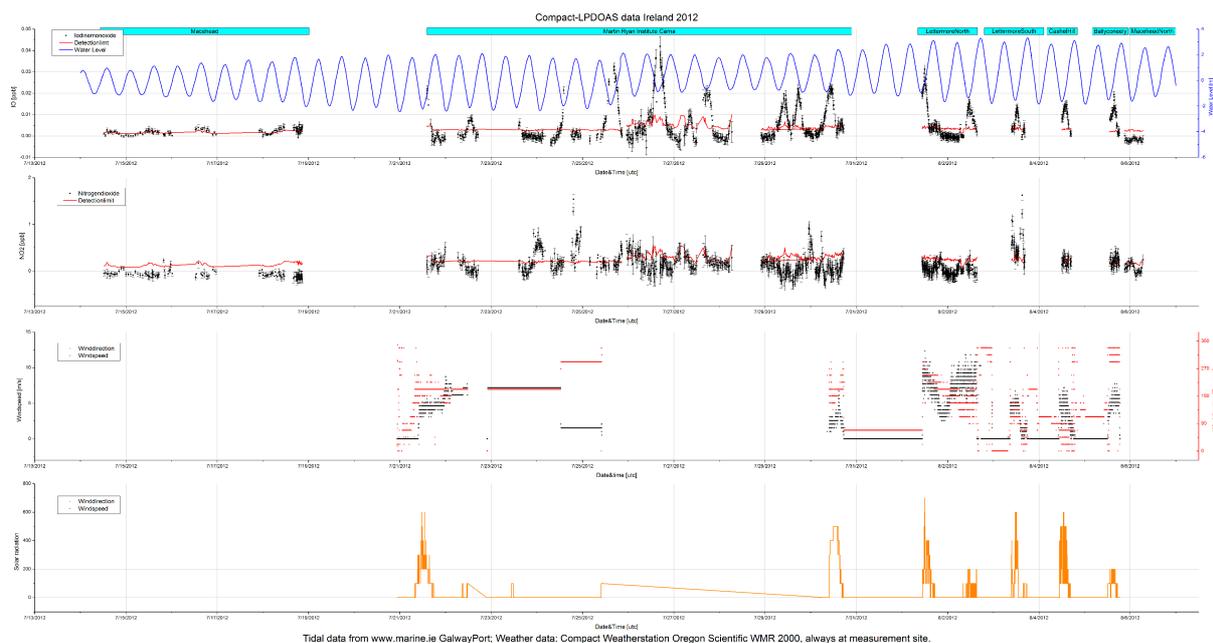


Figure 3: Preliminary results of the mobile LP-DOAS and weather data of a mobile weather station.

Observations of the mobile CE-DOAS confirm these observations. Measurements at Mace Head (15th - 20th of July and 6th of August) feature a much lower concentration than observed on any other location (Figure 4). At Mace Head two emission areas could be identified (Figure 1), where strong emissions of the laminaria digitata only arise shortly on very low tides.

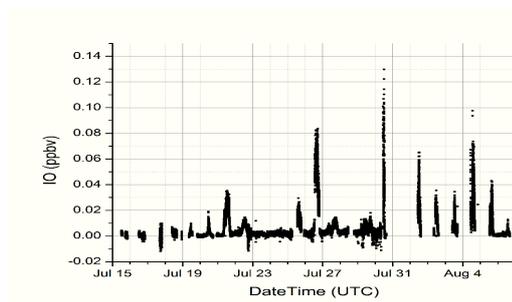


Figure 4: Preliminary results of the mobile CE-DOAS instrument.

Outcome and future studies

Strong variations of IO levels at different measurement locations with concentrations varying one order of magnitude indicate very strong variability in RHS emissions. Concentrations at Mace Head are much lower and significantly underestimate the total RHS emissions. Even at unfavourable weather conditions with rain and wind, several 10 ppt IO could be observed at other locations. Mace Head just show enhanced locally

emitted IO concentrations if very low tides match with sunny weather conditions, a very rare phenomenon at this site. Thus a review of RHS emissions at coastal sites is necessary. Any conclusions on regional and global scale of RHS emissions, its influence on ozone depletion and particle formation has to be reviewed. We could clearly correlate higher IO concentrations to specific macro algae. Similar mobile measurements are planned for other coastal sites to prove strong spatial variability and RHS emission strength.

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