



## Trace analysis of short-lived iodine-containing volatiles emitted by different types of algae

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Atmospheric iodine chemistry in the lower troposphere gained more attention in the last decade, because of its role in depleting tropospheric ozone and accelerating the ozone destroying capacity of other halogen species [1]. The iodine oxides formed during this reaction may also undergo further oxidation and form polyoxides which then can act as cloud condensation nuclei [2]. Precursors of both reactions are gaseous molecular iodine ( $I_2$ ) and volatile iodocarbons. Both  $I_2$  and iodocarbons are emitted by different kinds of macroalgae, whereby the emission of  $I_2$  dominates [3]. Iodocarbons are also released by different kinds of microalgae and it is assumed that also  $I_2$  is released by these algae.

Here we present the results of the measurement of iodine containing volatiles emitted by eight different macroalgae found in the intertidal zone and microalgae, two pure cultures and two net samples. To measure  $I_2$  emission from macroalgae an on-line time-of-flight aerosol mass spectrometric method was used [4] to determine the emission rates and to investigate temporally resolved emission profiles. The molecular iodine emissions from microalgae were measured using a recently developed denuder sampling technique and GC-MS method [5]. Iodocarbons were preconcentrated on solid adsorbent tubes and measured using thermodesorption-GC-MS.

The results of the macroalgae experiments showed that Laminariales were found to be the strongest  $I_2$  emitters. Time series of the iodine release of *L. digitata* and *L. hyperborea* showed a strong  $I_2$  emission when first exposed to air followed by an exponential decline of the release rate. For both species  $I_2$  emission bursts were observed. For *L. saccharina* and *F. serratus* a more continuous  $I_2$  release profile was detected, however, *F. serratus* released much less  $I_2$ . For *A. nodosum* and *F. vesiculosus* the  $I_2$  emission rates were slowly increasing with time (1h-2h) until a more or less stable  $I_2$  emission rate was reached. The lowest  $I_2$  emission rates were detected for the red algae *C. Crispus* and *D. sanguinea*. Total iodocarbon emission rates showed almost the same general trend, however, the total iodocarbon emission rates were about one to two orders of magnitude lower than those of molecular iodine, demonstrating that  $I_2$  is the major iodine containing volatile released by the investigated seaweed species. The dependency of  $I_2$  and iodocarbon emission on the ozone level was investigated, the interplant variability in  $I_2$  emission was too high to see a trend for this compound, but a clear dependency of iodocarbon emission from the ozone level (0-150 ppb  $O_3$ ) was found for *L. digitata*.

The results of the microalgae experiments showed that the pure cultures of *mediopyxis helysia* and *coscinodiscus wailesii* and the net samples of microalgae emitted iodocarbons (iodomethane, iodochloromethane, iodobromomethane and diiodomethane). Although no ozone dependency was found for the halocarbons, the ozone measurements showed that the depletion of ozone was quite different for the different algae species.

### References

- [1] Read et al. (2008) Nature 453, 1232–1235. [2] O'Dowd C. et al. (2002) Nature 417, 632–636. [3] Carpenter L. et al. (2005) Environ. Sci. Technol. 39, 8812–8816. [4] Kundel M. et al. (2011) Anal. Chem. DOI: 10.1021/ac202527a. [5] Huang R.-J. et al. (2009) Anal. Chem. 81, 1777–1783