

Copper Catalyzed Oceanic Methyl Halide Production

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ABSTRACT

Methyl halides are catalysts for stratospheric ozone depletion and their production and uptake has been measured in many of Earth's biomes. To assess the potential environmental impact of these compounds, it is important to understand their chemical cycling throughout these earth systems. Iron had previously been identified to contribute to methyl halide production in soils and oceans. Copper is able to undergo similar chemical oxidation reactions as iron, but remains to be examined. I conducted tests on seawater samples from the San Francisco Bay, comparing four different treatments that studied the impact of sunlight and copper sulfate addition. I tested samples using a gas chromatograph-mass spectrometer (GC/MS) machine and calculated flux rates for methyl chloride and methyl bromide. Samples with copper sulfate addition and sunlight exposure averaged higher positive flux rates for methyl chloride and methyl bromide than samples in other treatments. Sunlight was discovered to be essential to this reaction as measurements for samples with copper sulfate but without sunlight exposure showed less methyl halide production. Additionally, samples with copper sulfate showed increased production of carbon dioxide and acidification of the water. Three possible mechanisms may underlie the measured methyl halide production reaction: a photochemical reaction utilizing sunlight, a biological reaction, or a suppression of normal uptake processes resulting in overabundant concentrations in the water. Future studies can examine these possibilities to narrow down the cause of the reaction.

KEYWORDS

San Francisco Bay, ocean-atmosphere exchange, photochemical reaction, oxidation reaction, metals

INTRODUCTION

Over the past few decades, ozone depletion has increased concern for human and environmental health as greater amounts of ultraviolet radiation penetrates 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 contributes to global warming events (United Nations Environment Programme 2011). Methyl halides, comprised of methyl bromide, methyl chloride, and methyl iodide, act as catalysts for stratospheric ozone depletion and contribute to these concerns (Montzka and Reimann 2011).

Measurements of overall global production of methyl halides differ from quantified global uptake of these compounds (Montzka and Reimann 2011). 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 (Montzka and Reimann 2011). 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 processes have contributed to increasing levels of methyl halides in the atmosphere (Montzka and Reimann 2011). Methyl halides exist in all earth systems, including the terrestrial and oceanic spheres, and can be produced in both abiotic and biotic environments (Redeker and Kalin 2012). Methyl halide flux measurements have been studied worldwide in ecosystems such as: grasslands, oceans, salt marshes, and the Arctic tundra (Li et al. 1999, Rhew et al. 2000, Teh et al. 2009, Rhew 2011). Additionally, anthropogenic production and use of methyl halides in industry and agriculture has contributed to their global budget and environmental impact (UNEP 1992). Methyl bromide is an important agricultural fumigant used to grow strawberries, tomatoes, and peppers (Schneider et al. 2003). The Montreal Protocol banned methyl bromide due to its detrimental impact on the ozone layer, which pressured the agriculture industry to seek alternative fumigants (Mayfield and Norman 2012). Further identification of anthropogenic sources of methyl halides would create opportunities for mitigating the effects of these compounds.

A terrestrial abiotic mechanism for methyl halide production involving iron and organic matter in soils suggests that new processes for production remain to be quantified (Keppler et al. 2000). This particular abiotic mechanism has only been tested in the terrestrial environment. 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 (Montzka and Reimann 2011). Iron's interaction within the marine environment has already been accounted for (Wingenter et al. 2004, Moore and Wang 2006). Copper however, which has similar oxidation properties to iron and can participate in these reactions, remains unstudied. Many anthropogenic pathways for copper addition to the oceans exist, primarily through leaching from boat antifouling paint, aquaculture nets, and brake pads (Davis et al. 2001, Schiff et al. 2004, Tsukrov et al. 2011). 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 marine 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 ocean water, I collected half liter seawater samples using half-gallon Ball brand glass mason jars. I collected a total of twenty samples of San Francisco Bay water from the Cal Sailing Club dock at the Berkeley Marina. 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.

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 room air. The sample jar was then connected 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 needed to be pre-concentrated before injection into the GC/MS. I pre-concentrated gases by capturing the 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. The GC/MS inlet line also had an Ascarite trap to capture carbon dioxide, and a magnesium perchlorate trap to prevent water vapor from entering the machine.

To evaluate the impact of 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 (Boyd et al. 2005), 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 carbon dioxide was emitted after copper sulfate addition, I measured the concentration of carbon dioxide in 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 which contains known amounts of methyl halide concentration. The calibration curve served as the baseline for methyl halide concentration comparison. I performed data analysis using Microsoft's Excel program and a coding system developed by Professor 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 computer 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 two isotope concentrations for methyl chloride, and similarly for methyl bromide 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 flux ($\text{nmol m}^{-2} \text{d}^{-1}$) 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 between pure seawater and seawater with copper samples had similar values; however the pH values measured for samples after copper sulfate addition were 100 times more acidic than before copper sulfate addition. Salinity measurements ranged from 7.87 to 8.00 parts-per-thousand for all samples, regardless of the addition of copper (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 and seawater samples was 5.11 to 5.96 (Fig. 2).

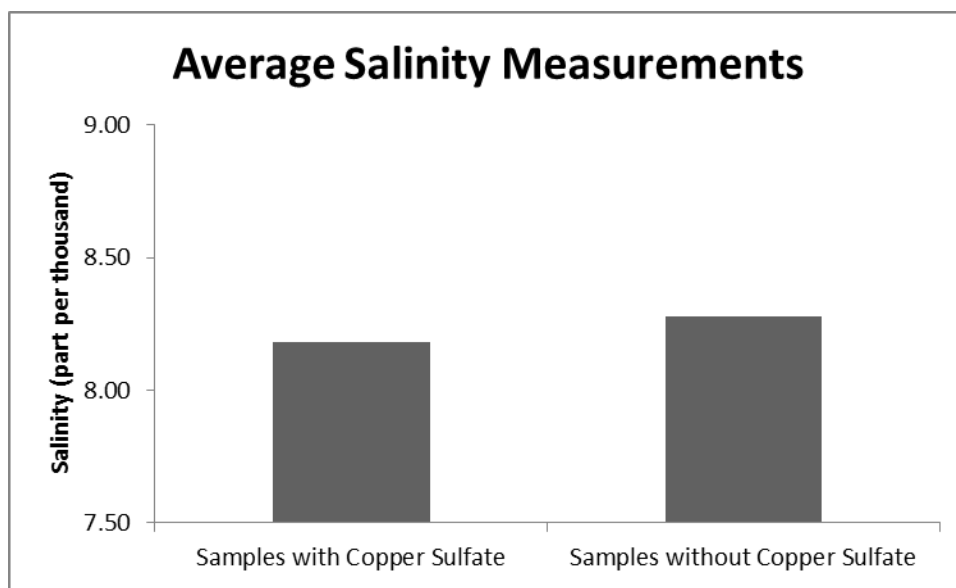


Fig. 1. Average Salinity Measurements comparing samples with and without copper sulfate addition. Samples do not show a marked difference in salinity, measured in part per trillion. N=10 per treatment

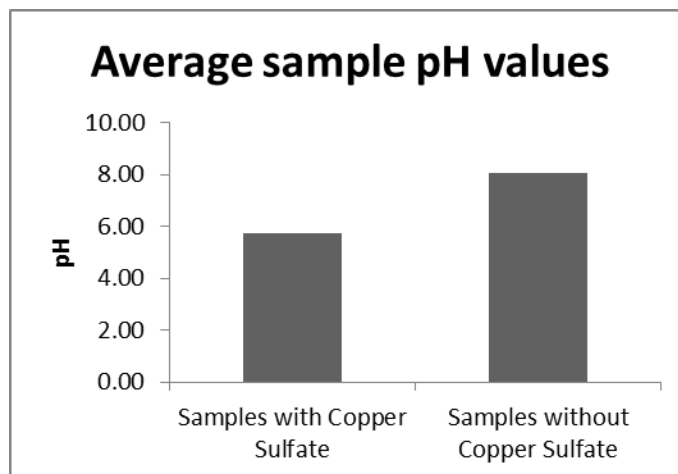


Fig. 2. Average pH measurements comparing samples with and without copper sulfate addition. Samples without copper sulfate show average oceanic pH levels of 8, while samples with copper sulfate added have acidic pH values of around 6. N=10 per treatment

In addition, I measured higher levels of carbon dioxide emissions from seawater samples that contained copper sulfate versus those samples without copper sulfate. 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 continue to rise over time (Fig. 3).

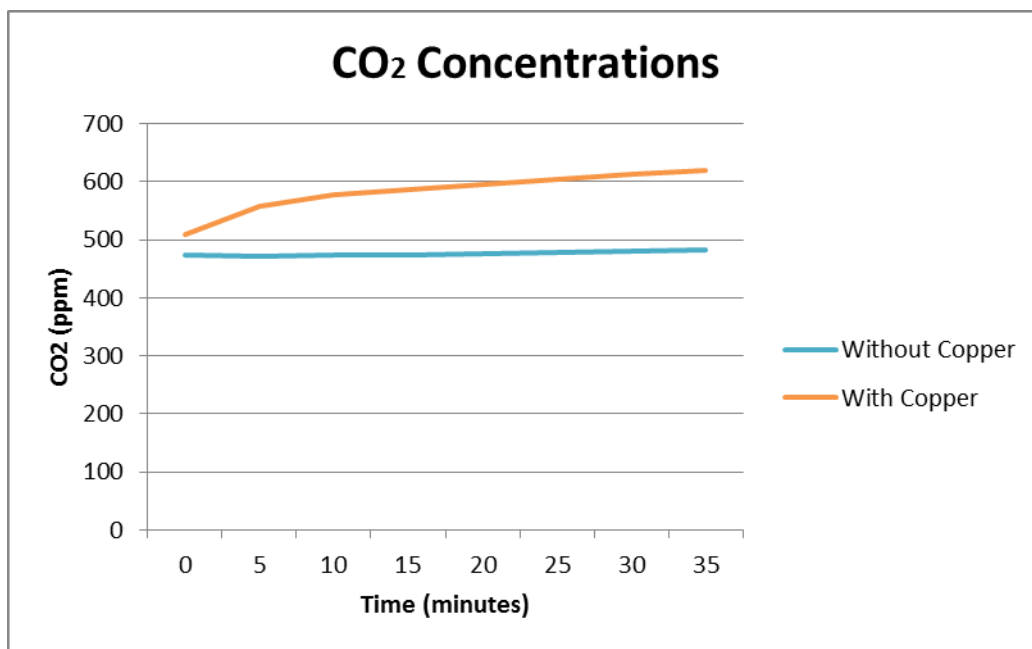


Fig. 3. Carbon dioxide concentration comparison between samples with and without copper sulfate. The concentration for samples without copper sulfate remains steady over time, however samples with copper sulfate show production of carbon dioxide over time.

Variable average flux measurements for methyl chloride and methyl bromide amongst the four treatments 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 samples that remained pure seawater. Samples exposed to sunlight showed greater variation in standard deviation for methyl halide flux measurements than measurements from samples aired in the shade.

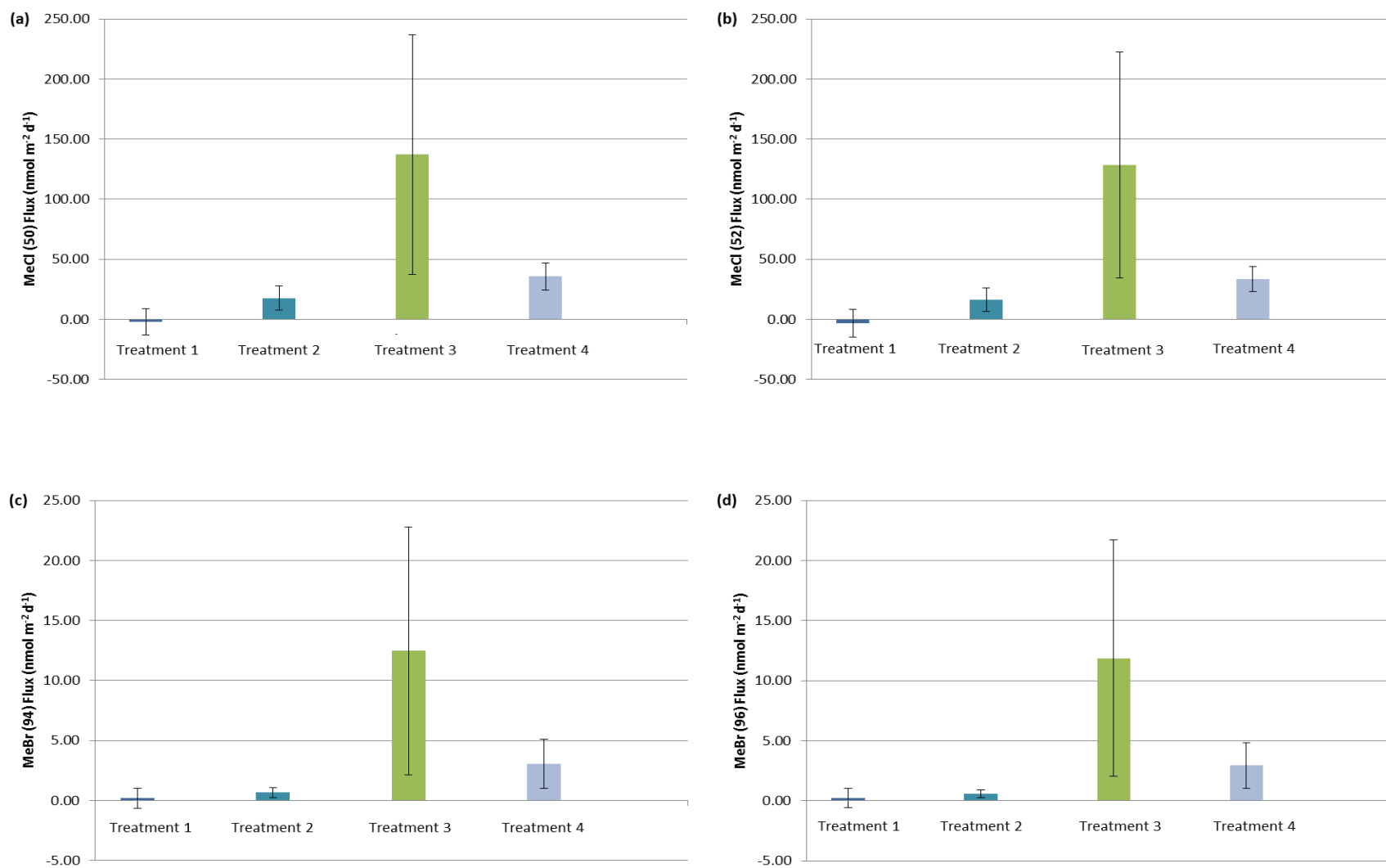


Fig. 4. Average methyl chloride and methyl bromide isotope flux measurements for testing treatments. Average flux measurements for (a) MeCl (50), (b) MeCl (52), (c) MeBr (94), and (d) MeBr (96) are reported for various treatments. Treatments 3 (N=4) and 4 (N=4) have copper sulfate added, while treatments 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.

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, oxidation, or prevention of oceanic consumption and uptake. In addition to increased levels of methyl chloride and methyl bromide, carbon dioxide was produced as a byproduct of copper additions, lowering pH levels to acidic values. Salinity however, remained constant even between 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.

Influence of copper on methyl halide production

The average flux measurements for methyl chloride and methyl bromide were highest for samples that contained copper sulfate and were exposed to 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 chloride were lower than measurements for samples that contained copper sulfate and were exposed to sunlight. This implies that copper sulfate addition alone does not enhance the concentration of methyl halides in the water, and exposure to sunlight acts as a major catalyst for the reaction to move forward. Possible explanations for the reaction are based off previous identified mechanisms for iron catalyzed methyl halide production.

Photochemical reaction

A likely driver of the reaction is a photochemical pathway involving a reaction between halides in seawater and sunlight. 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. Questions still remain as to the exact chemical processes and variables involved in the reaction, and future tests could assess this lack in knowledge.

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 (Santore et al. 2001, Pascal et al. 2010) and 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 which would lead 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. Methyl halides in the oceans are produced by bacteria (Brownell et

al. 2010) while also being broken down by microorganisms (Cox et al. 2012). The addition of copper could have disrupted these processes by killing these organisms and preventing the natural chemical cycle, which may cause 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 (Mari 2008) and can detrimentally alter the toxicity of metals (Pascal et al. 2010). Increasing salinity levels can alter the reactivity of chemicals in seawater and affect hydrophobicity of trace metals such as copper (Turner 1998, Turner and Mawji 2005). 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 merely adding copper 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 and seawater must be occurring. This conclusion is supported by the acidic pH values measured from samples with copper added to seawater, suggesting that slight acidification of the seawater must be occurring as carbon dioxide is produced (Pascal et al. 2010, Bates et al. 2012). This experiment shows that a number of other important reactions occur and there is need for further study to critically examine each effect.

Limitations

The greatest limitation for this study stems from the uniqueness of the study site. The San Francisco Bay is an estuary that collects freshwater from the San Joaquin and Sacramento rivers and connects to the Pacific Ocean. The intermixing of freshwater and saltwater at this junction provides unique characteristics for the water samples, but findings here may not be applicable to

independent freshwater or saltwater bodies. Future studies could examine the influence of specific bodies of water by comparing samples from the Pacific Ocean to samples collected from freshwater sources such as the Sacramento River. By recording the salinity and pH of these water samples, the effects of water chemistry composition on methyl halide production could be further expanded.

Alternate methods for sample testing could be implemented to confirm the reliability of data. As a result of 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 of the gases in the air and water to test methyl halide concentrations in the water. There are more precise methods for analyzing compounds in water by stripping gases from the water sample itself (Moore et al. 1996, Lu et al. 2010) but because of the limitations of laboratory equipment I opted in favor of a simpler testing design. 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 also 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 $10 \text{ nmol m}^{-2} \text{ d}^{-1}$, which is within the limits reported in the literature (Rhew et al. 2003, Rhew 2011). The standard deviation for treatment 3 samples was quite large; however this amount of variation is common for samples exposed to sunlight (Richter and Wallace 2004). 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

Future projects can potentially investigate the mechanism of production identified in this study. Keppler et al. (2000) reported an abiotic methyl halide production pathway during an oxidation reaction between organic soil matter and iron. Immediate tests could examine the

effects of increased organic matter, such as humic acid, to determine if a photochemical reaction proves feasible. Altering the organic matter content within samples will confirm that a similar reaction is occurring in seawater samples; if methyl halide production is greater in samples with increased organic matter, then it is likely that a similar oxidation reaction mechanism is contributing to their production.

Another simple experiment consists of measuring the amount of radiation exposure the samples receive while they are being aired out. Comparing sample radiation exposure levels to measured methyl halide fluxes could determine if a correlation between the two variables exists. If flux measurements increase with increasing radiation levels, then the influence of sunlight on the mechanism is demonstrated.

Conclusions

Copper was successfully identified as a possible variable in methyl halide production in seawater, similar to previous reports of iron's role in methyl halide production. Samples with copper sulfate addition showed increased average flux of methyl chloride and methyl bromide into the air. However, this reaction was found to be highly dependent on the presence of sunlight to drive the process forward. The results support a possibility of an oxidation reaction between copper and marine organic matter to create increased methyl halide concentration, which may be verified through future experimentation.

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