Observations of IO Hot-Spots at Coastal Sites with the Combination of a Mobile CE- and LP- DOAS Instrument

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Aerosol Clouds, and Trace gases Research InfraStructure Network

Tropospheric Iodine at Coastal Sites

In coastal regions iodine atoms are set free via photolytic destruction of short lived iodinated hydrocarbons or I_2 molecules emitted from the seaweed. The emissions arise mainly during low tide if they are exposed to the air and are especially enhanced if simultaneously solar radiation is high.

Iodine affects the atmospheric chemistry in different ways:

- Important role in the process of ozone depletion. Iodine reacts quickly with O_3 to form IO. Self and cross reactions with IO, XO leads to autocatalytic destruction of O_3.
- Are precursors of particle bursts (I_2 not CH_2I_2 seems to be the main precursor for particle formation in coastal areas). Probably the OIO self reaction or the reaction of OIO with IO form higher oxides, which get further oxidised and or cross-react to form particles.
- Affects the HO_2/OH and NO_2/NO ratio.
- Oxidise DMS from phytoplankton.
- Uptake of inorganic iodine compounds (e.g. HOI, INO_3) leads to the liberation of chlorine and bromine from sea salt aerosols.

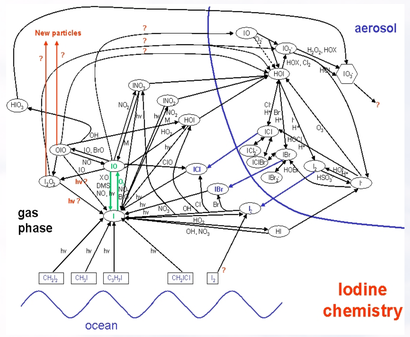


Figure 1: Schematic overview on the atmospheric iodine cycle in the marine boundary layer. Adapted from [Pechtl et al., 2006]

Measurement Techniques

Measurements of seaweed emitted reactive iodine species have mostly been carried out at Mace Head research station at the Irish West Coast using long-path differential optical absorption spectroscopy (LP-DOAS) [e.g. Alicke et al., 1999; Saiz-Lopez et al., 2004; Peters et al., 2005]. Derived are average concentrations over several 100m. However, information about the spatial distribution of reactive iodine species and emissions of different species (e.g. Laminaria, Ascophyllum) in the field are still rare. In order to study if reactive iodine species are actually located in so-called „hot-spots“, we combine LP-DOAS with the new in-situ Cavity Enhanced (CE)-DOAS technique.

LP-DOAS (averaged over several 100m)

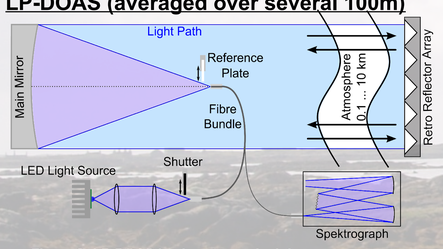


Figure 2: LP-DOAS basic set-up principle.

- Measures the absorption of the trace gases on a light path of 100m -10km
- Royal blue LED light source
- Telescope with f=50cm transmit the light to a retro reflector array and receive it again

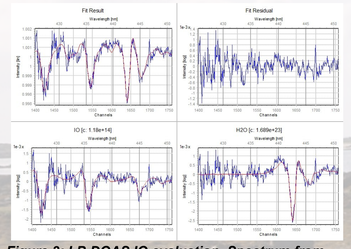


Figure 3: LP-DOAS IO evaluation. Spectrum from 02/06/2011 12:01 UTC measured at MRI over 1890m (Retro 3). IO concentration 12.4 ± 2.2 ppt.

- Light is spectrally analysed by a OMT spectrometer (resolution ~0.8nm)
- IO analysis range 425-451nm
- Detection limit ~1ppt (2km single light path)

CE-DOAS (in-situ)

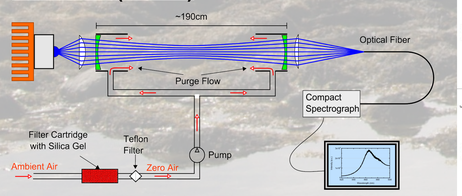


Figure 4: CE-DOAS basic set-up principle.

- Absorption path between two high reflective mirrors (~2m distance), peak reflectivity 445nm
- Light path up to 8km
- Royal blue LED light source
- Absorption path open (no reactions on walls and tubes possible), purge flow at mirrors prevent contamination
- ~25kg, mobile → set-up in the algae field during low tide possible

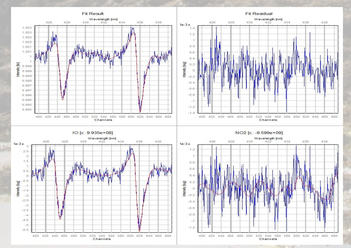
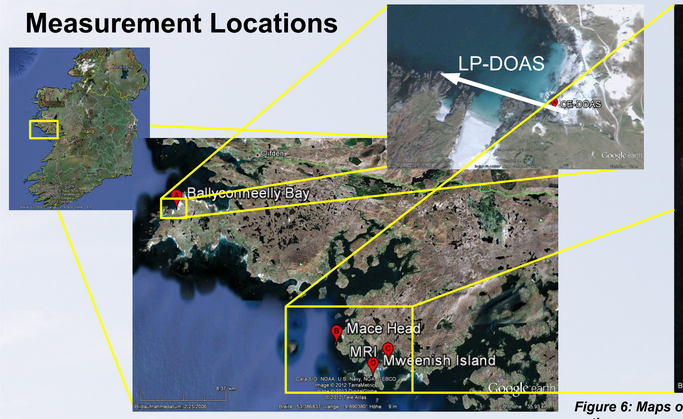


Figure 5: CE-DOAS IO evaluation. Spectrum from 03/06/2011 14:26 UTC measured at MRI . IO concentration 39.5 ± 1.6 ppt.

- Light is spectrally analysed by a Avantes spectrometer (resolution ~0.6nm)
- IO analysis range 425-440nm
- Light path calibration with Helium and ring-down
- Detection limit ~1ppt

Measurement Locations



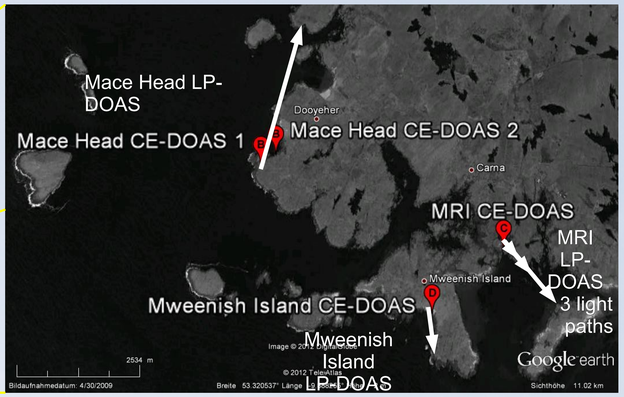


Figure 6: Maps of the measurement locations: with red letters CE-DOAS and white arrows LP-DOAS light paths.

Martin Ryan Institute (MRI)

- Surrounded by large algae fields of Ascophyllum Nodosum
- During low tides algae are exposed to the air over several 1000m²

LP-DOAS:

- Measurement over three light paths: Retro1 (266m) only over Ascophyllum algae, Retro2 (566m) over mainly Ascophyllum and some Laminaria, Retro3 (1890m) like 2 but additionally over water

CE-DOAS:

- During low tide located in the algae field (Figure 12), else on shore

→ Both instruments observe IO up to ~60ppt

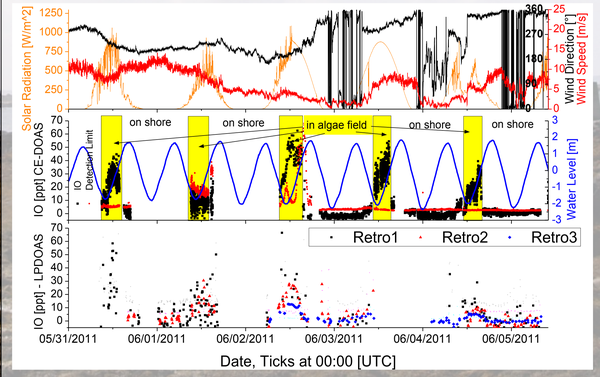


Figure 7: Meteorological data and IO values from MRI. During low tide very high IO concentrations of up to ~60ppt are observed in the algae field with both instruments. Note that the short LP-DOAS light path (Retro1) has a larger detection limit and measurement error (not drawn for simplicity)

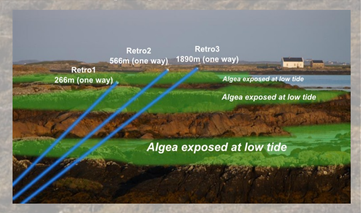


Figure 8: LP-DOAS light paths set-ups over the algae field.

Conclusions

- Combination of LP-DOAS + mobile CE-DOAS can observe IO hot-spots
- IO concentrations are locally very high (up to ~70ppt) even at bad weather conditions
- Averaged LP-DOAS concentrations are at most locations (incl. Mace Head) a factor of ~10 lower
- IO levels in Ascophyllum algae fields are higher due to their large extend in comparison to the small Laminaria fields

Mweenish Island

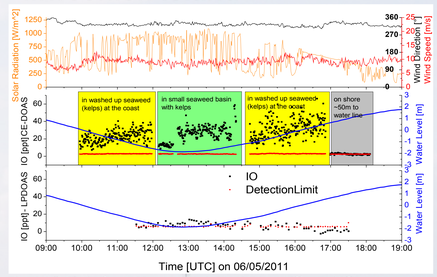


Figure 9: Data from Mweenish Island. Very dfferent IO concentrations from both instruments indicate local hot-spots.

- Beach with washed up algae (partly Laminaria)
- Locally Laminaria algae in deep water
- LP-DOAS light path over 855m along the coast
- CE-DOAS in the washed up algae and above Laminaria

local hot-spot: very high IO levels at the algae (up to 70ppt) which can not be found with LP-DOAS

Ballyconneely Bay

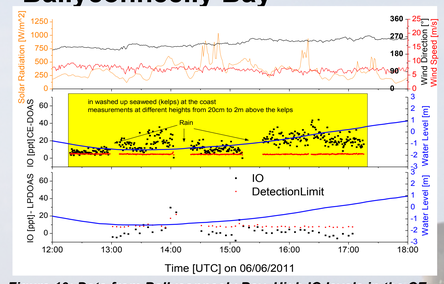


Figure 10: Data from Ballyconneely Bay. High IO levels in the CE-DOAS over the washed up algae can not be found in the LP-DOAS.

- Beach with washed up algae (Laminaria)
- LP-DOAS light path over 501m along the coast
- CE-DOAS in the washed up algae field (1m thick)
- Bad weather conditions with regular short rains
- Locally still relative high IO levels up to 40ppt

→ Iodine emissions even at bad weather conditions

Mace Head

- Measurements during MaCloud field campaign
- Bad weather conditions with strong wind and rain
- LP-DOAS light path over 3080m along the coast could not observe IO
- CE-DOAS at two different locations could still observe IO up to 30ppt

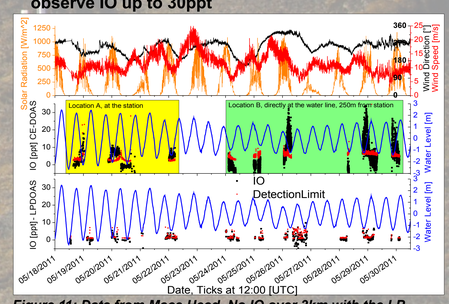


Figure 11: Data from Mace Head. No IO over 3km with the LP-DOAS, but still locally observed at the shore with the CE-DOAS.

Figure 12 (Background): Picture at the MRI. CE-DOAS in the algae field (Ascophyllum Nodosum) during low tide.

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References

Alicke, B; Hebestreit, K; Stutz, J; Platt, U. (1999), **Iodine oxide in the marine boundary layer.** *Nature*, 397(6720), 572-573

Pechtl, S., E. R. Lovejoy, J. B. Burkholder, and R. von Glasow (2006), **Modeling the possible role of iodine oxides in atmospheric new particle formation**. ACP, Vol. 6, 503 – 523.

Peters C., et al. (2005), **Reactive and organic halogen species in three different European coastal environments**, ACP 5, 3357–3375.

Saiz-Lopez, A., J. A. Shillito, H. Coe, and J. M. C. Plane (2006), **Measurements and modelling of I2, IO, OIO, BrO and NO3 in the mid-latitude marine boundary layer**. ACP, Vol. 6, 1513 – 1528.