

Methyl Halide Production by Periphyton Mats from the Florida Everglades



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Introduction

Methyl halides (methyl chloride, CH₃Cl and methyl bromide, CH₃Br) are trace gases with natural and anthropogenic origins. The majority of these gases are formed naturally by the oxidation of organic matter, when in the presence of iron and halide ions, or produced by enzyme mediated methyl transferase reactions^{1,2}. Once generated, CH₃Cl and CH₃Br transport chlorine and bromine into the stratosphere, where chlorine and bromine play an important role in atmospheric chemistry through catalytic cycles. These cycles ultimately help to contribute to ozone destruction within the stratosphere.

Coastal wetlands, such as the Florida Everglades, are one location where methyl halide production have been proposed to be elevated due to high primary production and high amounts of ionic halogens. This region also provides an unique study environment due to salt water intrusions which occur during storm or low marsh water level-high tide events. Periphyton mats, a collection of benthic algae, microbes, fungi, and detritus, are ubiquitous features within the Florida Everglades and are considered to a dominant portion of the standing crop^{3,4}. Previous studies have shown that algae and fungi are sources of methyl halides; however, periphyton mats as a whole have not been previously studied as a potential source of methyl halides^{5,6,7}. *The purpose of this study is to present novel research in clarifying the role of periphyton in the overall production of CH₃Cl and CH₃Br. Our results can then be used to provide better estimates for the global budgets of these compounds, since they are currently poorly understood. In addition, this research will also help to clarify how varying concentrations of salinity will affect methyl halide production originating from periphyton mats within the Florida Everglades and similar locations.*

Methods

- All periphyton utilized in this experiment was collected from sites Taylor Slough 2 (T2) and Taylor Slough 3 (T3) within the Florida Everglades.
- Samples were initially collected in September 2011 from TS 2 and 3 with fresh samples being collected from TS 2 in August 2012.
- Microcosms, containing periphyton and artificial marsh water, were subsequently set up in a research greenhouse under constant temperature and photoperiods (~30 ° and 14 hour light/8 hour dark cycle) to simulate conditions found naturally in the Everglades (Fig. 1).
- Once reestablished, ~ 45 to 90 grams (w.w.) of periphyton was selected at random for each time course experiment.
- Nine (~200 mL) quartz tubes, containing periphyton (25 g/L or 50g/L) and salt water (0, 0.1, 1.0, or 10‰), were prepared for each time course experiment.
- Quartz tubes were then exposed to continuous 30°C temperature and 12 hour dark/light cycles in an incubator (Fig. 1).
- Water samples were analyzed at 0, 24, 48, and 72 hours to determine the concentration and production rate of CH₃Cl and CH₃Br in periphyton samples using a gas chromatograph coupled with an electron capture detector (GC-ECD).



Figure 1: (Left) Periphyton microcosms in research greenhouse (Right) Quartz tubes with periphyton samples in an incubator.

Results

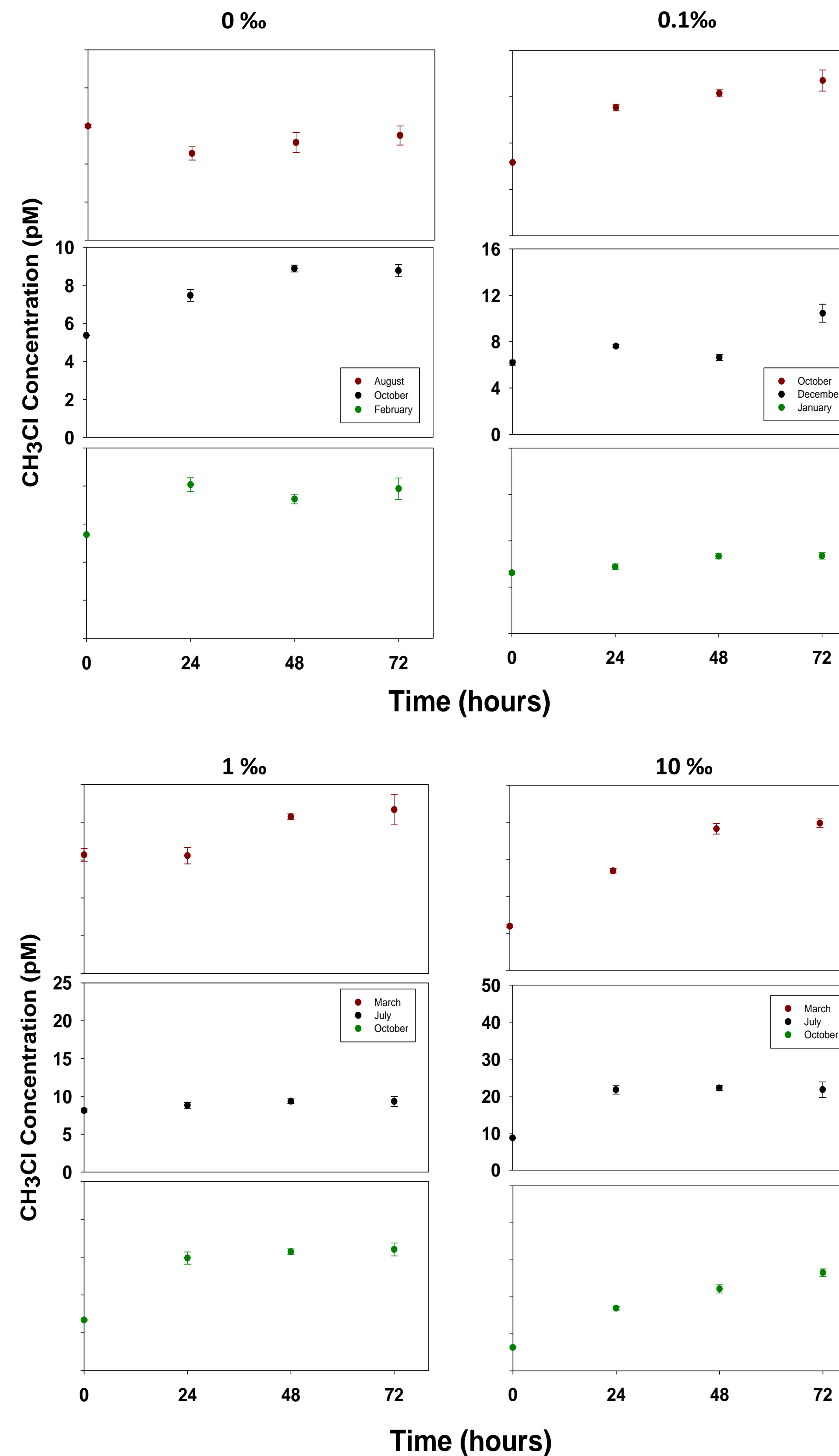


Figure 2: Methyl chloride (CH₃Cl) concentration, per gram of periphyton, over time for 0‰ (Top Left), 0.1‰ (Top Right), for 1‰ (Bottom Left), 10‰ (Bottom Right) salt water treatments for three trials. March and July experiments used periphyton samples collected in August 2011. October-February experiments used periphyton collected in August 2012. Symbol legend denotes month when trial was performed. Standard error bars are noted.

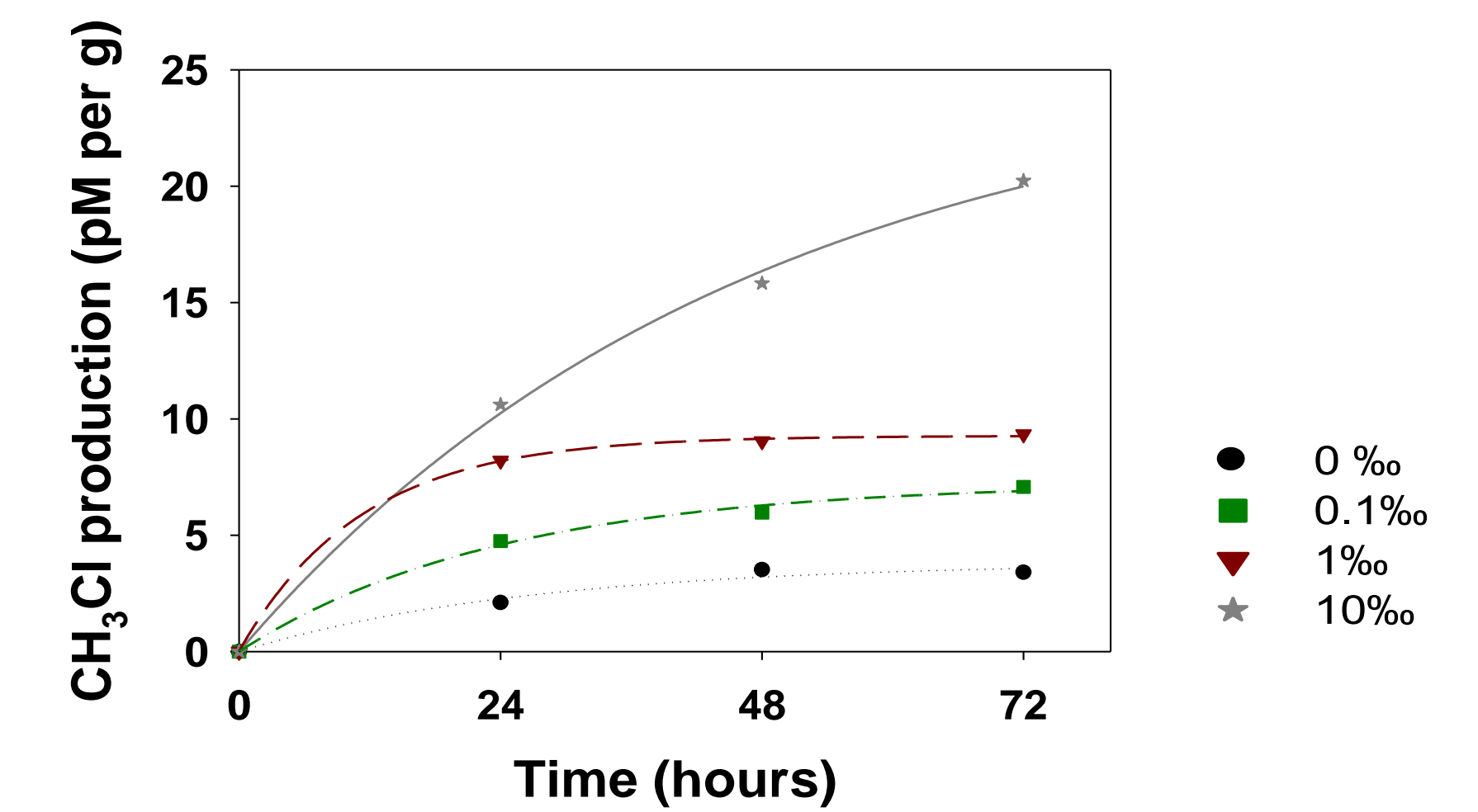


Figure 3: Methyl chloride, CH₃Cl, production (pM per g) for all salt water treatments during the month of October 2012.

Summary

- We found that the concentration of methyl chloride, at maximum, increased by approximately 3.4 pM, 7.1 pM, 9.3 pM and 27.9 pM over a 0 to 72 hour range for 0‰, 0.1‰, 1‰ and 10‰ treatments, respectively (Fig.2).
- Even though variation exists between experiments within the same salt water treatment, the overall CH₃Cl production does increase with increasing levels of salinity (Fig. 3).
- No significant change in CH₃Br, over time, has been found for all treatments.
- Initial results also suggest that time since collection or amount of time spent in refrigeration, till placement in a microcosm, may influence the amount of CH₃Cl produced over time (Fig.3).
- Overall, this research has shown that periphyton mats are a source of CH₃Cl, but further research is needed to help clarify the role of periphyton in CH₃Br production.
- This research has also shown that increased salinity does have a positive effect on the production of CH₃Cl from periphyton mats, which is important in areas that are prone to salt water intrusions due to storm or low marsh water level-high tide events.

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