Volatile short lived iodocarbons from biotic and abiotic sources affecting atmospheric chemistry

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Atmospheric Iodine chemistry in the lower troposphere gained more attention in the last decade, because of its ozone depleting capacity [1]. The oxides formed during this reaction may also undergo further oxidation and form polyoxides which then play a role in new particle formation [2]. Precursors of both reactions are iodocarbons found in the marine atmosphere. These Iodocarbons are emitted by different macroalgae [3] and are also produced by abiotic reactions [4]. The investigation of both release pathways is the aim of the presented study.

The method developed uses thermodesorption gas chromatography negative chemical ionisation mass spectrometry TD-GC-NCI-MS. Using the negative ionisation mode the method detection limits were reduced by on order of magnitude compared to electron impact. (LOD: Iodomethane 2.01 pg, Iodethane 0.98 pg, Iodchloromethane 0.26 pg, Iodbromomethane 7.37 pg, Diiodmethane 8.61 pg)

To investigate the biotic release pathway we treated different algae species with various ozone mixing ratios and measured iodocarbon and inorganic iodine release of the algae. We found a correlation on ozone concentration and iodine as well as organo-iodine release. A good correlation was found for iodine release and place of growth, meaning that algae growing above or in the intertidal zone release less iodine than algae in the sublittoral zone.

 σ investigate the abiotic pathways of forming iodocarbons a chamber experiment was done using particulate HOI and fulvic acid. The particles were formed by an atomizer and crossed a chamber with a residuance time of 160 seconds. Even after this short reaction time the formation of iodomethan was seen.

[1] Read *et al.* (2008) *Nature* **453**, 1232–1235. [2] O'Dowed *et al.* (2002) *Nature* **417**, 632–636. [3] Nightingale *et al.* (1995) Limnol. Oceanogr. **40**, 680–689. [4] Carpenter *et al.* (2005) *Environ. Sci. Technol.* **39**, 8812–8816.

Rapid changes in North Atlantic deep ocean circulation during the MIS 5a/4 glacial inception

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Earth's climate during the Plio-Pleistocene epoch has been characterised by oscillations between glacial and interglacial conditions, thought to be related to changes in the Earth's orbit, as well as feedbacks including variations in atmospheric CO_2 and ice albedo. Detailed examination of the last glacial termination (and earlier terminations) has revealed that millennial-scale changes, probably involving variation in the Atlantic meridional overturning circulation (AMOC), play a critical role in the mechanism of glacial termination. Conversely, very little is known about the AMOC during the onset of glacial conditions and the associated millennial-scale variability.

Here, we investigate North Atlantic deep ocean circulation during the Marine Isotope Stage 5a to 4 glacial inception ~70, 000 years ago, an interval which contains Dansgaard-Oeschger events 19 and 20 and also marks the onset of full glacial conditions, involving a rapid lowering of sea-level an abrupt decrease in atmospheric CO₂. Using a range of geochemical and sedimentological methods applied to marine sediment cores, we present high resolution (100-200 year) proxy reconstructions of deep water circulation and chemistry from depth transects in both the eastern and western North Atlantic. The chronology of the cores is tightly constrained, enabling us to examine the precise timing of deep ocean chemistry and circulation changes with respect to the decrease in sea-level and atmospheric carbon dioxide.

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