



Unexpected consequences of increasing CO₂ and ocean acidity on marine production of DMS and CH₂ClI: Potential climate impacts

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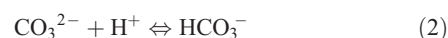
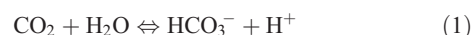
[1] Increasing atmospheric mixing ratios of CO₂ have already lowered surface ocean pH by 0.1 units compared to preindustrial values and pH is expected to decrease an additional 0.3 units by the end of this century. Pronounced physiological changes in some phytoplankton have been observed during previous CO₂ perturbation experiments. Marine microorganisms are known to consume and produce climate-relevant organic gases. Concentrations of (CH₃)₂S (DMS) and CH₂ClI were quantified during the Third Pelagic Ecosystem CO₂ Enrichment Study. Positive feedbacks were observed between control mesocosms and those simulating future CO₂. Dimethyl sulfide was 26% (±10%) greater than the controls in the 2x ambient CO₂ treatments, and 18% (±10%) higher in the 3xCO₂ mesocosms. For CH₂ClI the 2xCO₂ treatments were 46% (±4%) greater than the controls and the 3xCO₂ mesocosms were 131% (±11%) higher. These processes may help contribute to the homeostasis of the planet. **Citation:** Wingenter, O. W., et al. (2007), Unexpected consequences of increasing CO₂ and ocean acidity on marine production of DMS and CH₂ClI: Potential climate impacts, *Geophys. Res. Lett.*, 34, L05710, doi:10.1029/2006GL028139.

1. Introduction

[2] Over the last 650,000 years, but prior to the industrial revolution, atmospheric CO₂ mixing ratios oscillated between 180 and 280 parts per million by volume (ppmv) [Petit et al., 1999; Siegenthaler et al., 2005]. By the end of 2005, atmospheric CO₂ mixing ratios reached 375 ppmv as measured at the National Oceanic and Atmospheric Administration's Mauna Loa Observatory (www.cmdl.noaa.gov). This additional CO₂ burden is a result of anthropogenic combustion of fossil fuels and other anthropogenic perturbations [Intergovernmental Panel on Climate Change (IPCC), 1995].

[3] Rising atmospheric CO₂ impacts the marine biosphere directly. Elevated CO₂ alters seawater carbonate

equilibria shifting inorganic carbon away from carbonate (CO₃²⁻) towards more bicarbonate (HCO₃⁻) and increased ocean acidity (equations 1 and 2).



[4] By the end of this century, it is expected that atmospheric CO₂ concentrations will rise by a factor of three relative to preindustrial values (280 ppmv) assuming the "business as usual" scenario IS92a [IPCC, 1995]. This will result in a cumulative pH drop of 0.4 units in mean surface seawater, a factor of three increase in hydronium (H⁺) concentration and a fall in CO₃²⁻ levels by ~50% since 1750 [Feely et al., 2004; Orr et al., 2005; Raven et al., 2005]. As stated above, atmospheric CO₂ concentrations are currently at their highest as recorded in paleohistory spanning the last 650 millennia [Petit et al., 1999; Siegenthaler et al., 2005]. Consequently, the current average ocean pH is at its lowest over this period. Furthermore, the rate of ocean acidity is climbing at a rate ~100 times faster than at any known time [Raven et al., 2005].

[5] Although the changes in ocean acidity can be predicted with great certainty, the consequences for marine organisms, their ecosystems and climate-relevant organic gas emissions are largely unknown. Recent studies have shown that some phytoplankton taxonomic groups favor CO₂ as their inorganic carbon source while others consume mostly HCO₃⁻ [Elzenga et al., 2000].

[6] Coccolithophorids such as *Emiliania huxleyi* and other marine microorganisms, including diatoms, produce dimethyl sulfide (DMS) [Haas, 1935; Gabric et al., 2001], which is a radiatively important trace gas [Charlson et al., 1987; Wingenter et al., 2004]. Dimethyl sulfide is produced by the enzymatic cleavage of dimethylsulfoniopropionate (DMSP) [DiTullio and Smith, 1995]. Viral activity also induces DMS production from DMSP [Malin et al., 1998] as does grazing of phytoplankton by microzooplankton [Archer et al., 2001]. In the atmosphere DMS is rapidly oxidized to sulfur dioxide (SO₂), which can form sulfate aerosols. As a result, emissions of DMS from ocean waters are a major source of cloud condensation nuclei (CCN) in the clean marine atmosphere [Bates et al., 1992; Clarke et al., 1998].

[7] Molecular iodine (I₂) and iodo-carbons such as chloroiodomethane (CH₂ClI) photolyze quickly in the atmospheric boundary layer, releasing atomic iodine (I) that

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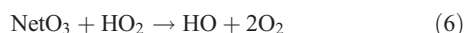
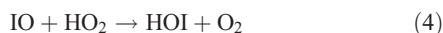
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can catalytically destroy ozone (O₃) [Jenkins *et al.*, 1991] via the following catalytic cycle,



[8] Unlike atomic Cl, or to a lesser extent Br, I does not react with hydrocarbons to form reservoir species. Thus, I atoms are very efficient in the catalytic removal of O₃. Because the chief atmospheric oxidant, the hydroxyl radical (HO), is produced primarily from O₃ and water vapor, the abundance of tropospheric O₃ is pivotal to the oxidative capacity of the atmosphere, which governs the lifetime of many climate relevant gases including methane (CH₄) and DMS. Photooxidation of iodocarbons can also lead to aerosol nucleation [O'Dowd *et al.*, 2002; Jimenez *et al.*, 2003].

2. Experiment

[9] A unique experiment was conducted between May 16 and June 9, 2005 at the Large-Scale Facilities at the Biological Station of the University of Bergen in Espesgrend, Norway (60.3° N, 5.2° E). The purpose of the experiment was (1) to examine the effects of increasing CO₂ and related changes in seawater carbonate chemistry on natural marine plankton communities, and (2) to monitor changes in climate-relevant organic gases produced and consumed by marine phytoplankton and other microorganisms during the Third Pelagic Ecosystem CO₂ Enrichment Study (PeECE III). Nine polyethylene bags (2 m diameter; submerged to 10 m) were moored to a raft. Unfiltered, nutrient-poor, post-bloom fjord water was pumped from a depth of 12 m and used to fill the enclosures and were then covered by gas-tight tents made of ETFE foil (Foiltec, Germany). The tents allowed for 95% transmission of the full spectrum of sunlight. A mixed layer was created by adding 0.6 m³ of freshwater to the upper 5 m of the mesocosms. The resulting stratification greatly diminished re-introduction of sediments into the surface layer. Throughout the study, the upper 5 m layer was gently mixed using aquarium pumps.

[10] The mesocosms were initially equilibrated to the following conditions: (1) three were at ambient levels of CO₂ (~375 ppmv; mesocosms M7-M9), (2) three were at levels expected at the end of this century (760 ppmv pCO₂ assuming IPCC's business as usual scenario; ISP92a, 2xCO₂; M4-M6), and (3) three were at 1150 ppmv pCO₂, as predicted for the middle of the next century (3xCO₂, M1-M3). After four days of CO₂ aeration target water column pCO₂ values were reached and the CO₂ treatments were stopped (day 0). A constant flow of air to the mesocosm headspace at initial CO₂ levels was continued throughout the experiment. On day 0 nutrients were added to stimulate bloom development. To promote a bloom of *E. huxleyi*, nitrate and phosphate were added in a ratio of 25:1, yielding initial concentrations of approximately 15 μmol L⁻¹ NO₃

and 0.6 μmol L⁻¹ PO₄. These nutrients and other physical, chemical and biological parameters were closely monitored during the development and decline of the bloom. Except for the different pCO₂ levels, the mesocosms were essentially the same as those described by Engel *et al.* [2005]. Phytoplankton and viruses were identified and enumerated by flow cytometry (FCM) as described by Marie *et al.* [1999].

[11] During PeECE III 4-liter samples of ocean water were collected from each of the mesocosms daily at approximately 9:45 a.m. and kept in a dark walk-in refrigerator maintained at fjord temperature (8° C). Extraction of gases [U.S. Environmental Protection Agency, 2003] from 25 mL aliquots began shortly after returning from the raft. A trap filled with activated carbon and a molecular sieve was used to further purify ultra high purity helium (He). The He was used to purge gases from a total of 220 mesocosm ocean water samples at a rate of 40 ml min⁻¹ into evacuated 2-L electropolished canisters (University of California, Irvine; UCI) equipped with a metal bellows valve (Nupro by Swagelok, Solon, OH). In order to assure a steady flow into the canisters, a passive sampler (Entech Instruments, Simi Valley, CA) was connected directly upstream of the canister valve. The canisters were flown air cargo to UCI and analysis began soon after arrival.

[12] Details of the six-channel gas chromatographic instrument and sample analysis employed at the UCI laboratory can be found elsewhere [Sive, 1998; Colman *et al.*, 2001; Blake *et al.*, 2003] and are outlined here. For each sample 1515 ± 1 cm³ (STP) were preconcentrated in a liquid nitrogen-cooled loop filled with glass beads. The sample were directed to six different gas chromatographic column/detector combinations. Electron capture detectors (ECDs, sensitive to halocarbons and alkyl nitrates), flame ionization detectors (FIDs, sensitive to hydrocarbons) and quadrupole mass spectrometer detectors (MSDs, for selected compound monitoring) were employed. The first column-detector combination was a DB-5ms column (J&W; 60 m, 0.25 mm I.D., 0.5-μm film thickness) output to a quadrupole MSD (HP-5973). The second combination was a DB-1 column (J&W; 60 m, 0.32 mm I.D., 1-μm film thickness) coupled to an FID (HP-6890). The third combination was a PLOT column (J&W GS-Alumina; 30 m, 0.53 mm I.D.) connected in series to a DB-1 column (J&W; 5 m, 0.53 mm I.D., 1.5-μm film thickness) with an FID. The fourth combination was a Cyclodex B column (J&W 60 m, 0.25 mm I.D., 0.25-μm film thickness), which was output to an FID. The fifth combination was a Restek 1701 column (60 m, 0.25 mm I.D., 0.50-μm film thickness) with an ECD. The sixth combination was a DB-5 (J&W; 30 m, 0.25 mm I.D., 1-μm film thickness) column connected in series to a Restek 1701 column (5 m, 0.25 mm I.D., 0.5-μm film thickness) coupled to an ECD.

[13] The analytical accuracy is 10% for DMS and 20% for CH₂Cl₂. The measurement precision for DMS is 3% at the levels observed during PeECE III and 8% for CH₂Cl₂. Both compounds were always a factor of 50 or more above their limits of detection.

3. Results

[14] Dimethyl sulfide production followed the development and decline of the phytoplankton bloom (Figures 1

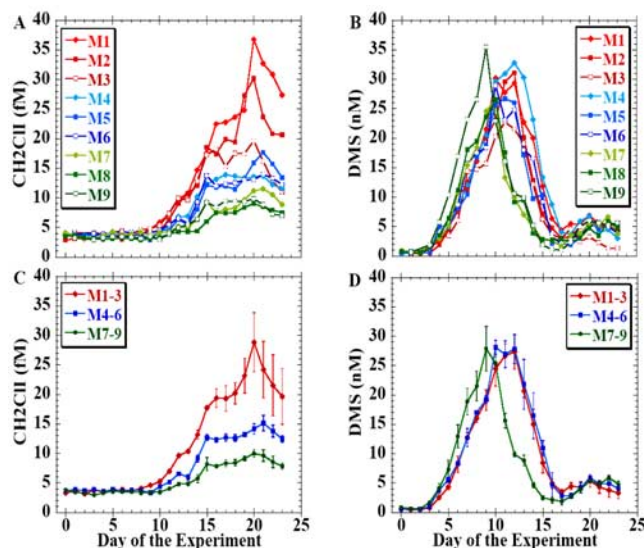


Figure 1. Time series of the evolution of CH₂CII and DMS concentrations in ocean water during PeECE III. (a, c) The concentrations of CH₂CII for each of the nine mesocosms and averages over the triplicate treatments, respectively. (b, d) Same as for Figures 1a and 1c but for DMS measurements. The initial day of the experiment was May 16, 2005. Green, $p\text{CO}_2 = 375$ ppmv; blue, 760 ppmv; red, 1150 ppmv.

and 2). Maximum DMS concentrations coincided with the peak in chlorophyll-*a* concentrations in the present day CO₂ treatment, but were delayed by 1–3 days relative to chlorophyll-*a* in the double and triple CO₂ treatments. The time integrated average amount of DMS was 26% ($\pm 10\%$ having a confidence interval (CI) of $\sim 90\%$) and 18% ($\pm 10\%$ or

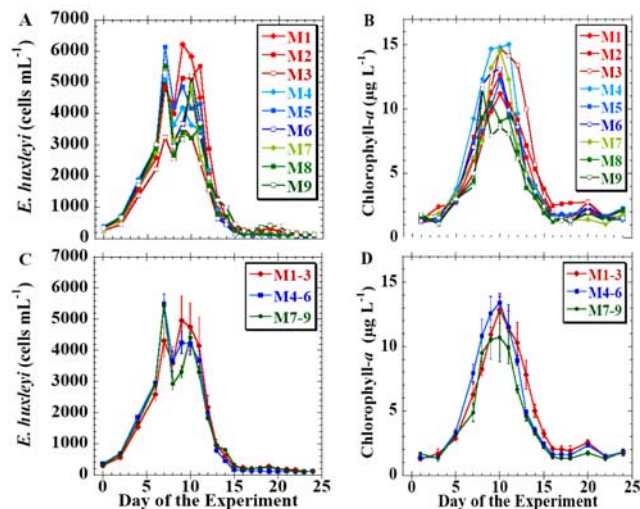


Figure 2. Time series of the evolution of *E. huxleyi* and Chlorophyll-*a* concentrations in ocean water during PeECE III. (a, c) The concentrations of *E. huxleyi* for each of the nine mesocosms and averages over the triplicate treatments, respectively. (b, d) Same as for Figures 2a and 2c but for Chlorophyll-*a*. Green, $p\text{CO}_2 = 375$ ppmv; blue, 760 ppmv; red, 1150 ppmv.

$\sim 80\%$ CI) higher in the 2x and 3xCO₂ mesocosms, respectively (days 0–17). Maximum abundances of the coccolithophore *E. huxleyi*, the dominant phytoplankton species during the bloom period and a major DMS producer, occurred at nearly the same time in all of the mesocosms (days 7–10 of the experiment). Their decline was chiefly a result of viral infection and occurred a day or two ahead of the DMS decline in the 2x and 3xCO₂ mesocosms (the dip in concentration on day 8 was associated with cloud cover). The peak in DMS correlated better with chlorophyll-*a* than with any other measured parameter, having an average correlation coefficient of 0.88.

[15] Chloriodomethane had its peak concentration much later than the maximum in chlorophyll-*a*, about 6–10 days (Figures 1 and 2). When integrating the CH₂CII concentrations over its peak period (days 8 through 23), the estimated abundance of CH₂CII was on average $\sim 46\%$ ($\pm 4\%$; CI > 98%) higher in the 2x ambient CO₂ mesocosms and about 131% ($\pm 11\%$; CI > 98%) higher in the 3xCO₂ mesocosms compared to the average of the ambient treatment. Besides the virus that infected *E. huxleyi*, other viral populations were detected and quantified in the mesocosms (A. Larsen, unpublished data). One, here named “Big Virus 1”, showed a dramatic CO₂ response (Figure 3) opposite of that observed for CH₂CII, with the greatest amount of Big Virus 1 measured in the control mesocosms. The integrated amount of Big Virus 1 was 33% ($\pm 16\%$; CI > 98%) and 66% ($\pm 18\%$; CI > 98%) lower on average in the 2x and 3xCO₂ treatments, respectively, between days 8 and 23, compared to the ambient treatment. The relationship between this virus and CH₂CII is not known at this time. We have previously found a virus - with a flow cytometric signature similar to that of Big Virus 1 - that infects nanoeukaryotic algae. From FCM results it is evident that several other nanoeukarotes were present in the mesocosms during PeECE III. However, the method that was used does not allow us to identify these further.

4. Discussion

[16] Differences in viral attacks and phytoplankton lysis could be responsible for differences in the production of DMS and CH₂CII. Changes in algal physiology in response to changes in CO₂, pH and CO₃²⁻ cannot be ruled out, nor can changes in aqueous chemistry induced by the CO₂ perturbations. Differences between zooplankton (K. Schmidt,

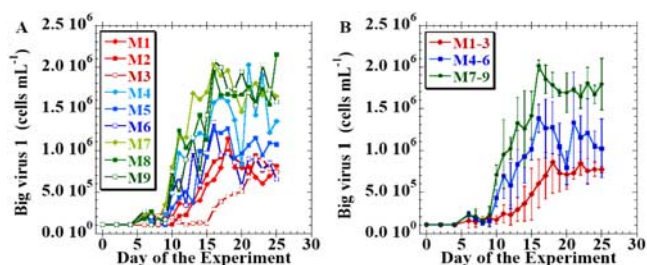


Figure 3. Concentrations of Big Virus 1 measured versus day of the experiment from ocean water during PeECE III. (a, b) The concentrations for each of the nine mesocosms and averages over the triplicate treatments, respectively. Green, $p\text{CO}_2 = 375$ ppmv; blue, 760 ppmv; red, 1150 ppmv.

personal communication, 2006) and copepod (Y. Carotenuto, personal communication, 2006) grazing rates between the three treatments were insignificant. The differences in DMS and CH₂CL concentrations may be viewed as a result of changes to the ecosystems as a whole brought on by the CO₂ perturbations.

[17] Emissions of CH₂CL to the atmosphere contribute to destruction of O₃ and to aerosol nucleation [O'Dowd *et al.*, 2002; Jimenez *et al.*, 2003]. Therefore, an increase in marine production of CH₂CL may impact marine boundary layer photochemistry and cloud radiative properties.

[18] If increasing atmospheric CO₂ leads to greater DMS, then this may contribute to planetary climate self regulation. At this point it is difficult to assess the impact of increasing marine DMS production observed during PeECE III. However, this experiment points to the need for similar work to determine the changes in other plankton communities in response to future CO₂ concentrations and any change in DMS production. Concurrently, continued efforts to determine changes in the extent of community distributions globally are needed [Iglesias-Rodríguez *et al.*, 2002]. Combining future experimental and modeling efforts will lead to a better understanding of the feedbacks between the future atmosphere and ocean.

5. Conclusion

[19] If the present rate of fossil fuel consumption continues it will take tens to hundreds of millennia for ocean chemistry to return to a state similar to present conditions [Raven *et al.*, 2005]. Observations of DMS and CH₂CL during the PeECE III CO₂/ocean acidity perturbation experiment demonstrate the potential for unintended and largely unpredictable consequences of future atmospheric CO₂ concentrations on climate-relevant organic gases that are produced and consumed in the marine environment. Additional DMS production in a higher CO₂ environment may help contribute to the homeostasis of the planet. It is critical that we understand the outcome of increasing ocean acidification in order to predict future climate more accurately. The consequences of future ocean acidification on climate are difficult to evaluate without additional empirical measurements and numerical modeling studies, because of many factors, including feedbacks. These and further results will allow those involved in developing environmental and energy policy to make more informed decisions on carbon use.

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