On-line monitoring of molecular iodine emissions from seaweed using a new mass spectrometric technique

M. Kundel✉, U.R. Thorenz, J. Petersen, R.J. Huang, N.H. Bings and T. Hoffmann

Johannes Gutenberg University, Department of Inorganic Chemistry and Analytical Chemistry, Duesbergweg 10-14, 55128 Mainz, Germany
✉mkundel@uni-mainz.de

Introduction: Molecular iodine (I_2) and iodocarbons are released by macroalgae and phytoplankton into the atmosphere. These volatile iodine containing compounds are involved in the tropospheric ozone depletion and the marine new particle formation. Recent studies suggest that biogenic emissions of molecular iodine rather than iodocarbons are the dominant source of reactive iodine atoms in the marine boundary layer [1]. Especially during low tide, when seaweed is exposed to atmospheric air, increased levels of I_2 were detected at different measurement sites [2],[3]. In this work we present a new application of the time-of-flight aerosol mass spectrometer (ToF-AMS) [4] for the determination of I_2 in real-time. Therefore incubation experiments with eight different seaweed species were performed in the presence of ozone (0-150 ppb). *Laminaria digitata*, *Laminaria hyperborea*, *Laminaria saccharina*, *Ascophyllum nodosum*, *Fucus vesiculosus, Fucus serratus*, *Chondrus Crispus* and *Delesaria sanguinea* were collected in the intertidal zone of Helgoland in May 2011. After harvesting, the seaweed samples were stored in running seawater at the Alfred-Wegener-Institute Helgoland. All samples were used within four days after harvesting. Release profiles of molecular iodine were measured using the newly developed ToF-AMS method. Furthermore the total iodine content of the seaweed was measured to determine emission rates of I_2. Contemporaneously with I_2 iodocarbon emission rates were determined and compared to I_2 emission rates.

On-line monitoring of I_2:

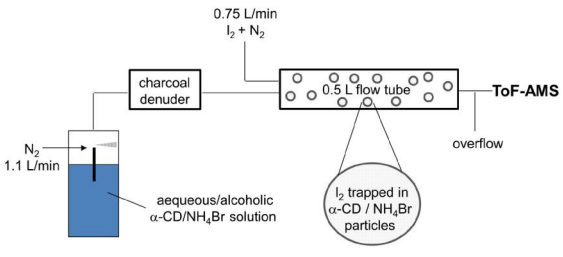

Fig.1: Selective uptake of I_2 into α-CD/NH_4Br particles

In order to use the high sensitivity of the ToF-AMS for I_2 measurements, I_2 has to be converted from the gas phase into the particle phase by α-CD/NH_4Br particles. Therefore a flow tube was mounted in front of the AMS. Br^- was added to α-CD to improve the inclusion complex. I_2 was quantified by the molecular ion at m/z 253.8. LOD of 300 ppt was achieved for 1 min time resolution and could be improved to 60 ppt for 30 min time resolution.

Seaweed incubation experiments:

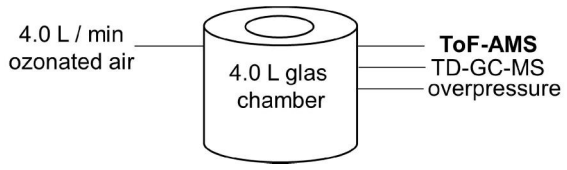

Fig.2: Experimental setup of the seaweed incubation experiments

Iodocarbon measurement: Iodocarbons were pre concentrated on thermodesorption tubes filled with Carbotrap and Tenax and off-line quantified using TD-GC-MS.
Total iodine measurement: Microwave assisted TMAH extraction followed by ICP-MS measurement was used for the quantification of total iodine in seaweed.

I_2 release profiles of different seaweed species at 50 ppb O_3

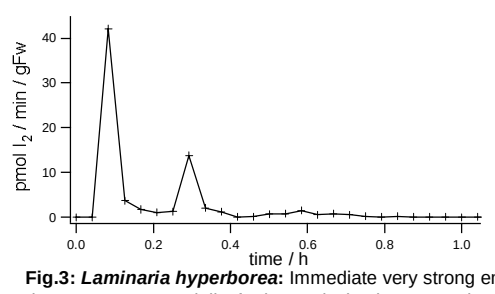

Fig.3: *Laminaria hyperborea*: Immediate very strong emission, decreases exponentially, further emission burst was detected

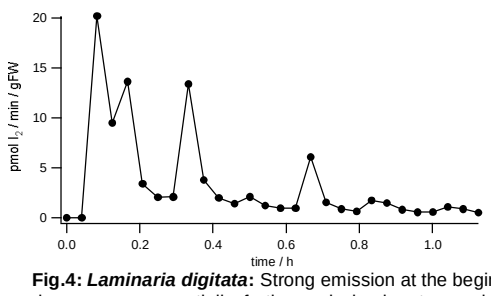

Fig.4: *Laminaria digitata*: Strong emission at the beginning, decreases exponentially, further emission burst were detected

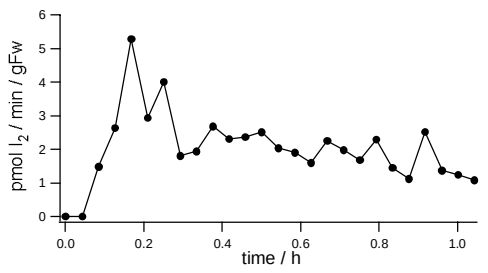

Fig.5: *Laminaria saccharina*: Strong emission at the beginning, decay less steep compared to the other Laminariales, remains stable after 0.3 hours.

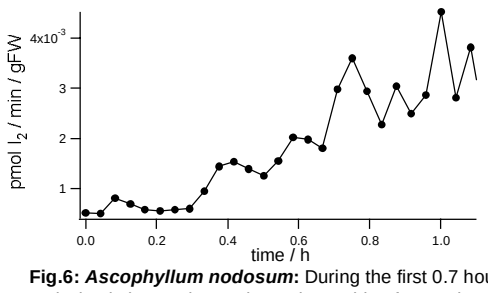

Fig.6: *Ascophyllum nodosum*: During the first 0.7 hours I_2 emission is increasing and remains stable afterwards

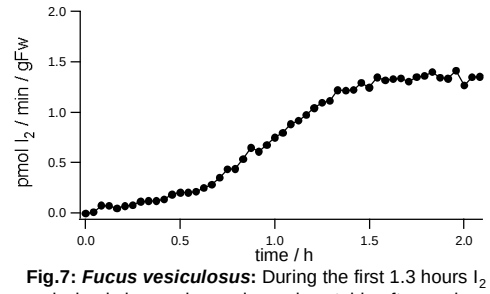

Fig.7: *Fucus vesiculosus*: During the first 1.3 hours I_2 emission is increasing and remains stable afterwards

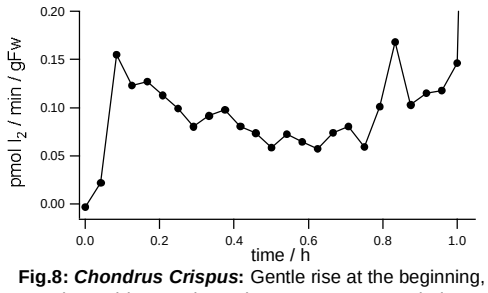

Fig.8: *Chondrus Crispus*: Gentle rise at the beginning, I_2 emission remains stable over the entire measurement period

Comparison of I_2 release with total iodine content and iodocarbon emission at 50 ppb O_3

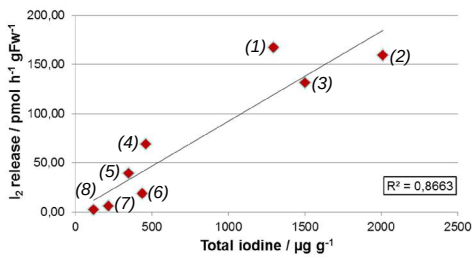

Fig.9: Dependency of I_2 release on total iodine content for eight different types of macroalgae

- I_2 release rates:
Laminaria hyperborea (1) ~ Laminaria digitata (2)
> Laminaria saccharina (3) >> Ascophyllum nodosum (4)
> Fucus vesiculosus (5) ~ Fucus serratus (6)
Chondrus Crispus (7) ~ Delesaria sanguinea (8)

- Correlation between I_2 release in the gas phase and total iodine content of the seaweed

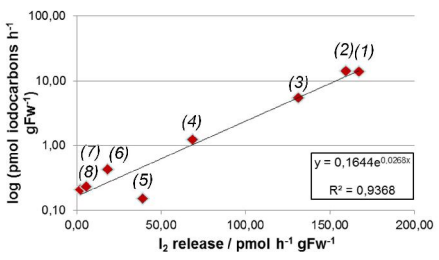

Fig.10: Dependency of total iodocarbon emission and I_2-release

- The strongest I_2 emitters are also the strongest iodocarbon emitters
- I_2 emission is 1-2 orders of magnitude higher compared to total iodocarbon emission
- Photolytic lifetime of I_2 is lower compared to iodocarbons

→ I_2 is the most important precursor for reactive iodine atoms in the marine boundary layer

Conclusions and Outlook:

- Selective uptake of gaseous I_2 into α-CD/NH_4Br particles inside a flow tube enables the on-line measurement of I_2 by ToF-AMS
- I_2 release profiles of different seaweed species were measured
→ Emission profiles of the Laminariales are in good agreement with previous studies performed by Ball et al. 2010.
→ *Fucus serratus, Fucus vesiculosus* and *Ascophyllum nodosum* showed increasing I_2 release rates with time until a stable I_2 emission was reached
- Linear correlation between total iodine content of seaweed and emission of I_2 was found
- Release rates of I_2 are 1 - 2 orders of magnitude higher than total iodocarbon emissions in our study
→ I_2 is the most important precursor for reactive iodine atoms in the MBL
- Detection limit (60 ppt, t_R= 30 min) has to be improved for field measurements
→ further optimisation of experimental parameters is required
- Future application: Simultaneous measurement of gaseous I_2 and particulate iodine by ToF-AMS in real-time

References: [1] McFiggans et al. (2004), Atmos. Chem. Phys., 4, 701-713.; [2] Mahajan et al. (2009), Geophys. Res. Lett., 36, L16803.; [3] Huang et al. (2010), Atmos. Chem. Phys., 10, 4823-4833.; [4] DeCarlo et al. (2006), Anal. Chem., 78, 8281-8289.; [5] Ball et al. (2010), Atmos. Chem. Phys., 10, 6237-6254.