Volatile short lived Iodocarbons from biotic and abiotic sources effecting atmospheres chemistry

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

Johannes Gutenberg University, Department of Inorganic Chemistry and Analytical Chemistry, Duesbergweg 10-14, 55128 Mainz, Germany

✉ute.thorenz@uni-mainz.de

Introduction:

Atmospheric Iodine radicals, formed from iodocarbons or molecular iodine, deplete tropospheric ozone and accelerate the ozone destroying capacity of other halogen species [1]. The oxides formed during this reaction may also undergo further oxidation and form polyoxides which then can react as cloud condensation nuclei [2]. The iodocarbons found in marine atmosphere are mainly produced via a biotic pathway from different kinds of macro- and microalgae. Additionally abiotic pathways of forming these reactive substances are known [3,4]. The production of iodocarbons in atmospherical particles is discussed.

An overview of the iodine related atmospherical reactions is given in Figure 1.

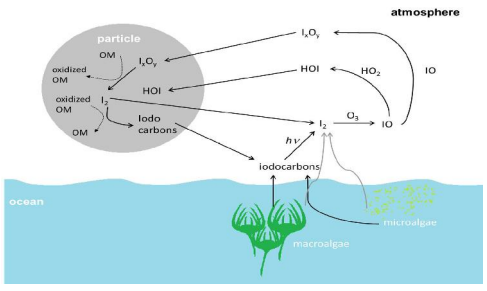

Figure1: Iodine related atmospheric reactions

Methods:

Air samples were pre concentrated on thermal desorption tubes and measured using a self-made thermal desorption device mounted on a GC-MS. The analytes were separated on a DB624 Durabond column. Measurement of the halocarbons was done using negative chemical ionisation mode with methane as reagent gas. Iodinated compounds (CH_3I, C_2H_5I, CH_2ICl, CH_2IBr, CH_2I_2, 1-C_3H_7I, 2-C_3H_7I, 1-nC_4H_9I, 2-nC_4H_9I,1-iso-C_4H_9I) were measured using the m/z 127, whereas brominated compounds (C_2H_5Br, CH_2BrCl, CH_2Br_2, $CHBrCl_2$, $CHBr_2Cl$, $CHBr_3$, 1,2-C_2H_4BrCl, 1,2-C_2H_4Br2, 1,2-$C_3H_6Br_2$, 1,3-C_3H_6BrCl, 1,2-$C_3H_6Br_2$) used m/z 79/81 in the typicall isotope ratio of 1:1.

A five point calibration was done in the range of 0.01 ng- 1.00 ng using the continuously diluted output of permeation tubes. These tubes were made by filling the pure standards in Teflon tubes which were sealed with stainless steel balls at both ends. The method detection limit was 0,003 - 0,088 ppt. For sample measurement the calibration was done in triplicate giving a method precision of 3-13%.

Biotic Sources :

During a measurement campaign at the Alfred Wegener Institute at Helgoland the dependency of Halocarbon and molecular iodine emission (using a TOF-AMS method, see Poster 3095) on ozone mixing ratios was investigated. Different macro algae *(Laminaria digitata, Laminaria saccharina, Laminaria hyperborea, Ascophyllum nodosum, Fuccus serratus, Fuccus vesiculosus, Chondrus crispus and Delesaria sanguinea)* were treated with air at different ozone concentrations to investigate weather the elevated oxidative stress leads to higher emission. Additionally the total iodine amount of these species was measured using ICP-MS.

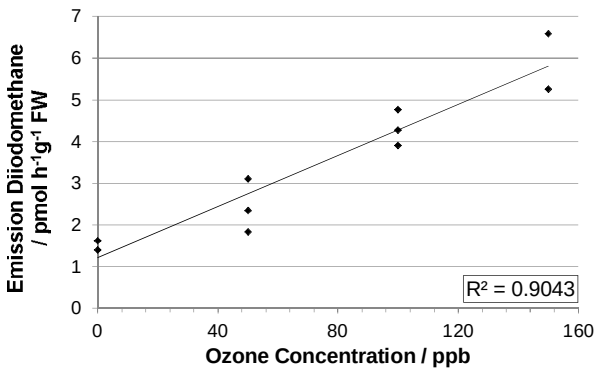

Figure 2: Ozone dependent emission of diiodomethane from *Laminaria digitata*

The experiments showed an enhanced halocarbon production of *Laminaria digitata* by oxidative stress using ozonized air, **Figure 2**. This was also found by Palmer et al. 2005 for higher ozone concentrations. Other kelps *(Laminaria saccharina, Ascophyllum nodosum Fuccus serratus and Fuccus vesicolosus)* halocarbon emissions showed no clear relationship.

A correlation for molecular iodine and iodocarbon emission was found. [Poster 3095]

The total iodine content and iodocarbon emission showed a exponential trend, **Figure 3.** This indicates that the emission of iodocarbons may be limited by total iodine content.

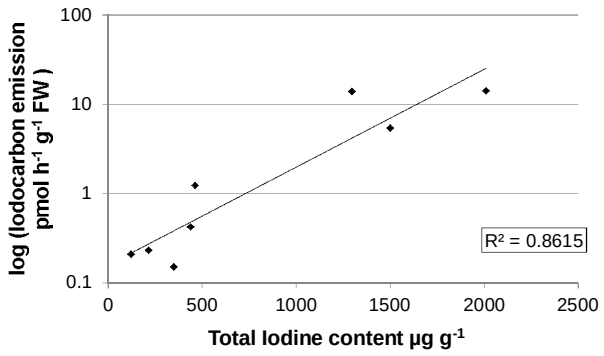

Figure 3: Iodocarbon emission and total Iodine content of different algae at 50 ppb ozone

Abiotic Sources :

Different chamber experiments were performed to investigate the abiotic pathways in halocarbon formation. In experiment 1, Fulvic Acid and HOI were mixed and atomized, to form particles of organic matter and oxidized iodine. These particles passed a chamber of 70 L. In this experiment the formation of iodomethane was observed (Figure 4). Since the Fulvic acid was already contaminated with Iodinated compounds new experiments with other material as organic matter are planned to verify the discussed reaction pathway via haloform reaction and to calculate constants of formation.

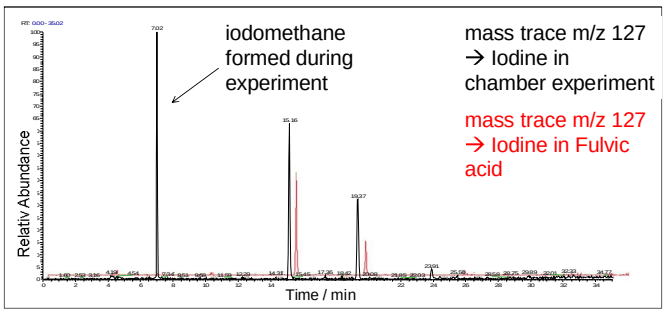

Figure 4: Formation of iodomethane in particle phase

Conclusion:

Oxidative stress by atmospheric relevant ozone mixing ratios enhances the halocarbon emission

The exponential trend of the iodocarbon emission and the total iodine content indicates iodine content as imitating factor

Abiotic formation of iodocarbons by Fulvic acid and HOI as it was described for bulk material [6] also takes place in the particle form

Outlook:

Microalgae are more abundant in the oceans and have higher impact on global climate models, therefore also different kind of microalgae will be target of future investigation.

Another abiotic model needs to be tested whereby Fulvic acid will be replaced by benzyl alcohol to be the organic reaction partner, HOI will be replaced by I_2O_5.

Different factors like pH, particle diameter, temperature and educt concentration need to be investigated.

References: [1] O´Dowd, C. et al. (2002) *Nature, 417*, 632-636 ; [2] Carpenter, L. et al. (1999). *J.Geophys.Res., 104,*1679–1689
[3] Mahajan, A. S. et al. (2010) *J.Geophys.Res., 115,*D20303; [4]Carpenter, L. et al. (2005) *Environ. Sci. Technol.,* 39, 8812-8816
[5] Palmer, C.J. et al. (2005) Environ. Chem. 2, 282-290 ; [6] Carpenter, L et al.(2005) Environ. Sci. Technol. 39, 8812-8816