



Emission of atmospherically significant halocarbons by naturally occurring and farmed tropical macroalgae

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Abstract. Current estimates of global halocarbon emissions highlight the tropical coastal environment as an important source of very short-lived (VSL) biogenic halocarbons to the troposphere and stratosphere, due to a combination of assumed high primary productivity in tropical coastal waters and the prevalence of deep convective transport, potentially capable of rapidly lifting surface emissions to the upper troposphere/lower stratosphere. However, despite this perceived importance, direct measurements of tropical coastal biogenic halocarbon emissions, notably from macroalgae (seaweeds), have not been made. In light of this, we provide the first dedicated study of halocarbon production by a range of 15 common tropical macroalgal species and compare these results to those from previous studies of polar and temperate macroalgae. Variation between species was substantial; CHBr_3 production rates, measured at the end of a 24 h incubation, varied from 1.4 to 1129 pmol g FW⁻¹ h⁻¹ (FW = fresh weight of sample). We used our laboratory-determined emission rates to estimate emissions of CHBr_3 and CH_2Br_2 (the two dominant VSL precursors of stratospheric bromine) from the coastlines of Malaysia and elsewhere in South East Asia (SEA). We compare these values to previous top-down model estimates of emissions from these regions and, by using several emission scenarios, we calculate an annual CHBr_3 emission of 40 (6–224 Mmol Br⁻¹ yr), a value that is lower than previous estimates. The contribution of tropical aquaculture to current emission budgets is also considered. Whilst the current aquaculture contribution to halocarbon emissions in this regional is small, the potential exists for substantial increases in aquaculture to make a significant contribution to regional halocarbon budgets.

1 Introduction

Over the past 30 yr, a number of incubation studies have investigated the production and emission of volatile low molecular weight halocarbons including the methyl halides (e.g. methyl iodide, CH_3I) and polyhalogenated compounds (e.g. bromoform, CHBr_3) from polar and temperate macroalgae (seaweeds) (e.g. Baker et al., 2001; Carpenter et al., 2000; Goodwin et al., 1997; Gschwend et al., 1985; Laturus, 1995; Manley and Dastoor, 1988; Marshall et al., 1999). Such studies have helped to quantify the production of halocarbons by macroalgae and develop our understanding of the complexity and variability involved in these biogenic processes.

Macroalgae concentrate halides from seawater (Küpper et al., 1998; Saenko et al., 1978) and it is believed that these halides act as antioxidants. In particular, iodine chemistry in phaeophytes as a response to oxidative stress at low tide has been well documented. A flux of internal iodine is observed during oxidative stress which can act as an antioxidant both within algal cells and also on the surface of the alga. Intercellular oxidation of iodine via haloperoxidase catalysed-reactions in the presence of H_2O_2 and other reactive oxygen species forms hypoiodous acids which may then react with nucleophilic acceptors such as ketones to produce halocarbons (Wever et al., 1991; Winter and Moore, 2009). Iodine may also be released onto the algal surface where it reacts with ozone (O_3) to form molecular iodine (I_2), which is now thought to be the dominant product from the iodine antioxidant response (Küpper et al., 2008; Palmer et al., 2005). A flux of bromocarbons as a product of a bromine antioxidant