

COS and CS₂ are sulfur compounds that are formed in natural waters. These compounds are also volatile, which leads them to move into the atmosphere and serve as critical precursors to sulfate aerosols. Sulfate aerosols are known to counteract global warming by reflecting solar radiation. One major source of COS and CS₂ stems from the ocean. While previous studies have linked COS and CS₂ formation in these waters to the indirect photolysis of organic sulfur compounds, much of the chemistry behind how this occurs remains unclear. This study examined this chemistry by evaluating how different organic sulfur precursors, water quality constituents, and temperature affected COS and CS₂ formation in natural waters.

In the first part of this thesis (chapters 2 and 3), nine natural waters ranging in salinity were spiked with various organic sulfur precursors (e.g. cysteine, cystine, dimethylsulfide (DMS) and methionine) exposed to simulated sunlight over varying exposures. Other water quality conditions including the presence of O₂, CO and temperature were also varied. Results indicated that COS and CS₂ formation increased up to 11× and 4×, respectively, after 12 h of sunlight while diurnal cycling exhibited varied effects. COS and CS₂ formation were also strongly affected by the DOC concentration, organic sulfur precursor type, O₂ concentration, and temperature while salinity differences and CO addition did not play a significant role.

To then specifically evaluate the role of DOM in cleaner matrices, COS and CS₂ formation was examined in synthetic waters (see chapters 4 and 5). In this case, synthetic waters were spiked with different types of DOM isolates ranging from freshwater to ocean water along with either cysteine or DMS and exposed to simulated sunlight for up to 4 h. Surprisingly, CS₂ was not formed under any of the tested conditions, indicating that other water quality constituents, aside from DOM, were responsible for its formation. However, COS formation was observed. Interestingly, COS formation with cysteine was fairly similar for all DOM types, but increasing DOM concentration actually decreased formation. This is likely due to the dual role of DOM on simultaneously forming and quenching the RIs. Additional experiments with quenching agents to remove select reactive intermediates (RI) (e.g. ³DOM* and •OH) further indicated that •OH was not involved in COS formation with cysteine but ³DOM* was involved. This result differed with DMS in that •OH and ³DOM* were both found to be involved. In addition, treating DOM isolates with sodium borohydride (NaBH₄) to reduce ketone/aldehydes to their corresponding alcohols increased COS formation, which implied that the RIs formed by these functional groups in DOM were not involved. Since ketones are known to form high-energy-triplet-states of DOM while

quinones are known to form low-energy-triplet-states of DOM, removing ketones from the system further supported the role of low-energy-triplet-states on COS formation. This was initially hypothesized by findings from the testes on DOM types. In the end there are several major research contributions from this thesis. First, cysteine and DMS have different mechanisms for forming COS. Second, adding O₂ decreased COS formation, but it did not stop it completely, which suggests that further research is required to evaluate the role of RI in the presence of O₂. Lastly, considering the low formation yields of COS and CS₂ formation from the organic sulfur precursors tested in this study, it is believed that some other organic sulfur precursors are missing which are likely to generate these compounds to higher levels and this needs to be investigated in future research.