

COPPER CATALYZED OCEANIC METHYL HALIDE PRODUCTION

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ABSTRACT

Methyl halides are found in all of Earth's biomes, produced naturally or through manmade means. Their presence in the atmosphere is problematic, as they catalyze depletion of stratospheric ozone. To understand the full environmental impact of these compounds, it is important to identify their chemical cycling processes. Iron increases methyl halide production in soils and oceans, yet copper's influence remains unknown despite its similar chemical oxidation properties to iron. I experimentally tested the effect of copper sulfate and sunlight on methyl halide fluxes in San Francisco Bay seawater. Samples exposed to copper sulfate and sunlight averaged higher positive flux rates than other treatments. Copper sulfate also increased carbon dioxide production and acidification of the water. The interaction of copper sulfate and sunlight in seawater suggests a new mechanism for methyl halide production, most likely via a photochemical reaction or through suppression of normal uptake processes causing overabundant concentrations.

INTRODUCTION

Concerns over human and environmental health have increased over the past few decades as depleting ozone layers allow greater amounts of ultraviolet radiation to penetrate the Earth's atmosphere. Increased ultraviolet radiation is linked to: growing rates of skin cancer and an increased frequency of ocular disease in humans, disruption of natural processes in the terrestrial and oceanic environments, and involvement in global warming events (1). Methyl halides, comprised of methyl bromide, methyl chloride, and methyl iodide, act as catalysts for stratospheric ozone depletion and contribute to these concerns (2).

Measurements of overall global production of methyl halides differ from quantified global uptake of these compounds (2). For example, methyl bromide's known sinks outweigh its known sources by approximately 35 Gg yr⁻¹, and more methyl chloride uptake than production is reported (2). Without fully understanding the various environmental pathways involved in the methyl halide lifecycle, the inconsistencies in overall quantification creates difficulties for methyl halide regulation as scientists and legislators are unable to specify target reduction areas.

Methyl halides occur naturally in the environment, but anthropogenic production has contributed to growing levels of methyl halides in the atmosphere (2). Methyl halides exist in all earth systems, including terrestrial and oceanic environments, and can be produced in both abiotic and biotic settings (3). Methyl halide flux measurements have been studied worldwide in various ecosystems such as: grasslands, oceans, salt marshes, and

the Arctic tundra (4, 5, 6, 7). Additionally, anthropogenic production and use of methyl halides in industry and agriculture have contributed to their global budget and environmental impact (8). Until the Montreal Protocol banned methyl bromide for its detrimental impact on the ozone layer, it served as an important agricultural fumigant used to grow strawberries, tomatoes, and peppers (9, 10). Continued identification of both known and unknown anthropogenic sources of methyl halides would create opportunities for additional mitigation.

A newly identified terrestrial abiotic mechanism for methyl halide production involving iron and organic matter in soils suggests that new processes for production remain to be quantified (11). This particular abiotic mechanism has only been tested in the terrestrial environment, but there is potential for its application in other systems. Aside from the many ecosystems in the terrestrial environment where methyl halides can be found, the marine environment plays a major role in the methyl halide lifecycle, acting as both a methyl bromide sink and methyl chloride source (2). Iron's interaction within the marine environment has already been accounted for (12, 13). Copper however, which has similar oxidation properties to iron and can participate in these reactions, remains to be examined. Many anthropogenic pathways for copper discharge to the oceans exists. Copper leaching from boat antifouling paint and aquaculture nets, and copper residue from automobile brake pads in urban runoff being the primary routes (14, 15, 16). By studying the interaction of copper and oceanic organic matter, an unaccounted, primarily anthropogenic driven methyl halide source could be revealed.

The objective of this experiment is to determine if there is a quantifiable change in oceanic methyl halide production when copper is added to seawater samples. By incubating samples of seawater with copper sulfate, I will determine if exposure to copper sulfate changes the flux of methyl halide species, indicating either a production or a loss of these compounds from the water.

METHODS

Study area and sample collection

To assess the reaction between copper and seawater, I collected half-liter seawater samples using half-gallon Ball brand glass mason jars from the Cal Sailing Club dock at the Berkeley Marina. I collected a total of twenty samples of San Francisco Bay water. Samples were stored in the lab refrigerator immediately after collection and after sample testing. Prior to sample collection, I washed all mason jars with deionized water, ethanol, and acetone to ensure purity of the jars. I designated ten jars of water as controls for the experiment, and left them as pure seawater samples without any copper sulfate. An additional ten jars were used as experimental samples, to which I added close to 0.3 grams of Copper (II) Sulfate reagent (Sigma-Aldrich, St. Louis, MO). The amount of copper sulfate added to the samples is greater than reported measurements of copper leaching into the oceans; however, the increased concentration was necessary to test the influence of copper addition on methyl halide production in the laboratory.

Sample testing

To observe the reaction, I exposed each sample to its specified treatment parameters and incubated samples at approximately thirty minute intervals. The twenty samples were separated into four different testing regimes that looked at the influence of copper sulfate and sunlight on methyl halide production. Samples in treatments 1 and 2 did not have copper sulfate added, but treatment 1 samples were exposed to sunlight while treatment 2 samples were not. Treatments 3 and 4 samples had copper sulfate but only treatment 3 samples were exposed to sunlight.

Each sample was first aired out on the balcony of McCone Hall, either in shade or direct sunlight for at least 1.5 hours. After this time period the sample was capped and sealed off from external air, and attached to the inlet system of the GC/MS (Agilent Technologies 6890N Network GC, Agilent 5973 inert mass selective detector). I injected 70 torr, or about 30 milliliters, of the headspace gas from each sample into the GC/MS machine over three time periods to obtain concentration measurements over time for each sample. The sample was constantly stirred with a magnetic Teflon coated stir bar during testing to ensure adequate gas exchange between the water and

air. After each sample injection, I added 10 milliliters of ambient air to the headspace of the sample jar to prevent a vacuum from forming.

I tested the samples at lab room temperature, approximately 20-23 degrees Celsius, and at atmospheric pressure. Because methyl halides exist in very scarce (part-per-trillion) levels in the atmosphere, the gas samples required a pre-concentration process before injection into the GC/MS. I pre-concentrated gases by capturing target compounds onto two cooled "U" shaped stainless steel traps prior to injection. The first trap was cooled with an ethanol-liquid nitrogen mixture at about -70 degrees Celsius and the second trap was cooled with pure liquid nitrogen. To ensure clean concentration readouts, the GC/MS inlet line had an Ascarite trap to capture carbon dioxide and a magnesium perchlorate trap to prevent water vapor from entering the machine.

To account for climate variables on methyl halide concentrations, I noted the salinity and pH of all samples immediately after collection. For samples with copper sulfate added, these variables were measured again after addition of copper sulfate. Measuring the pH and salinity is important because copper availability in water is known to be highly dependent upon environmental conditions (17), and these variables could influence the outcome of the reaction I hope to measure. Using Oakton Instruments Waterproof SaltTestr probe and Waterproof pH Testr 3+ double junction probe (Oakton Instruments, Vernon Hill, IL, USA), I measured the pH and salinity of samples at room temperature, about 20 to 23 degrees Celsius. Additionally, upon suspecting that large concentrations of carbon dioxide were emitted after copper sulfate addition, I measured the carbon dioxide concentration of samples using a LiCor water vapor and carbon dioxide analyzer (LI-840A CO₂/H₂O Analyzer).

Data analysis

To analyze the GC/MS readouts, I compared the data from all seawater samples against a calibration curve created from a lab ambient air standard with known amounts of methyl halide concentration. The calibration curve served as the baseline for methyl halide concentration comparison. I performed data analysis on Microsoft's Excel program and a coding system developed by Robert Rhew. During this process, I eliminated bad runs and made labeling adjustments to the remaining data. I calculated the concentration in part-per-trillion values for methyl chloride and methyl bromide from the area under the curve from the GC/MS readouts. I separately compared each sample's methyl chloride and methyl bromide concentrations with those of the calibration curve standard to determine if there was a major difference in concentration for either compound. Additionally, I calculated concentrations for methyl chloride and methyl

bromide using their two major isotopes, methyl chloride 50 and 52 and methyl bromide 94 and 96. Comparing the isotope concentrations allowed me to cross reference my values to ensure that the correct concentration of each methyl halide was accounted for. Finally, to determine if net production of methyl halides occurred in the water, I calculated methyl chloride and methyl bromide fluxes ($\text{nmol m}^{-2} \text{s}^{-1}$) for all samples using concentration over time values. Positive flux indicates a flow of methyl halides from the water to the air, representing production in the water. Negative flux describes a flow of methyl halides from the air into the water.

RESULTS

Salinity measurements for pure seawater and seawater with copper sulfate samples had similar values, however, the pH values for samples containing copper sulfate were 100 times more acidic. Salinity measurements ranged from 7.87 to 8.00 parts-per-thousand for all samples, regardless of the addition of copper sulfate (Fig. 1). Average sample pH measurements showed a wider range; the average pH for pure seawater samples had a range of 7.98 to 8.11 while the average for copper sulfate seawater samples was 5.11 to 5.96 (Fig. 2).

Average Salinity Measurements

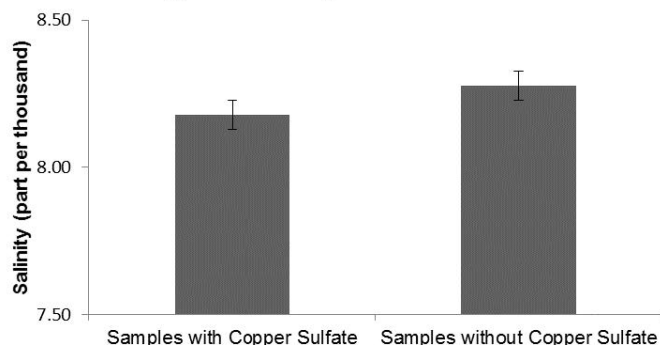


Figure 1. Average Salinity Measurements comparing samples with and without copper sulfate addition. Samples do not show a marked difference in salinity, measured in part per trillion. Error bars indicate standard error. N=10 per treatment.

In addition, I measured higher emission levels of carbon dioxide from seawater samples with copper sulfate versus those without. Measured carbon dioxide concentration from the LiCor machine showed a steady concentration range of 400 to 500 parts-per-million over the course of an hour for pure seawater samples. However, the addition of copper sulfate caused the concentration of carbon dioxide to immediately increase and rise over time (Fig. 3).

Variable average flux measurements for methyl chloride and methyl bromide amongst the four treatments

Average Sample pH Values

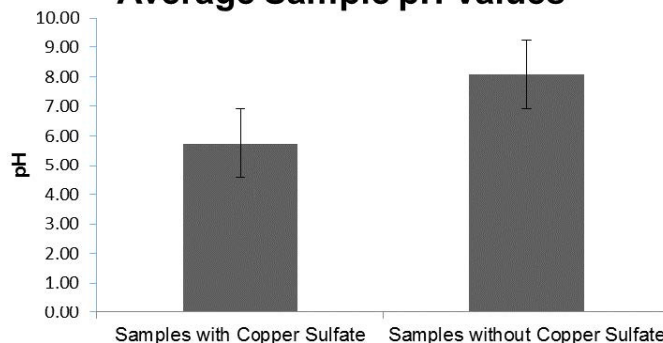


Figure 2. Average pH measurements comparing samples with and without copper sulfate addition. Samples without copper sulfate show average oceanic pH levels of 8, while samples with copper sulfate added have acidic pH values of around 6. Error bars indicate standard error. N=10 per treatment.

CO2 Concentrations

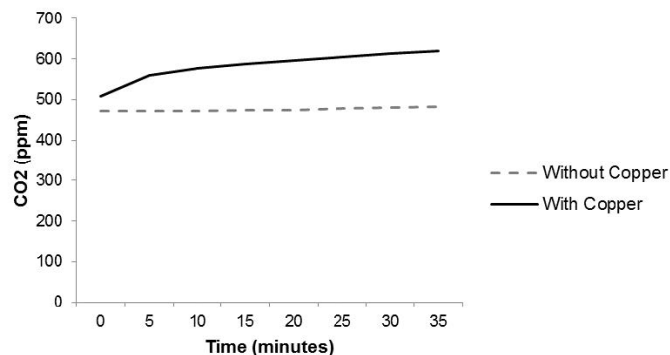


Figure 3. Carbon dioxide concentration comparison between samples with and without copper sulfate. The concentration for samples without copper sulfate remains steady over time, however samples with copper sulfate show production of carbon dioxide over time.

signified a difference in methyl halide production contingent upon treatment parameters. Treatment 3 samples, which were exposed to copper sulfate and sunlight, showed the greatest positive average flux for both methyl chloride and methyl bromide (Fig. 4). Flux rates between isotope species for methyl chloride and methyl bromide were found to agree, which supports the correctness of the data. Average flux measurements for methyl chloride and methyl bromide were greater for samples with copper sulfate added than for pure seawater samples. Samples exposed to sunlight showed greater variation in standard deviation for methyl halide flux measurements than measurements from samples aired in the shade.

DISCUSSION

Methyl halide production is contingent upon the presence

of both copper and sunlight; copper addition alone does not foster greater than normal levels of methyl bromide and methyl chloride production in samples. Although the exact mechanism to explain this reaction remains unknown, possible options include photochemistry, a biologic reaction, or prevention of oceanic consumption and uptake. In addition to increased levels of methyl chloride and methyl bromide, carbon dioxide was

Influence of copper on methyl halide production

The average flux measurements for methyl chloride and methyl bromide were highest for samples exposed to copper sulfate and sunlight, while samples undergoing other treatments displayed smaller fluxes. Comparing measurements for all samples with copper sulfate addition showed that without exposure to sunlight, the flux measurements of methyl bromide and methyl

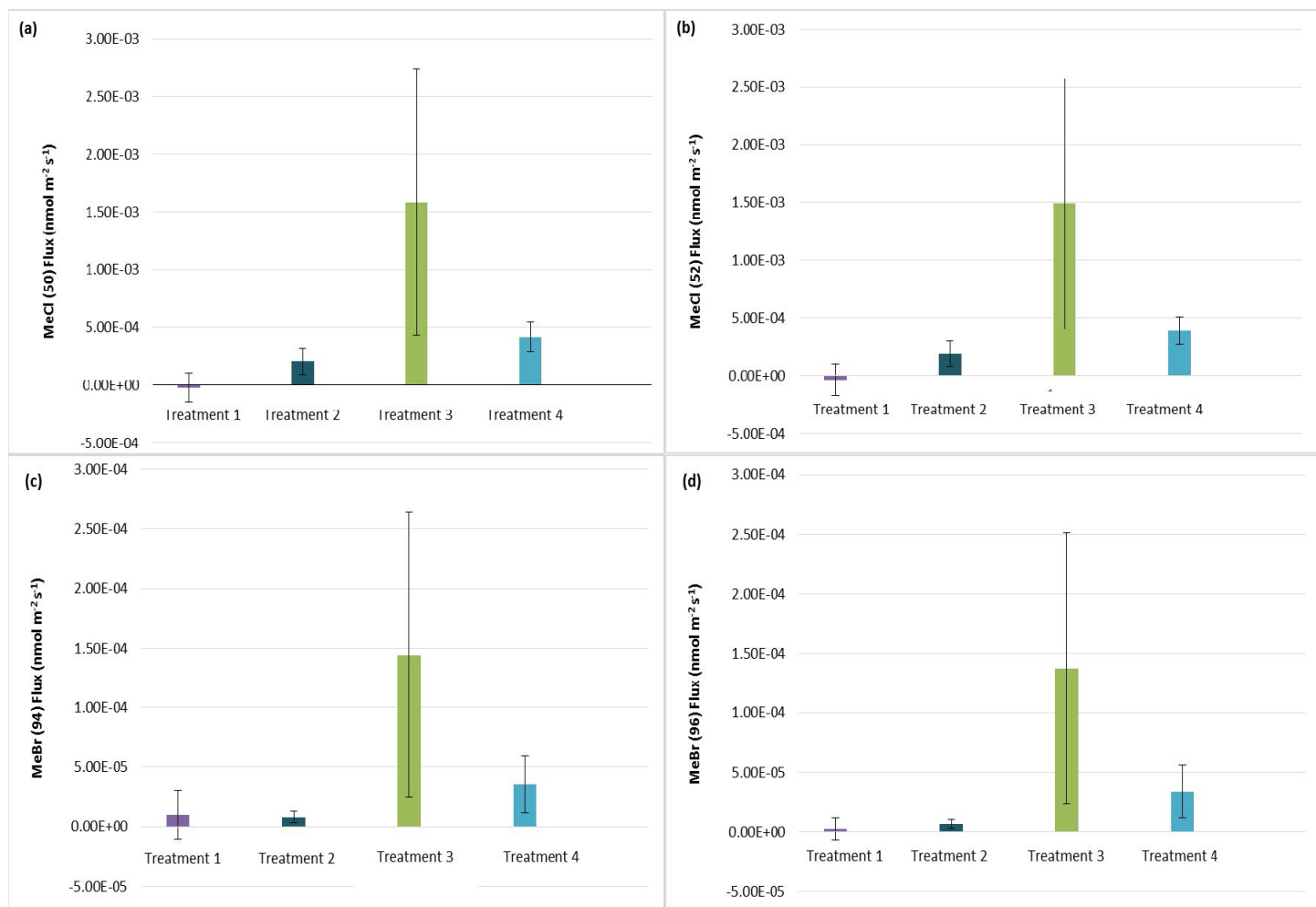


Figure 4. Average methyl chloride and methyl bromide isotope flux measurements for testing treatments. Average flux measurements for (a) MeCl (50), (b) MeCl (52), (c) MeBr (94), and (d) MeBr (96) are reported for various treatments. Treatments 3 (N=4) and 4 (N=4) have copper sulfate added, while treatments 1 (N=2) and 2 (N=5) do not. Treatments 1 and 3 are exposed to sunlight and Treatments 2 and 4 were incubated in the shade. The error bars indicate one standard deviation. values of around 6. Error bars indicate standard error. N=10 per treatment

produced as a byproduct of copper sulfate addition, lowering pH levels to acidic values. Salinity however, remained constant among samples with and without copper sulfate. Future research studying the effects of organic matter in seawater or levels of sunlight exposure prior to sample measurement could aid in identifying the mechanism driving the production of methyl halides in copper seawater samples.

chloride were lower than measurements for samples containing copper sulfate and exposed to sunlight. This implies that copper sulfate addition alone does not enhance the production of methyl halides in the water, and exposure to sunlight acts as a major catalyst for the reaction to move forward.

The standard deviations for all treatment flux measurements coincide with those reported in the literature. For treatments 1, 2, and 4, the standard

deviation for flux measurements was on the order of 10^{-4} nmol $m^{-2}s^{-1}$ (4, 18). Although the standard deviation for treatment 3 samples was quite large, this amount of variation is common for samples exposed to sunlight (19) and results indicate a definite positive flux of methyl halides from the water to the air. Possible drivers of this reaction are based on previously identified mechanisms for iron catalyzed methyl halide production.

Photochemical reaction

A likely driver of the reaction is a photochemical pathway involving sunlight and halides in seawater. Concentrations of methyl chloride and methyl bromide increased with longer exposure time to sunlight, supporting a possible photochemical production pathway. Richter and Wallace (2004) identified a purely photochemical production pathway for methyl iodide production in the Atlantic Ocean. Moore (2008) also reported that dissolved organic oxygen reacting with chlorine and sunlight generated methyl chloride in seawater. However, Moore (2008) reports that pH levels above 7.7 were more conducive to methyl chloride production than lower pH levels. Copper addition was shown to decrease the pH of samples from 8 to 5; but contrary to Moore's study conclusions, the decreased pH did not seem to deter methyl halide production. Rather, the copper worked in conjunction with sunlight to increase the rate of methyl halide flux from the water. Considering the greater methyl chloride and methyl bromide flux measurements in samples with copper sulfate and sunlight, the implication of sunlight as a driver for the reaction is highly plausible.

Biological reaction

A biologically driven reaction can also enhance methyl halide production in the oceans. Richter and Wallace (2004) compared unfiltered seawater samples to filtered seawater samples and found that unfiltered seawater samples showed greater amounts of methyl iodide production. Unfiltered seawater differs from filtered seawater by retaining the biological organisms during the testing process. I did not filter my samples which leaves open the possibility for a biological pathway. However, copper is toxic to many organisms at high levels of exposure (22, 23) and adding copper sulfate should have removed biological organisms from the samples. As I only saw greater methyl halide fluxes in those samples with copper added, a biological reaction seems unlikely for this experiment.

Uptake suppression

Rather than producing new methyl halides, copper and sunlight could have acted to prevent the uptake of methyl halides in the water. Reducing uptake would create a build-up of concentration in the water, leading to

removal of excess methyl halides into the air. Wingenter et al (2004) attributed increased oceanic methyl bromide in iron fertilized patches to this suppression mechanism. In the ocean, methyl halides are produced by bacteria (24) and broken down by microorganisms (25). Adding copper sulfate could have removed these organisms and stopped this chemical cycle, causing a build-up of methyl halides in the water.

Byproducts of copper and seawater interaction

Salinity and pH are two important climate factors for studying reactions in the marine environment. Changes in ocean pH levels can affect the atmospheric-oceanic flux of compounds (26) and can detrimentally alter the toxicity of metals (21). Increasing salinity levels can alter the reactivity of chemicals in seawater and affect hydrophobicity of trace metals such as copper (27, 28). Salinity measurements from the samples showed no significant change in salinity between pure seawater samples versus those of seawater and copper samples. Turner and Mawji (2005) found that increased salinity can decrease the hydrophobicity of copper in estuary waters. Although shifts in salinity may affect how copper reacts in the water, I found that adding copper sulfate to seawater does not considerably change the salinity.

The pH measurements between sample treatments, however, changed drastically. Immediately after copper sulfate was added to seawater, carbon dioxide concentrations increased in those samples, indicating that an exothermic reaction between the copper sulfate and seawater must be occurring. This conclusion is supported by the acidic pH values measured from samples containing copper sulfate, suggesting that slight acidification of the seawater must be occurring as carbon dioxide is produced (21, 29).

Limitations

Alternate methods for sample testing could be implemented to confirm the reliability of data. Working within the limitations of equipment in the laboratory, I relied on the assumption that constant disturbance to the water by a stir bar would create a state of equilibrium between the gases in the air and water to test methyl halide concentrations in the water. A more precise method for analyzing compounds in water is by stripping gases from the water sample itself (30, 31). Direct measurements of methyl halides using the stripping method may provide more precise measurements than the present method, but the equilibrium assumption was sufficient to test the general hypotheses for the study. Despite these limitations the results still show significant findings that give rise to questions that may be studied with future experiments.

The relatively small sample size prevents a

direct application of these findings to the general study system. A sample size of at least thirty samples would lead to greater confidence in the results and lend itself to statistical analysis. However, the standard deviation for flux measurements for treatments 1, 2, and 4 were on the order of 10^{-4} nmol m⁻² s⁻¹, which is within the limits reported in the literature (4, 18). The standard deviation for treatment 3 samples was quite large; however this amount of variation is common for samples exposed to sunlight (19). Although the sample size is limiting, the small variation in flux measurements for both methyl chloride and methyl bromide speak to the quality of the study results as a first indication for a possible production pathway.

Future directions

The influence of sunlight on methyl halide production was undiscovered until the latter half of the experimentation period. Future projects can clarify the role of sunlight in the mechanism by varying the amount of radiation and length of exposure to sunlight. Comparing radiation exposure levels to measured methyl halide fluxes could determine a possible correlation between the two variables. If flux measurements increase with increasing radiation levels, then the influence of sunlight on the mechanism is demonstrated.

Conclusions

Addition of copper sulfate to seawater samples invokes a positive methyl halide flux from the sea to the air, indicating possible production of methyl halides from the reaction with copper sulfate. However, copper sulfate alone does not drive this reaction forward and environmental factors such as sunlight play a major role. Future experimentation could determine if this positive flux is indeed due to new production, similar to iron's role in methyl halide production, or if it is caused by a disruption of normal methyl halide uptake processes. More importantly these results show that not all methyl halide chemical cycling in the environment is accounted for, and future studies should not only test new study systems but also re-examine known production pathways with different study parameters to ensure that all possibilities are explored.

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