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## Light and brominating activity in two species of marine diatom

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#### 1. Abstract

Marine organisms mediate the formation of volatile inorganic (e.g. HOBr) and organic halogens (e.g. CHBr<sub>3</sub>) and contribute to the sea-to-air emission of bromine and iodine. This air-sea halogen exchange has implications for atmospheric chemistry. It is important to establish the physiological function of halogen metabolism in key groups of marine organisms to permit predictive model development. In this study a series of laboratory experiments was performed to investigate the link between the availability of photosynthetically active radiation (PAR) and brominating activity, as measured by the bromination of phenol red, in two cold-water marine diatoms (Thalassiosira antarctica, CCAP 1085/25; Porosira glacialis, CCMP 668). Brominating activity in T. antarctica was found to change in response to short term changes in photon flux density and to have a strong positive linear relationship with gross photosynthetic rate up to 260  $\mu$ mol O<sub>2</sub> (mg chla)<sup>-1</sup> hr<sup>-1</sup>. Experiments performed across multiple diel cycles showed that light-phase brominating activities in T. antarctica were a factor of 2.8  $(\pm 1.0)$  higher than those measured in the dark. Whilst P. glacialis showed no response to short term changes in PFD, measurements across a number of diel cycles revealed that light-phase brominating activities in this diatom were significantly higher than those in the dark by a factor of 1.3 ( $\pm 0.3$ ). The addition of 0.1  $\mu$ M H<sub>2</sub>O<sub>2</sub> to the medium of *T. antarctica* cultures led to a significant increase in brominating activity by a factor of 2.4 (±0.3) relative to noaddition controls but no such response was seen in P. glacialis. These results suggest that there is a link between PAR light availability and brominating activity in marine diatoms but that the nature of this relationship differs between species. By establishing a potential link with common ecosystem model state variables (light and photosynthesis) this work provides the first step towards developing a predictive capability for brominating activity in the marine environment. More work is needed to assess the potential for developing generalised parameterisations between PAR light availability and brominating activity in diatom species representative of a wider range of ocean regions.

### 2. Introduction

A wide range of marine organisms are known to be involved in the production of halogenated organic (e.g. CHBr<sub>3</sub>, CH<sub>2</sub>I<sub>2</sub>) and inorganic species (I<sub>2</sub>, HOI) including bacteria (e.g. Fuse *et al.*, 2003), cyanobacteria (e.g. Smythe-Wright et al., 2006; Hughes et al., 2011), microalgae (e.g. Moore et al., 1996; Hill and Manley, 2009; Hughes et al., 2013), seaweeds (e.g. Goodwin et al., 1997; Manley and Barbero, 2001) and invertebrates (Fielman et al., 1999). Despite this, many questions remain regarding the physiological and ecological functions of these halometabolites (Manley et al., 2002; Johnson et al., 2011). There is also still considerable uncertainty regarding the biogeochemical importance of biogenic volatile halogens; most specifically those that have a relatively low molecular weight (e.g. CHBr<sub>3</sub>, I<sub>2</sub>) and contribute to the transfer of halogens from the ocean reservoir to the atmosphere (McFiggans et al., 2004; Hughes et al., 2012; Ziska et al., 2013). This is of interest as once in the atmosphere the halogens are involved in ozone cycling (Platt and Honninger, 2003), new particle formation and can control the formation of cloud condensation nuclei (CCN) by precursors such as dimethyl sulphide (DMS, von Glasow et al., 2004). Whilst their biological and biogeochemical roles are often considered separately, predicting spatial and temporal variability in sea-air volatile halogen fluxes and hence the importance of this for atmospheric processes now and into the future requires an understanding of how environmental conditions control halogen metabolism in key groups of organisms.

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