

Methyl chloride production by calcareous periphyton mats from the Florida Everglades

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ABSTRACT: Methyl chloride (CH₃Cl) is a trace gas with natural and anthropogenic sources that plays an important role in stratospheric ozone catalytic cycles. Here, we report on research to quantify the production of CH₃Cl in response to varying levels of salinity from calcareous periphyton mats found within the Florida Everglades, USA, the first measurements of their kind. Periphyton were collected from the Everglades and exposed to continuous, artificially simulated 12 h dark: 12 h light cycles, in both freshwater and varying concentrations of saltwater. Water samples were collected and analyzed to determine the resulting production rate of CH₃Cl. We found that periphyton produced CH₃Cl in both freshwater and all concentrations of saltwater (24 to 208 fmol CH₃Cl gDW⁻¹ periphyton h⁻¹ after 24 h) and that there was a significant positive effect of salinity on the production rate of CH₃Cl ($r^2 = 0.993$, $p < 0.001$). Our results indicate that rising sea levels as predicted by climate models will increase production rates of CH₃Cl in coastal periphyton wetlands that could be inundated with high salinity seawater. Furthermore, other natural sources of CH₃Cl may also respond through similar mechanisms to sea level rise and salt water intrusion resulting from global climate change.

KEY WORDS: Salinity · Stratospheric ozone depletion · Methyl halides

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INTRODUCTION

Methyl chloride (CH₃Cl) is a trace gas with both natural and anthropogenic origins. Due to its moderately long atmospheric lifetime (~1.2 yr), it transports chlorine to the stratosphere, where it plays an important role in stratospheric ozone loss (Harper 2000, Rhew 2011, Hu et al. 2013). Currently, CH₃Cl contributes ~15 to 20% of the stratospheric chlorine and is considered to be the most abundant volatile halocarbon in the atmosphere (Harper 2000, WMO 2011). Because stratospheric ozone catalytic cycles have been altered by humans, anthropogenic sources of CH₃Cl are currently being regulated under the Montreal Protocol and its amendments. Consequently, anthropogenic sources of CH₃Cl are decreasing, thereby increasing the relative importance of natural

sources. Recent work on measurements of CH₃Cl trapped in firn air and ice indicate that anthropogenic sources may only be responsible for a small portion of the CH₃Cl budget, suggesting that increases in CH₃Cl concentrations over the last 100 yr could be due to natural sources (Trudinger et al. 2004, Williams et al. 2007). Therefore, further studies that specifically address natural sources of CH₃Cl are required to better understand their roles in the global CH₃Cl budget.

Large uncertainties in the CH₃Cl budget are apparent when the literature is reviewed (WMO 2007, 2011) (Table 1). Some studies have estimated that only ~50 to 67% of known CH₃Cl sources are accounted for in its global budget (Butler 2000, Redeker et al. 2002). In contrast, some modeling studies have shown that CH₃Cl sinks and sources are

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Table 1. Estimated source and sink strength for methyl chloride (CH_3Cl) in its global budget

Source or sink	Strength (Gg yr^{-1})
Source	
Tropical/subtropical vegetation	820–8200 ^{a,b}
Tropical senescent or dead leaves	30–2500 ^{a,b}
Biomass burning	325–1125 ^a
Oceans (global net sea-to-air flux)	210–480 ^c
Fungi	43–470 ^a
Salt marshes	50–440 ^{a,b}
Wetlands	48 ^a
Mangroves	11 ^b
Rice paddies	2.4–4.9 ^a
Other anthropogenic sources	30–290 ^a
Subtotal	1569–13569
Sink	
Reaction with OH^-	3180–4100 ^{a,b}
Loss to the stratosphere	100–300 ^{a,b}
Marine boundary layer Cl^- reaction	93–370 ^{a,b}
Microbial soil degradation	100–1600 ^{a,b}
Loss to polar ocean waters	93–145 ^{a,b}
Subtotal	3566–6515
Total (sources – sinks)	–1997 to 7054
^a WMO (2007); ^b WMO (2011); ^c Hu et al. (2013)	

more or less balanced (Lee-Taylor et al. 2001, Yoshida et al. 2004).

CH_3Cl emissions are most prevalent in subtropical and tropical climates due to elevated temperatures and biological activity found in these regions (Butler 2000, Rhew et al. 2000). Hu et al. (2010) found that annual coastal emissions of CH_3Cl were greatest (0.7 Gg yr^{-1}) between 0 and 35° N latitudes. Coastal wetlands such as the Florida Everglades, USA, are one location where CH_3Cl emissions may be elevated due to the subtropical climate, ample sunlight, and increased levels of ionic halogens. These conditions help to drive the biogenic production of CH_3Cl through methyl chloride transferase reactions and abiotic oxidation–reduction reactions (Butler 2000, Rhew et al. 2000).

The Florida Everglades provide a useful study environment due to salt water intrusions which occur during storm or low marsh water level–high tide events. Previous studies have attributed CH_3Cl emissions in salt marshes to saltwater intrusion (Rhew et al. 2002, Manley et al. 2007, Blei et al. 2010). According to Butler (2000), salt marshes make up less than 0.1% of the global surface area but could be producing 10% of the global budget for CH_3Cl . As global climate changes, the amount of land exposed to salt water intrusions may increase dramatically due to rising sea levels. Saha et al. (2011) proposed that sea

levels may rise by 1 to 2 m in southern Florida by 2100, demonstrating the importance of quantifying CH_3Cl emissions within the Florida Everglades and other similar karstic wetlands.

Calcareous periphyton mats are a collection of benthic algae, microbes, fungi, and detritus that are often attached to benthic, submerged, or floating surfaces (La Hee & Gaiser 2012). They are a ubiquitous feature within the Florida Everglades and are considered to be a dominant portion of the standing crop within this ecosystem (Gaiser et al. 2011). Periphyton mats play an important ecosystem function within the Everglades by removing calcium carbonate from the water column and depositing it as marl soils (Scheidt et al. 2000). This deposition process alters phosphorus availability and oxygen levels, and ultimately food web composition (Brown & Wright 2009, La Hee & Gaiser 2012). Previous studies have shown that algae, a major component of periphyton (Gribble 2003), and fungi (Redeker et al. 2004) are sources of CH_3Cl . However, periphyton mats as a whole have not previously been studied as a potential source of CH_3Cl . Here, we report on research that quantified the production of CH_3Cl in response to varying levels of salinity from calcareous periphyton mats found within the Everglades.

MATERIALS AND METHODS

Study sites and periphyton sampling

All periphyton samples were collected during the wet seasonal period from Taylor Slough 2 (TS 2) and Taylor Slough 3 (TS 3), within the boundaries of the Everglades National Park (ENP), Florida, USA (Fig. 1). Taylor Slough flows south into Florida Bay and is the second largest path of moving surface water located on the eastern side of ENP (Armentano et al. 2006). TS 2 and TS 3 are predominately freshwater marsh sites. However, TS 3 receives saltwater intrusions occasionally, as evidenced by the presence of red mangroves *Rhizophora mangle* (Armentano et al. 2006). Periphyton samples were initially collected in September 2011 from TS 2 and TS 3 and then again in August 2012 from TS 2 only. All periphyton grab samples were randomly collected and subsequently placed in gallon-size Ziploc® bags and coolers. After collection, all samples were shipped back to Portland State University, Portland, OR, and either immediately placed under refrigeration or placed in microcosms in a research greenhouse.

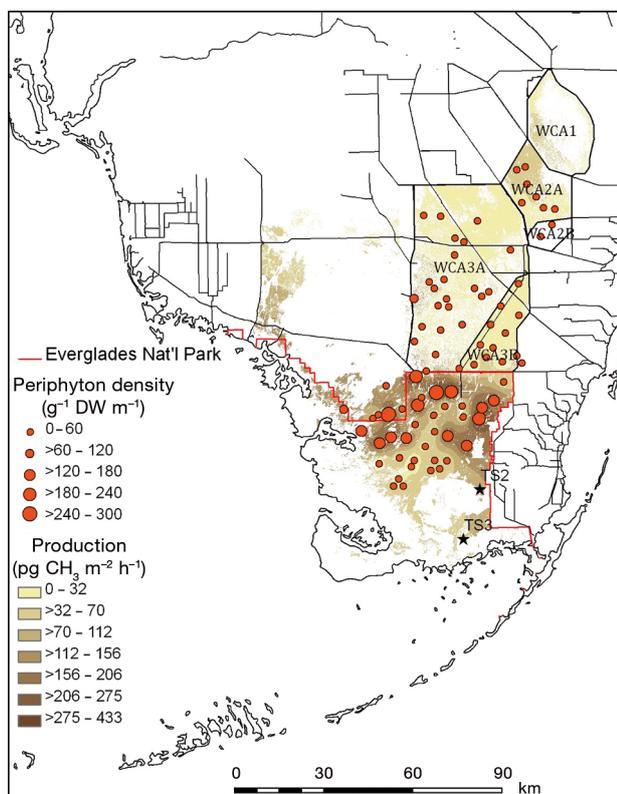


Fig. 1. Locations (stars) of periphyton sampling at Taylor Slough 2 and 3 (TS 2 and TS 3) within the Everglades National Park, FL, USA. Distribution of estimated methyl chloride (CH_3Cl) production based on freshwater production rates is also shown. Orange dots represent periphyton dry weight biomass measured by Lee et al. (2013). WCA: Water Conservation Area

Microcosms

Collected periphyton samples were randomly placed in $36.2 \times 31.1 \times 14.3$ cm (9.5 l) polypropylene pans, containing a 1.5 to 2 cm base layer of calcium carbonate rocks. The base layer was present to simulate the substrate found naturally in the Florida Everglades. All microcosms were placed in a research greenhouse with constant temperatures and photoperiods (30°C and 14 h light:10 h dark cycles). Each container received artificial marsh water containing sodium bicarbonate (NaHCO_3), potassium chloride (KCl), magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), and calcium chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) (10 cm depth). All proportions for the trace elements were made according to methods described in Jones & Amador (1992). After initial filling, all polypropylene pans were refilled twice a week to restore original water levels with 18.1 megaohms water (Barnstead Nanopure

Diamond Lab Water System). All periphyton microcosms were allowed to re-establish before use for a period of 4 to 6 wk.

Experimental methods

Once reestablished, approximately 45 or 90 g wet weight (WW) of periphyton was randomly selected from one of the microcosms in the research greenhouse. After removal of dead vegetation, calcium carbonate substrate, and excess water, 5 or 10 g WW periphyton samples were sliced into 9 subsamples. Experiments from March 2012 to mid-August 2012 contained 5 g and later increased to 10 g to optimize signal strength. Dry weight (DW) was determined by placing periphyton samples in a $\sim 80^\circ\text{C}$ muffle furnace, where they were allowed to dry until a constant weight was reached.

Each of the 9 subsamples were placed in a ~ 200 ml quartz tube and filled with ~ 160 ml of either artificial marsh water (0%) or with additional sodium chloride (NaCl) and sodium bromide (NaBr) at concentrations of 0.1, 1, 5, or 10%. Each quartz tube was equipped with a 1-way stopcock valve and plunger. After the addition of both periphyton and water, each quartz tube was inverted 3 to 4 times for a more homogeneous sample, followed by the removal of any headspace. All quartz tubes were then placed in a low temperature diurnal illumination incubator (VWR International, model 2015) with preset temperature and photoperiods (30°C and 12 h dark:12 h light cycles). Three 55 ml samples of the quartz tube water (0, 0.1, 1, 5, or 10%) were initially analyzed using a gas chromatograph coupled with an electron capture detector (GC-ECD) to determine the initial concentration of CH_3Cl in the water. After 24 h, one quartz tube was removed and all of the sample water was transferred to a second quartz tube with a 1-way stopcock valve and plunger. Over a 3.5 to 4 h time period, 3 samples ranging from 45 to 55 ml were analyzed using the GC-ECD. This procedure was repeated for 2 additional quartz tubes, for a total of 9 samples during the first sampling time period. The full procedure was repeated again at 48 and 72 h ($n = 9$ for each sampling time).

Gas chromatograph with GC-ECD

A gas chromatograph (GC) (Hewlett Packard series II 5890) coupled with an electron capture

detector (ECD) and a pre-concentration system was used to analyze all CH₃Cl concentrations (Bullister & Weiss 1988, Huset 2007, Raffel 2013). All water samples were injected into a glass stripping chamber, sparged for 20 min with helium, concentrated onto a ca. -40°C trap consisting of Porasil C and Porapak T, and injected into a GC column for chromatographic separation and analysis. CH₃Cl peak areas were analyzed for accurate quantification using the Agilent EZChrom SI (version 3.2) software. Calibration of the analytical system was achieved by introducing 3 different volumetric aliquots (each in triplicate) of an 8.12 ppb methyl chloride reference gas (Scott Specialty Gases). We achieved an average precision of ~2%, which was based on replicate analyses of samples.

Data analysis

A Kruskal-Wallis test and subsequent pairwise comparisons (Dunn's Method) were used to ascertain differences between production rates measured in different experiments. Pearson's correlation coefficients were calculated to assess a possible relationship between salinity and CH₃Cl production using SigmaPlot software. Alpha level was set at 0.05 for all statistical analyses.

RESULTS

We found that calcareous periphyton mats produced CH₃Cl in all freshwater trials and sampling periods and in the majority of saltwater treatments. In only one of the 1‰ treatment trials was there no CH₃Cl production during the first 24 h sampling period (Table 2, Fig. 2). Production rates significantly decreased between 24 and 48 h in the majority of the experiments; therefore, we considered the production rates from the first period as the most representative of the production rates. We suspect that an unknown component became limiting after the first 24 h period, which is the general response expected within an enclosed, relatively small volume container.

Production rates from the periphyton at low salinity levels (0.1, 1‰) were not significantly different than the freshwater treatments (0‰). However, the 5 and 10‰ production rates were significantly higher (Table 3). Overall, we found a significant positive relationship between CH₃Cl production and salinity ($r^2 = 0.993$, $p < 0.001$) (Fig. 3).

Table 2. Average methyl chloride (CH₃Cl) production rates for all trials in the freshwater (0‰) and saltwater treatments (0.1, 1, 5, and 10‰). Standard deviations and number of replicates are noted for each sampling time and water treatment

Salinity (‰)	Average CH ₃ Cl production (fmol gDW ⁻¹ periphyton h ⁻¹)	n
24 h		
0	34 ± 13	25
0.1	35 ± 31	27
1	35 ± 58	27
5	131 ± 21	27
10	208 ± 60	24
48 h		
0	17 ± 14	26
0.1	21 ± 22	27
1	43 ± 28	27
5	88 ± 28	27
10	159 ± 64	26
72 h		
0	15 ± 8	17
0.1	22 ± 14	27
1	31 ± 29	27
5	77 ± 13	27
10	121 ± 45	25

Table 3. Kruskal-Wallis and subsequent Dunn's Method test results to determine if the 24 h readings in the salt water treatments (0.1, 1, 5, and 10‰) were significantly different from the 24 h reading in the freshwater treatment (0‰). Difference of ranks, Q, and p-values are noted. Significant results in **bold**

Salinity (‰) 24 h	Diff of ranks	Q	p-value
0 and 0.1	1.56	0.15	>0.05
0 and 1	1.28	0.12	>0.05
0 and 5	52.94	5.06	<0.05^a
0 and 10	73.24	6.80	<0.05^a

^a0‰ rates are not equal

DISCUSSION

To our knowledge, this is the first documented field or laboratory-based study that has investigated CH₃Cl production from calcareous periphyton mats. Our study has shown that calcareous periphyton mats produce CH₃Cl and that there is considerable variability in CH₃Cl production within each salinity treatment. This variability could be due to bottle effects or a naturally occurring phenomenon. Other researchers have found large variability in CH₃Cl production rates in field-based studies from rice paddies (Redeker et al. 2002), temperate grasslands (Rhew & Abel 2007), coastal salt marshes (Rhew et al. 2002), and temperate forest litters (Blei & Heal 2011).

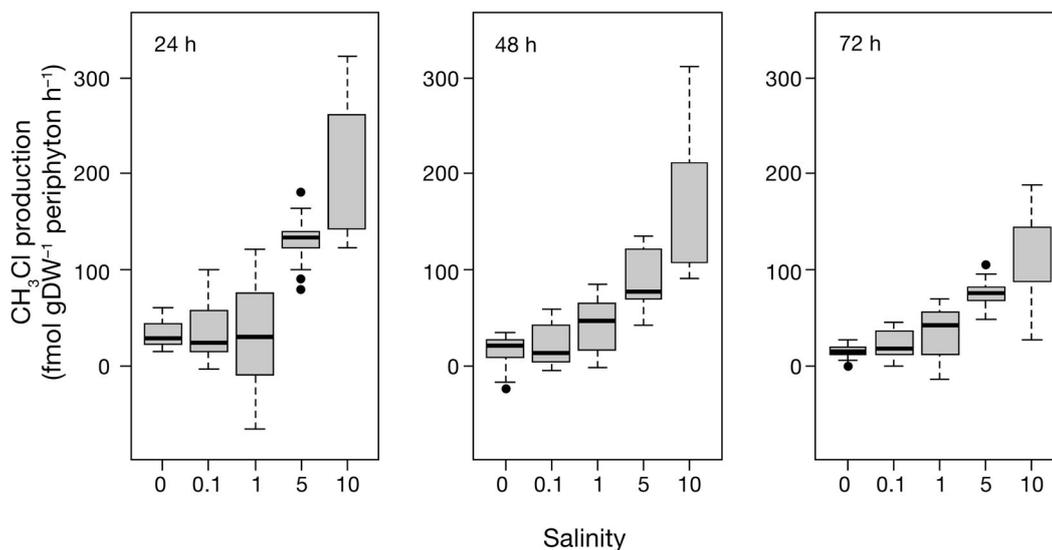


Fig. 2. Methyl chloride (CH_3Cl) production by calcareous periphyton mats per gram of dry weight over time for 0, 0.1, 1, 5, and 10‰ salt water treatments. Shaded boxes reflect production values between the first and third quartile; median value is indicated by the horizontal solid line. Dashed lines show the distance between the lowest and highest values for the majority of salinity treatments in this study. Outliers are noted (●)

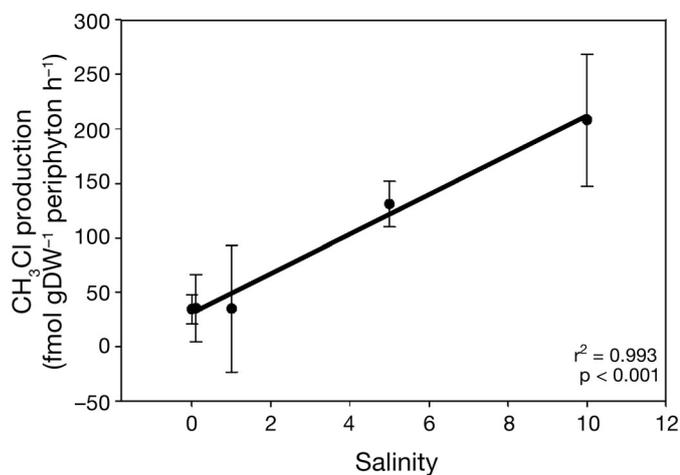


Fig. 3. Mean methyl chloride (CH_3Cl) production (fmol gDW^{-1} periphyton h^{-1}) versus salinity after 24 h. Standard deviations are noted. Equation of the line is CH_3Cl production = $29.973 + 18.189(\text{Salinity})$

Confirming our original hypothesis, we found a significant relationship between CH_3Cl production rate and salinity. The pooled production rate ($208.1 \text{ fmol gDW}^{-1}$ periphyton h^{-1}) in the highest salinity concentration (10‰) was about 6 times greater than the production rate ($34.0 \text{ fmol gDW}^{-1}$ periphyton h^{-1}) found in the freshwater trial. Our analysis provides strong evidence for increased CH_3Cl production for coastal freshwater environments under a global climate change-induced sea level rise scenario.

Methyl chloride studies

The majority of scientific research involving CH_3Cl production rates has focused on field-based studies. Due to methodological differences, our estimated production cannot be directly compared to the results of these field studies. However, one advantage to our study is that we isolated periphyton from other potential sources of CH_3Cl in an ecosystem setting. In addition to the work presented here, other laboratory-based studies for CH_3Cl production from organisms have been conducted, including white rot fungi and marine red algae (Wuosmaa & Hager 1990), ectomycorrhizal fungi (EMF) (Redeker et. al 2004), and marine phytoplankton (Scarratt & Moore 1998).

Wuosmaa & Hager (1990) studied whole cells of white rot fungi and marine red algae and found they produced 292 and $1250 \text{ fmol CH}_3\text{Cl g}^{-1} \text{ h}^{-1}$, respectively, during peak production periods. During our 10‰ treatment (208 fmol g^{-1} periphyton h^{-1}), we found average production values within this same magnitude.

The freshwater CH_3Cl production rates we report here (34 fmol g^{-1} periphyton h^{-1}) are 2 orders of magnitude smaller than the lowest rates reported for EMF ($2475 \text{ fmol CH}_3\text{Cl g}^{-1}$ fungi h^{-1}) in another laboratory-based study (Redeker et. al 2004), while our 10‰ saltwater treatment (208 fmol g^{-1} periphyton h^{-1}) resulted in rates that were approximately

one order of magnitude smaller than the low estimates found in the same EMF study. Since periphyton mats are a collection of benthic algae, microbes, fungi, and detritus, species composition would have an important role in the amount of CH_3Cl produced. The exact species composition of our periphyton samples is unknown, but our production values may be lower due to lower concentrations of CH_3Cl producing species.

Integrated South Florida production

To get a rough estimate of the total CH_3Cl produced across the Everglades, we extrapolated the measured production rates throughout the Water Conservation Areas (WCAs) and the Everglades National Park using available measurements of periphyton mass (Lee et al. 2013) and vegetation cover (Fig. 1). To our knowledge, no maps of periphyton within the Everglades exist, so instead we used sawgrass *Cladium* sp. as a proxy for periphyton because these 2 communities are closely associated with one another (Ewe et al. 2006) and digital vegetation maps are readily available (Welch et al. 1999, D. Gann pers. comm.). We estimated the total integrated periphyton biomass across the WCAs and National Park lands to be 1.7×10^{11} g. All periphyton was treated as freshwater since salinity drops rapidly inland from the coast. Assuming a 180 d hydroperiod during which the periphyton is producing CH_3Cl , the annual production for South Florida is 1.2 to 1.7 kg CH_3Cl . This estimate places calcareous periphyton mats as a relatively small source of CH_3Cl for the South Florida region.

Our results indicate that rising sea levels (as predicted by climate models) will increase production rates of CH_3Cl in coastal periphyton wetlands that will be inundated with high salinity seawater. However, our regional extrapolation suggests that this may be a small addition to the global CH_3Cl budget, although other natural sources of CH_3Cl may also respond through similar mechanisms to sea level rise and salt water intrusion resulting from global climate change.

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