

Emissions of Volatile Organic Compounds from Marine Environments
Lexie Gardner
Advisor: Professor Drew Gentner
Second Reader: Professor Juan Lora
December 21, 2022

A Senior Essay presented to the faculty of the Department of Earth & Planetary Sciences, Yale University, in partial fulfillment of the Bachelor's Degree.

Abstract

Volatile organic compounds (VOCs) play a key role in influencing atmospheric chemistry, air quality, and climate. Biogenic VOCs account for the majority of volatile organic compounds and have been shown to be in active flux with the environment. Until recently, the ocean had not been viewed as an important source or sink for VOCs, and it remains an understudied environment, particularly in coastal regions. This paper reviews the state of current literature as well as explores preliminary research from the Yale Coastal Field Station for three compounds of interest: acetone, isoprene, and dimethyl sulfide. Acetone, dimethyl sulfide, and isoprene all impact the oxidative capacity of the environment, along with cloud albedo, and have been determined to be in active air-sea exchange. Literature shows the ocean acts as a net source for DMS and isoprene. There is discrepancy for the net flux of acetone, as it has been shown to emit from and deposit into the ocean in different regions. Preliminary data from the YCFS shows a clear vertical gradient for acetone, but DMS and isoprene do not have as clear of patterns. Past studies combined with the preliminary YCFS data highlight the need for further research on air-sea exchange of VOC compounds.

Introduction

Air-water surface interactions are important for local, regional, and global air quality. The ocean is known to emit particles through droplets (eg. seaspray) and particle conversion (eg. secondary marine aerosols) (Mayer et al., 2020). Known emissions of compounds include a range of volatile organic compounds (VOCs) from acetone to dimethyl sulfide (DMS) (Phillips et al., 2021). VOC emissions are important factors in atmospheric chemistry and are known to contribute to both ozone production and secondary organic aerosol (SOA) formation, which affect air quality, human health, and climate (Park et al., 2013). Biogenic VOCs (BVOCs) make up 90% of all VOC emissions worldwide and emissions from oceans are relatively understudied (Guenther et al., 1995).

The ocean is an established source of VOC emissions, and coastal dynamics are known to affect the transport of air pollution to surrounding regions (Upstill-Goddard, 2006). However, there is a lack of understanding regarding the air-ocean fluxes of VOCs, with only a few compounds having been studied. Additionally, there is an understudied range of functionalized compounds emitted from marine systems that may be important for regional and long-range atmospheric chemistry including sulfur and nitrogen containing species.

DMS is one sulfur containing species of interest as its oxidation products have climate impacts and it makes up the majority of atmospheric organic sulfur (Phillips et al., 2021). It is produced as algae decomposes, much of which occurs anaerobically. Once emitted DMS has implications for nearby air-quality and once oxidized, the products of DMS act as cloud condensation nuclei, affecting cloud formation potential (Charlson et al., 1987).

Additional compounds of interest include acetone and isoprene. Acetone is highly prevalent in the atmosphere and plays a key role in influencing tropospheric ozone formation and thus the oxidation capacity of the atmosphere (Dixon et al., 2014). Previous studies have shown that the ocean predominantly acts as a sink for acetone, with emission hotspots in biologically active areas (Sinha et al., 2007, Phillips et al., 2021). Isoprene is known to be emitted from vegetation, but its emission from marine environments is less well understood. Recently, it has been shown that isoprene is emitted from the ocean surface as a product of oxidation of marine algae (Pacifico et al., 2009, Phillips et al., 2021).

The two main objectives of this project are to (1) determine the present state of literature on the topic of air-sea fluxes, with attention to coastal regions, and (2) present a methodological development case study for an air-sea flux project occurring on the Long Island Sound of Connecticut. The preliminary results of this study will be discussed briefly in the context of how they align with past work done in the field of air-sea exchange.

Background

Emissions of biogenic VOCs occur both terrestrially and in marine environments, but terrestrial environments are more well studied than marine environments. BVOCs can significantly alter the oxidative capacity of the atmosphere, increase pollution, and contribute to secondary organic aerosol formation, thus leading to both human health and environmental issues. Therefore, understanding the fluxes of VOCs with the natural environment is crucial to determining sources and sinks of pollutants.

VOCs, and their subsequent oxidation products, have been linked to many human health conditions. VOC emissions can lead to the creation of urban smog and tropospheric ozone, both of which adversely affect human health (Soni et al., 2018). The cardiovascular and respiratory systems are the most vulnerable to VOC based pollutants. VOCs, and their lower volatility oxidation products, can cause respiratory tract irritation and lung inflammation (Kampa & Castanas, 2008). VOCs are precursors to SOA, which is a primary component of particulate matter

(ie. PM_{2.5} and PM₁₀). Particulate matter contributes to both respiratory and cardiovascular issues due to its small size and ability to penetrate deep into the lungs (Kampa & Castanas, 2008). These health issues can occur with acute exposure at high concentrations as well as with chronic exposure to lower concentrations.

Fluxes of BVOCs with the environment are also important to understand due to their role in tropospheric chemistry and the global radiative budget. Emission rates of BVOCs play a critical role in controlling the concentration of both hydroxyl radicals (OH[·]) and ozone (O₃) in the troposphere, influencing atmospheric oxidation capacity (Guenther et al., 1995, Hackenberg et al., 2017). Additionally, oxidation products of BVOCs can form particulates and cloud condensation nuclei, which can affect the radiative forcing of the atmosphere and thus influence climate (Phillips et al., 2021).

Atmospheric Chemistry

Once emitted, VOCs undergo transformational processes and both chemical and physical removal in the troposphere. Emissions of VOCs as well as nitrogen and sulfur containing compounds and their subsequent transformation in the atmosphere result in ozone and secondary particulate matter formation as well as acid deposition (Atkinson, 2000). Common VOC reaction pathways, including intermediate radicals, are illustrated in Figure 1. Chemical transformations include reactions with ozone, the hydroxyl and nitrate radicals (NO₃), and photochemical reactions (Atkinson & Arey, 2003).

The oxidation efficiency of the atmosphere is determined by the concentration of oxidants, such as hydroxyl radicals, ozone, and nitrate radicals (Jung et al., 2022). Hence, ozone is of high importance in atmospheric chemistry as large quantities are created and destroyed by various chemical reactions in the troposphere—including oxidation cycles of non-methane hydrocarbons, such as isoprene. VOCs can act as a source or a sink for both tropospheric ozone and hydroxyl radicals, which influences the oxidative capacity of the atmosphere (Phillips et al., 2021). The oxidative capacity of the atmosphere refers to its ability to process chemical compounds through photochemical reactions with oxidants (Jung et al., 2022). This has profound impacts on air quality and climate.

VOCs can also be oxidized into lower volatility products, which can condense into particles and form cloud condensation nuclei, or into highly soluble products that then deposit or transform into secondary organic aerosols (Sander, 2015; Goldstein & Galbally, 2007). SOA have the ability

to influence the radiation balance of the atmosphere by scattering incoming solar radiation and can modify cloud microphysics (Shaw et al., 2010). SOA is also a primary component of particulate matter which can be detrimental to human health.

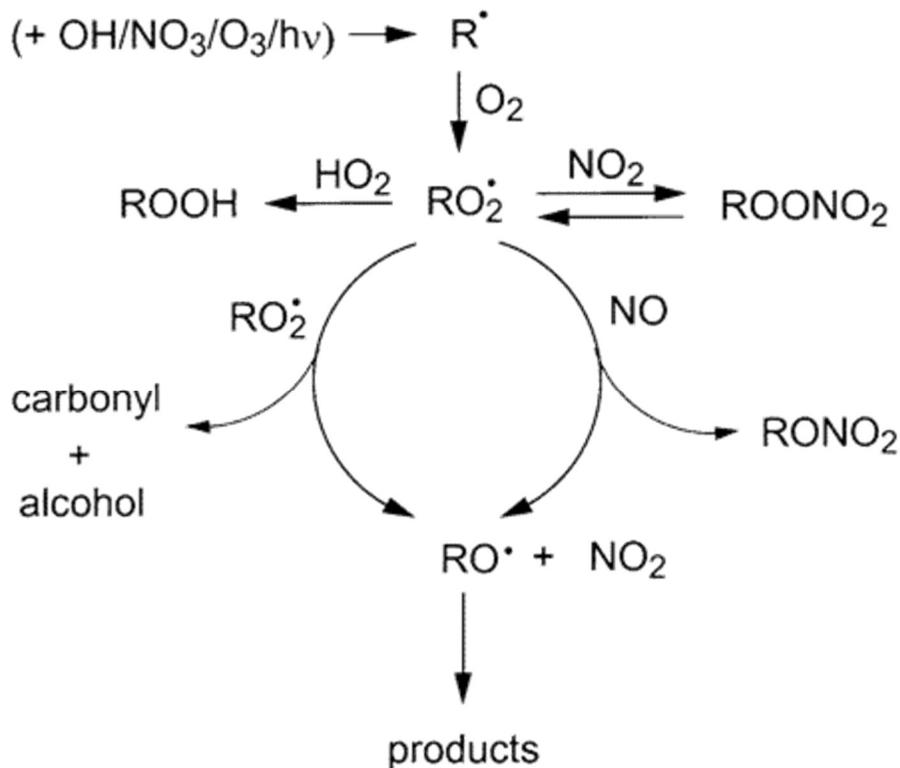


Figure 1 Typical schematic of atmospheric chemistry pathways for VOC reactions with hydroxyl and nitrate radicals, ozone, and light. (Atkinson & Arey, 2003).

Ecosystem fluxes of compounds

Terrestrial and marine environments are the largest source and sink of VOCs, including reactive trace gases, making biospheric fluxes a key controller of the oxidative state of the atmosphere (Monson & Holland, 2001). Land-air fluxes have been studied more comprehensively than air-ocean fluxes and thus provide a nice framework for the importance of understanding ecosystem emissions and deposition of VOCs.

Terrestrial ecosystem VOC fluxes

Air-land fluxes of VOCs are fairly well studied, especially in regions with large land areas occupied by forests. These terrestrial flux studies have highlighted the importance of characterizing the compounds in exchange with the environment, as they impact air quality and global budgeting of greenhouse gases. Due to their ability to influence atmospheric chemistry and thus local and regional pollution, quantifying emissions from terrestrial sources has become

increasingly needed to understand controls on urban pollution. While common VOCs like isoprene and methanol have been the subject of land-air flux studies for many years, the importance of trace gases in flux with the environment is a relatively new area of research. A tandem of studies in 2012 and 2013 in an orange grove in California illustrated fluxes of common VOCs as well as unexplored VOCs (Fares et al., 2012, Park et al., 2013). These studies showed a wide range of previously unexplored VOCs exist in the atmosphere and are in active exchange with the environment. Furthermore, the methods for determining vertical gradients of compounds as well as flux calculations were illustrated in a way that can be replicated in coastal marine environments.

Marine VOC Fluxes

Understanding VOC fluxes in marine environments (Figure 2) is important for determining oceanic sources of compounds that influence local and regional air quality as well as contribute to pollution. Marine VOC fluxes are thought to be primarily mediated in two ways: (1) turbulent and diffusive transfer and (2) through bubble ebullition at the air-water interface (Upstill-Goddard, 2006). However, the controlling processes of marine VOC emissions and aerosol formation are still poorly understood (Yu & Li, 2021).

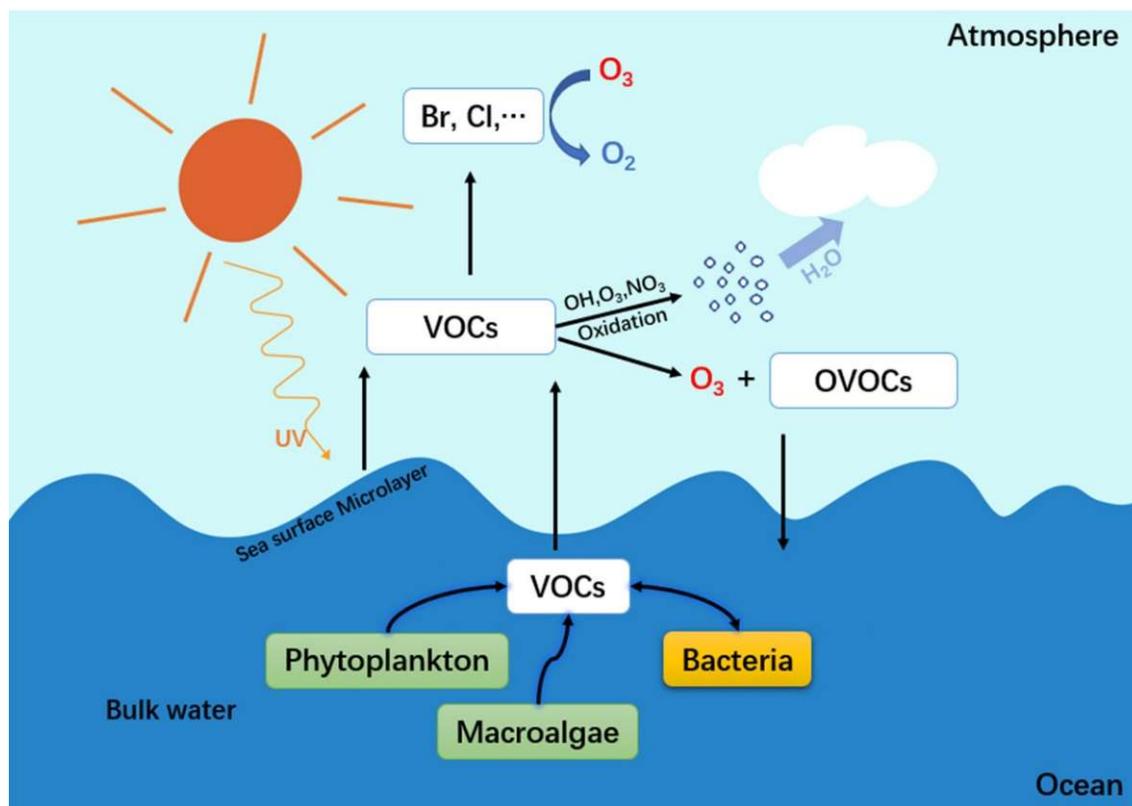


Figure 2 Simplified schematic of VOC generation within and emission from the ocean, atmospheric chemistry of VOCs, and deposition of VOCs into the ocean. (Yu & Li, 2021)

Turbulent and diffusive transport can be described by the concept of a diffusive sub-layer on either side of the air-water interface (Upstill-Goddard, 2006). These sub-layers create resistance for gas transfer, leading to the development of concentration gradients on either side of the interface. The sublayer that causes the rate limiting step in transfer between the atmosphere and ocean is determined by the affinity each compound has for being in the aqueous phase (Upstill-Goddard, 2006). This is often described by the Henry's constant of a given compound. It is expected that compounds with higher Henry's constants will have a greater affinity for the aqueous phase and will more readily partition into the ocean while compounds with lower Henry's constants will show greater emission from the ocean's surface (Sander, 2015). For compounds that are soluble (ie. higher Henry's constant), there is greater resistance to gas exchange in the atmospheric sub-layer than in the aqueous sub-layer, whereas for sparingly soluble gases, the aqueous sub-layer provides greater resistance (Upstill-Goddard, 2006). Most compounds of interest fall into the latter category; thus, their emission is limited by transport through the aqueous sub-layer.

The concept of diffusive sub-layers has given rise to several models of gas transfer in aqueous environments. The most widely accepted model is surface renewal in which turbulent eddies beneath the aqueous sub-layer continuously and randomly renew the water within the sub-layer (Upstill-Goddard, 2006). This aids in maintaining a concentration gradient within the sub-layer, which drives partitioning of compounds between the gas and aqueous phases.

Bubble ebullition at the sea surface is primarily driven by surface winds and cause direct emissions of aerosols composed of sea salt and organics (Yu & Li, 2021). These are classified as primary organic aerosols (POA). Marine SOA are formed through atmospheric oxidation of VOCs emitted from the ocean (Yu & Li, 2021). Marine organic aerosols (both POA and SOA) can impact climate directly—through scattering solar radiation—and indirectly—by acting as cloud condensation nuclei and altering cloud properties (reflectivity, extent, and lifetime). Previous studies have found higher concentrations of organics in aerosols in coastal areas than over the open ocean, thus highlighting the need for a greater understanding of VOC fluxes in coastal areas.

VOC emissions from marine environments have been shown to impact both oxidant loadings and SOA formation in the atmosphere through studies and modeling efforts (eg. Mayer et al., 2020, Novak & Bertram, 2020). However, most studies focus on air-sea exchange of gases in remote marine environments. While this is important for global budgeting of certain compounds, coastal

environments are usually very biogeochemically and physically dynamic meaning the results from remote regions cannot be extrapolated to include coastal regions (Phillips et al., 2021).

Past Studies on Compounds of Interest

There are many compounds of interest for air-sea flux research, some of which are better studied than others. Acetone and DMS have received more attention than other VOCs due to their prevalence in the environment and known influence over cloud microphysics. Isoprene accounts for around half of all non-methane hydrocarbons, and thus is influential in atmospheric chemistry.

Dimethyl Sulfide

Dimethyl sulfide was originally recognized as a compound of interest in 1987 when the CLAW hypothesis was proposed. The CLAW hypothesis suggests the creation of a feedback mechanism in which DMS is emitted into the troposphere by phytoplankton where it undergoes oxidation to sulfate particles (Andreae & Crutzen, 1997). These sulfate particles then act as cloud condensation nuclei, the concentration of which can alter cloud albedo and in turn, climate. Large scale changes in climate affect phytoplankton populations and locations in the ocean, thus closing the feedback loop (Andreae & Crutzen, 1997).

DMS is a product of dimethyl sulfoniopropionate (DMSP) in the surface ocean (Novak & Bertram 2020). DMSP has wide variations in intracellular concentration between different phytoplankton species in the ocean, making it difficult to predict regional DMS concentrations using chemical or physical parameters (Andreae & Crutzen, 1997). Once DMS has been created in the marine mixed layer, it is subject to several removal mechanisms, including emission to the atmosphere. Past studies on the photooxidation of DMS have shown it is mainly oxidized by the OH radical, which leads to production of sulfur dioxide, methyl sulfonic acid, dimethyl sulfoxide, and dimethyl sulfone (Andreae & Crutzen, 1997). Low volatility products formed from the oxidation chemistry of DMS and the OH radical can further oxidize to sulfate, which contributes to new particle formation (Novak & Bertram, 2020).

Andreae et al. performed one of the first studies on concentrations of DMS in both remote and more coastal marine environments in 1985. Five sites were chosen and concentrations of DMS were monitored at each using gas chromatography. The study found that in remote marine areas, DMS concentrations remain high and do not vary much, while DMS concentrations in the continental region showed greater variability. Similarly, the remote marine sites showed greater diurnal variability than the continental site (Figure 3). The reduced diurnal variability at the

continental site was attributed to OH^- oxidation not being the dominant reaction pathway for DMS in the presence of urban influenced (ie. polluted) air masses (Andreae et al., 1985). The study also took air mass origin into account for the continental site. When air mass trajectories were correlated with DMS concentrations, they found that the lowest concentrations of DMS occurred when air masses originated over the North American continent (Andreae et al., 1985). This study verified the emerging idea that DMS is emitted from marine sources and not from biogenic or anthropogenic continental sources.

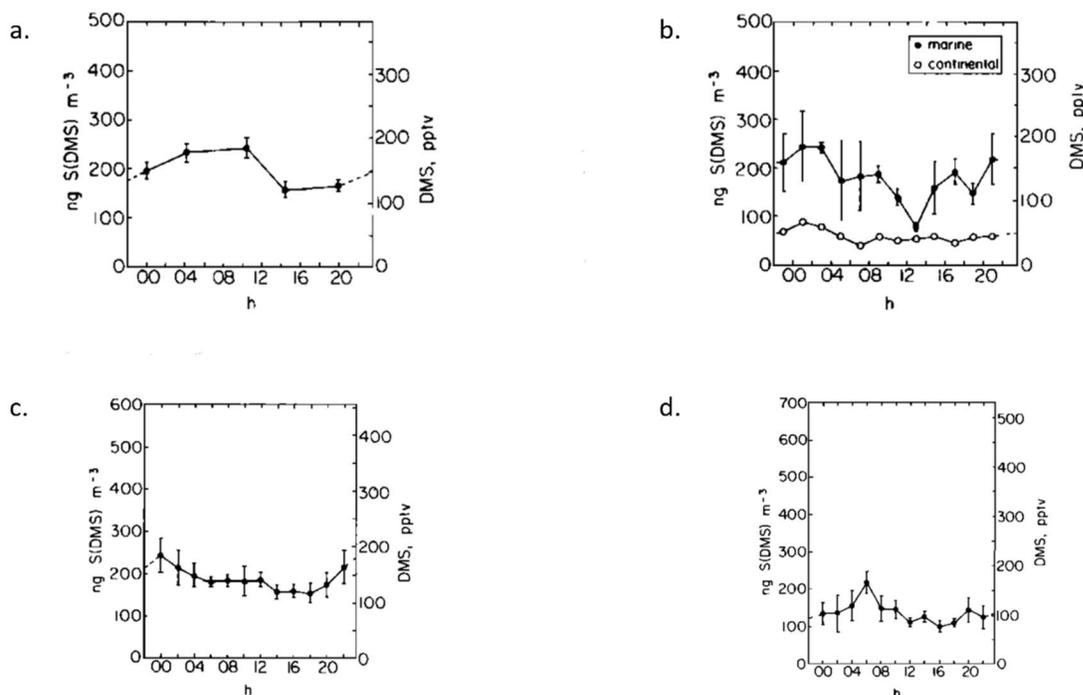


Figure 3 Diurnal profiles for each of the 5 study sites. (a): DMS concentrations in the remote Equatorial Pacific in 1982; (b): DMS concentrations in North Atlantic (1984) for both remote marine (solid dots) and continental (open circles); (c): DMS concentrations in Cape Grim (1984); (d): DMS concentrations in the Bahamas (1983) (Andreae et al., 1985).

More recently, coastal environments have received more attention due to the connection of DMS to biological marine species. Sinha et al. created several mesocosms to study the controls of BVOC fluxes at the air-ocean interface. These BVOCs included DMS, acetone and isoprene (the latter two are discussed below). In the mesocosms, DMS was always emitted from the water into the air and emission intensity was consistent throughout the day with no indication of sunlight intensity dependence (Sinha et al., 2007).

Phillips et al. conducted a study at Penlee Point Atmospheric Observatory on the coast of the southwest UK to determine air-sea fluxes of acetone, acetaldehyde, and DMS during the spring,

using eddy covariance. Air-water exchange was investigated in two distinct marine ecosystems: an open water region and a more terrestrial influenced sound with two estuary feeds. The mean eddy covariant fluxes from the study showed that DMS had a net sea-to-air emission in both locations (Figure 4). The sound location had reduced DMS emission which the authors contributed to lower wind speeds combined with lower seawater concentrations of DMS. The contributions of the estuaries indicate that coastal regions with freshwater influence will have differing controls on fluxes and thus vertical gradients.

There is consensus among literature that DMS is emitted from the ocean into the atmosphere, in both open ocean and coastal environments. However, fewer studies have focused on coastal environments where complex land-sea dynamics may influence controls on DMS emissions, namely the presence of marine organisms that contain DMSP.

Acetone

Acetone is a common oxygenated VOC and is the second most abundant atmospheric carbonyl compound (Dixon et al., 2014, Fischer et al., 2012). It influences the availability of nitrogen oxides and is a source of hydroxyl radicals in the upper troposphere, indicating that it alters the oxidative capacity of the atmosphere (Fischer et al., 2012). The ocean is thought to play a major role in controlling atmospheric acetone levels, as oceanic photochemical and biological processes can produce and consume acetone (Fischer et al., 2012). The ocean's role in atmospheric budgeting of acetone was not considered until 2002, and since then there has been much debate about the net direction of acetone (ie. if the ocean acts as a source or sink) (Taddei et al., 2009).

The first two major studies regarding acetone flux with seawater yielded opposite results. A 2002 model of the global acetone budget concluded that the ocean must act both as a source and a sink in order for acetone concentrations to match aircraft observations over oceans (Jacob et al., 2002). The study proposed a source in the South Pacific and a sink in the Arctic Ocean to align with atmospheric observations of acetone concentrations. Additionally, to complete the global budgeting of acetone, a net global source was proposed (Jacob et al., 2002). In 2005, one of the first near surface studies was performed regarding vertical fluxes of acetone. Measurements were made aboard a cruise throughout the Pacific in the spring/early summer. The study found that acetone fluxes measured by eddy covariance were all negative, indicating a net flux into the ocean, regardless of the location of the ship (ie. coastal or remote) (Marandino et al., 2005).

Later studies continued to refine the hypothesis of net oceanic production or deposition for acetone. The 2007 Sinha et al. mesocosm study found that the direction of acetone flux was correlated to both the presence of phytoplankton and sunlight. Throughout the study acetone exhibited a strong diurnal profile with a maximum flux in the early afternoon and a minimum flux in the morning (Sinha et al. 2007). When there was no sun or insufficient sunlight, there was a net deposition of acetone into the ocean, whereas in the presence of strong sunlight acetone was emitted from the ocean. Additionally, higher concentrations of phytoplankton corresponded to higher concentrations of acetone emitted (Sinha et al., 2007). Data from a transatlantic research vessel supported the mesocosm study, as eddy covariance calculations yielded areas of both emission and deposition. The study found that acetone had a net emission in the subtropics, but net deposition at higher latitudes (Yang et al., 2014). However, the directional flux was not found to be correlated with the concentration of dissolved organic matter in the ocean.

Recent studies in coastal environments have shown acetone has unidirectional fluxes into the ocean, as indicated by negative vertical gradient and eddy covariance calculations (Figure 4). It has also been shown that terrestrially influenced air can lead to higher concentrations of acetone in the coastal marine atmosphere which consequently leads to greater deposition into the ocean (Phillips et al., 2021).

While acetone is one of the better studied compounds with regards to air-ocean fluxes, it is clear that there is still a lack of understanding surrounding the controls of acetone emission from, or deposition into, the ocean. It is clear the ocean plays a role in the global acetone budget; however further research is needed in order to determine the net source and sink potentials of marine environments.

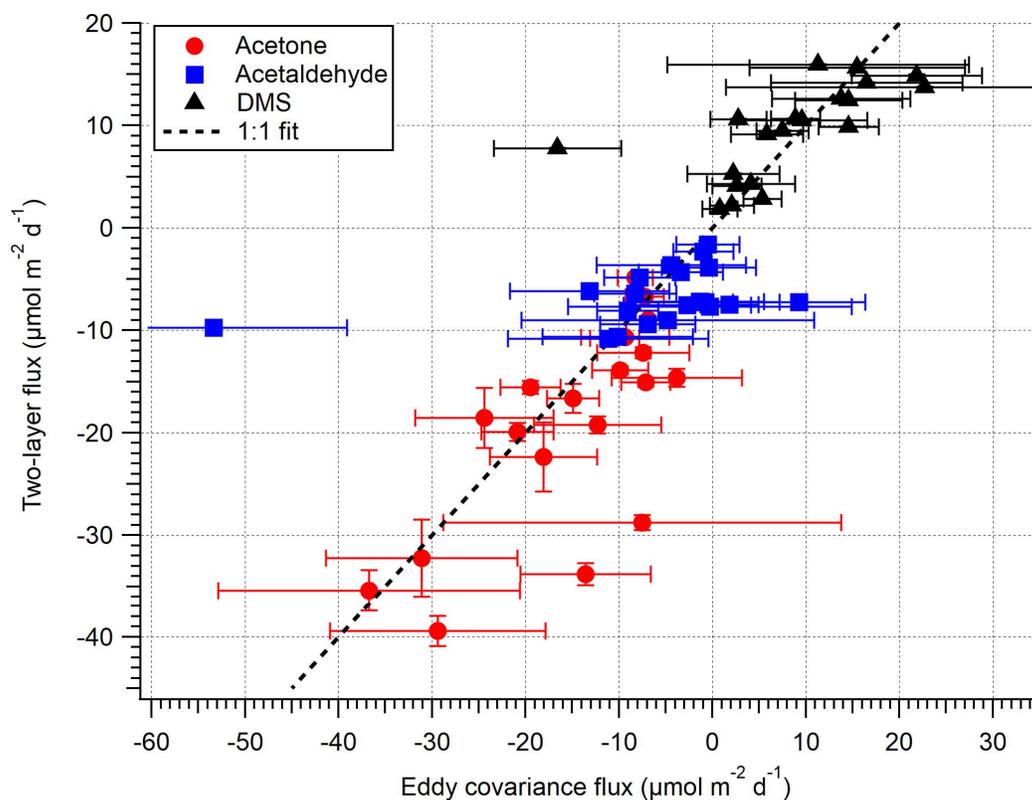


Figure 4 Eddy covariance flux plotted against two-layer flux for acetone, acetaldehyde, and DMS, with error bars. 1:1 fit line plotted in background. Negative eddy covariance and two-layer flux indicate net deposition, while positive eddy covariance and two-layer flux indicate net emissions. (Phillips et al., 2021).

Isoprene

Isoprene accounts for approximately half of all biogenic nonmethane hydrocarbon emissions (Hackenberg et al., 2017). The primary source of isoprene is terrestrial plants, but it has been established that it is also produced by marine algae as a secondary metabolic product (Pacifico et al., 2009, Phillips et al., 2021). The carbon-carbon double bonds make isoprene highly reactive with nitrate, hydroxyl radicals, and ozone, thus it has a short atmospheric lifetime. The oxidation of isoprene aids in regulating concentrations of tropospheric ozone and methane (Pacifico et al., 2009). Additionally, isoprene is a precursor for secondary organic aerosols, thus influencing the radiative balance of the atmosphere.

The presence of isoprene in ocean water was first established in 1992, but relatively few studies have been performed on air-sea fluxes since then (Shaw et al., 2010). Between 1997 and 2001, three studies on air-sea fluxes of select biogenic alkenes, including isoprene, were performed at a remote coastal location in Ireland. Each of these three studies showed distinct diurnal profiles of isoprene concentration with sharp peaks occurring mid-day and the lowest concentrations

occurring at night (Lewis et al. 1997, Lewis et al., 1999, Lewis et al., 2001). These mid-day peaks were correlated with times of highest light and temperature—both of which are known environmental controls on isoprene (Pacifico et al., 2009).

Hackenberg et al. performed a more comprehensive analysis of isoprene fluxes from the ocean using data from four cruises throughout the Atlantic and Arctic oceans. All the data collected was from more remote ocean locations, and all isoprene fluxes remained fairly constant throughout the day, contradicting the Lewis et al. studies (Hackenberg et al., 2017). However, the magnitude of isoprene fluxes was comparable to past studies (Figure 5).

More recently, Uning et al. measured isoprene fluxes using a floating flux chamber outfitted with adsorbent cartridges. Samples were analyzed using thermal desorption GC-MS. The study compared open ocean fluxes with coastal regions and found that isoprene emissions were evenly distributed throughout the varying regions. However, isoprene fluxes were correlated with both regional upwelling as well as dissolved inorganic nitrogen concentrations (Uning et al., 2021). This suggests that fluxes of isoprene may correspond to surface water nutrients in upwelling regions.

Since its discovery in seawater nearly 30 years ago, subsequent studies have consistently shown that the ocean is a source of isoprene. However, controls on emissions are not well understood and there is discrepancy regarding any diurnal patterns of emissions correlating to light and temperature. Further constraining marine sources and daily patterns of isoprene emission are important for understanding coastal atmospheric chemistry as well as remote marine radiative balance.

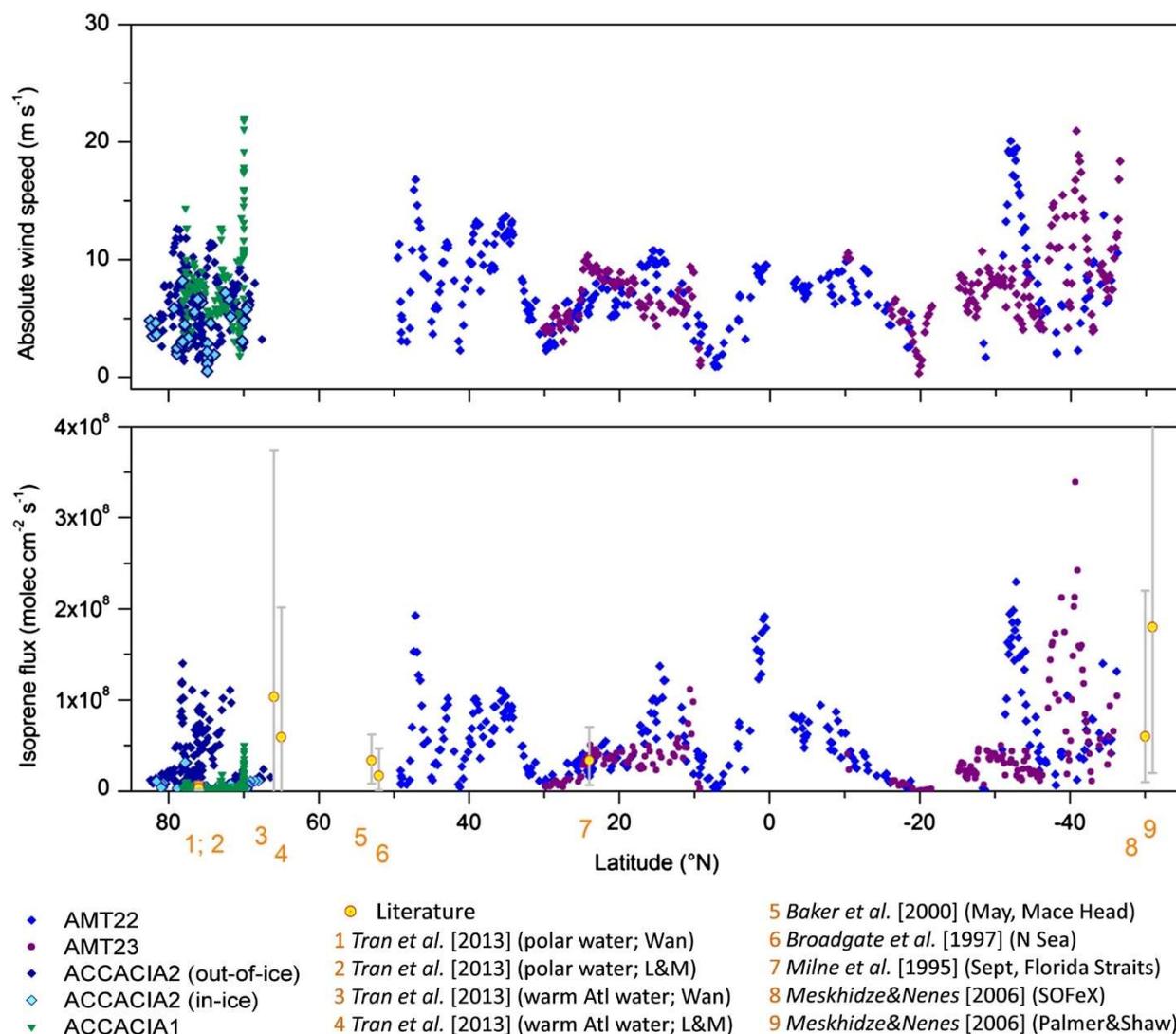


Figure 5 Results from four ocean cruises throughout the Arctic and Atlantic Oceans (shown in varying shades of blue and purple) compared to results of Isoprene fluxes from past studies (shown at yellow dots with corresponding study number shown beneath). (Hackenberg et al. 2017)

Methodological Development Case Study

The Yale Coastal Field Station is a data collection hub for the NASA AEROMMA campaign. The goal for this site is to aid in determining accurate atmospheric chemistry and aerosol dynamics in the marine environment (“AEROMMA Goals”). As part of this study, a high-resolution mass spectrometer was stationed at YCFS to perform online measurements of VOCs for the purpose of calculating vertical gradients and eddy covariance.

Site Characterization

The Yale Coastal Field Station is located on the Long Island Sound in Guilford, CT (41.2583°N, 72.7312°W) (Figure 6). The YCFS is in the NYC metro area, however its position minimizes local urban influences from Connecticut (Rogers et al., 2020). Ambient air quality samples were collected at three vertical heights above the ocean surface: 0m, 5m, and 10m. The



Figure 6 Satellite Image of Connecticut and Long Island Sound with location of the Yale Coastal Field Station marked in red. Image obtained from Google Earth.

sampling inlets at each height are positioned facing south towards the Long Island Sound in order to capture onshore air-flow and reduce air mass contributions from inland urban areas. Air mass samples were collected and analyzed using online Vocus proton transfer reaction time of flight mass spectrometry (PTR-ToF-MS). PTR-MS is highly sensitive and is optimal for analysis of VOC mixtures at low concentrations (Lindinger & Jordan, 1998). Each sampling cycle consisted of 20 second sampling intervals at each of the three inlet heights (0m, 5m, and 10m), followed by a 10-minute sampling period at the 10m inlet for eddy-covariant flux measurements. Each inlet line had the same tubing length to avoid varying retention times of air within the inlet lines.

Wind data was also collected using a sonic anemometer to determine the origin of the air masses being sampled. Upon analysis, it was confirmed that average wind direction was south to north, meaning that there was primarily onshore flow (Figure 7).

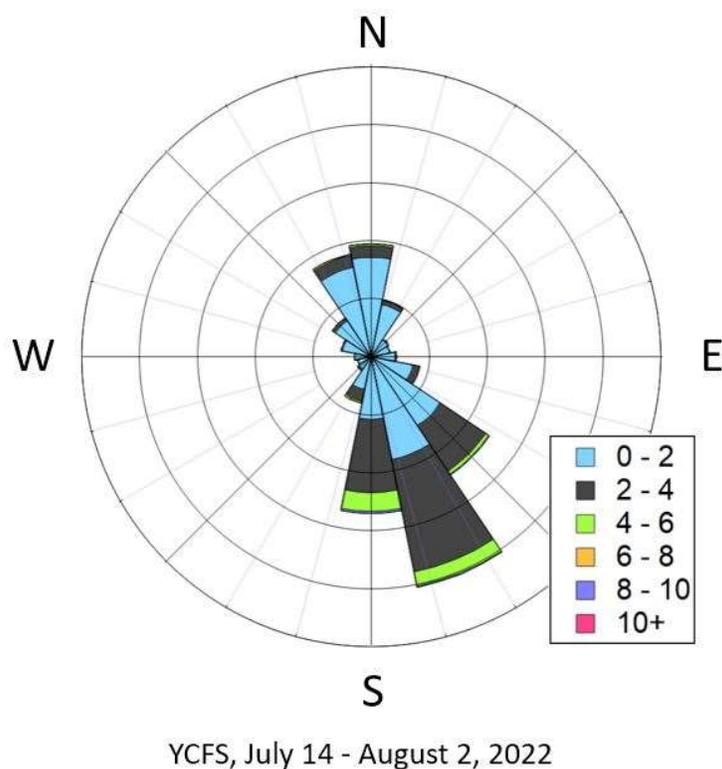


Figure 7 Wind rose showing direction and speed of average winds from sonic data collected at YCFS from July 14, 2022 – August 2, 2022.

Preliminary Results

A brief look at some of the data collected at the YCFS shows that the vertical gradients of acetone at this site are consistent with that of previous studies, but the vertical gradients of DMS and isoprene are less clear. All data analyzed for these three compounds was collected on July 24, 2022. Only the isoprene data was averaged down from the raw 10 Hz to 1 second averages.

The diurnal profile of acetone ion abundance from July 24, 2022, show variability throughout the day with a peak in the late morning around 11:00 AM (Figure 8A). However, it is not possible to tell if this is a prevailing trend until the rest of the data is analyzed. Additionally, the profile may be consistent with daily changes in wind direction, so the origin of the air mass being sampled may be from an urban influenced area. Acetone abundances show clear variations between the different inlet heights as shown in Figure 8B. When onshore wind flows are considered (in early morning)—therefore reducing contributions from inland urban locations—the inlet closest to the waters surface consistently had lower ion abundances than the middle inlet, which was lower than

the top inlet. This pattern suggests the ocean acts as a net sink for acetone, which is supported by the high Henry's constant of acetone, indicating that acetone is relatively soluble (Sander, 2015).

The results for DMS are not as clear as for acetone. Consistent with literature, there does not appear to be a diurnal profile (Figure 9A). The first two sampling periods of the day are inconsistent with the rest of the day; however, it is unclear what is driving the variability in the abundance of DMS. DMS is detected at each of the inlet heights with slightly higher ion abundances of DMS at the 0m inlet than the 5m and 10m inlets (Figure 9B). The slightly higher levels of DMS near the ocean surface do indicate emission, as is consistent with past studies. The relatively low ion abundances and limited vertical gradation of DMS, may be explained by the transport, and consequent dilution, of DMS from further offshore as opposed to production of DMS near the coast.

Data from July 24, 2022, for isoprene was averaged down to one second intervals from the 10 Hz raw data, so direct comparisons to DMS and acetone must be made with caution. The averaged data shows high variability in isoprene concentrations for each of the three inlets throughout the day, with elevated concentrations at each inlet in the afternoon (Figure 10A). This may be due to a change in wind direction from onshore flow to terrestrial based winds. Looking at a sampling period with onshore wind flow, there is not a clear gradient in ion abundance between the three inlets (Figure 10B).

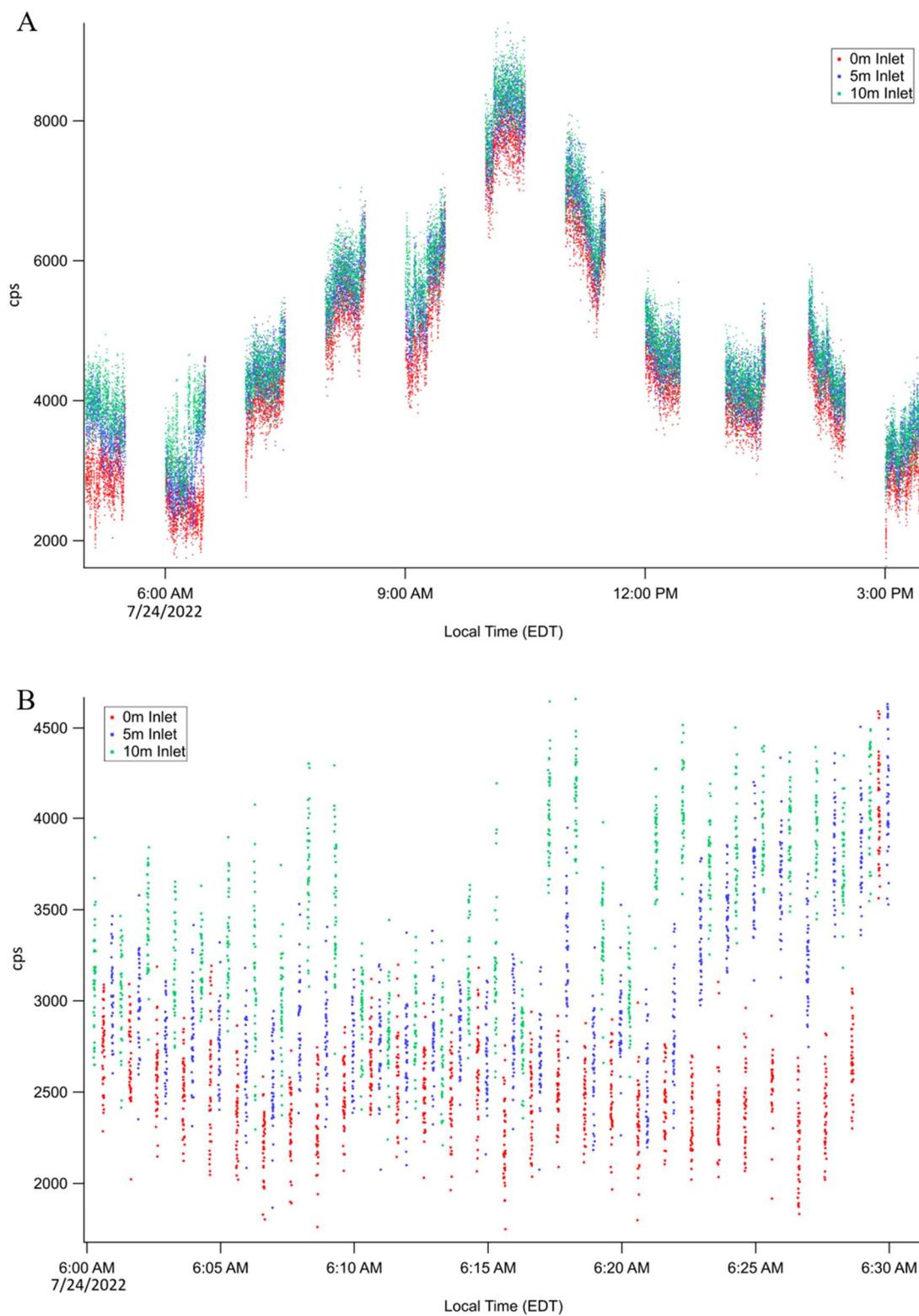


Figure 8 Ion abundance of acetone at the YCFS during July 24, 2022, sampling period. Panels: (A) Diurnal profile of ion abundance of acetone (shown as counts per second (cps) on y-axis). Gaps in data are due to removed eddy covariance data sampling. (B) Representative 30-minute sampling period (6:00 AM – 6:30 AM) during onshore wind flow.

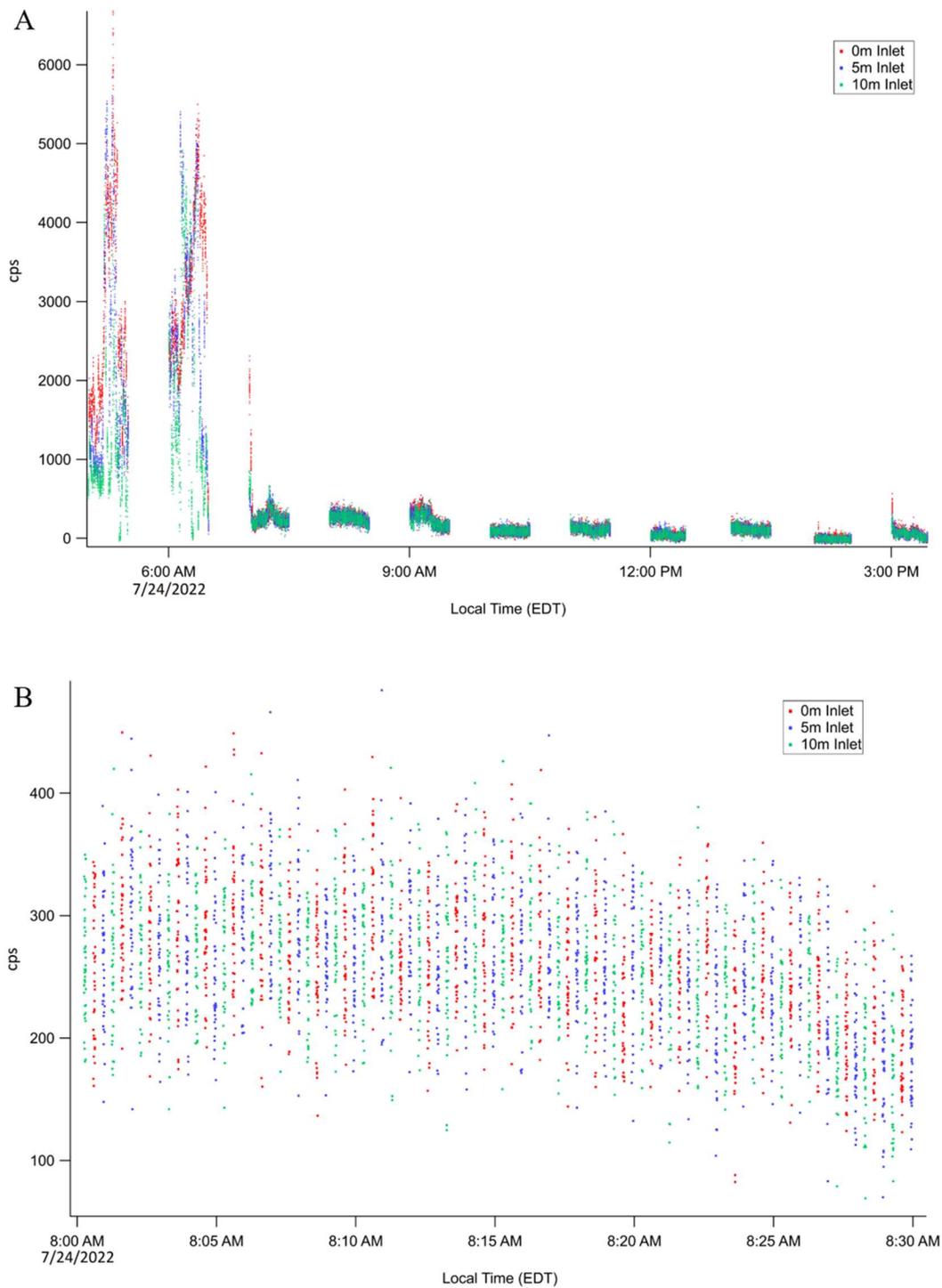


Figure 9 Ion abundance of DMS at the YCFS during July 24, 2022, sampling period. Panels: (A) Diurnal profile of ion abundance of DMS (shown as counts per second (cps) on y-axis). Gaps in data are due to removed eddy covariance data sampling. (B) Representative 30-minute sampling period (8:00 AM – 8:30 AM) during onshore wind flow.

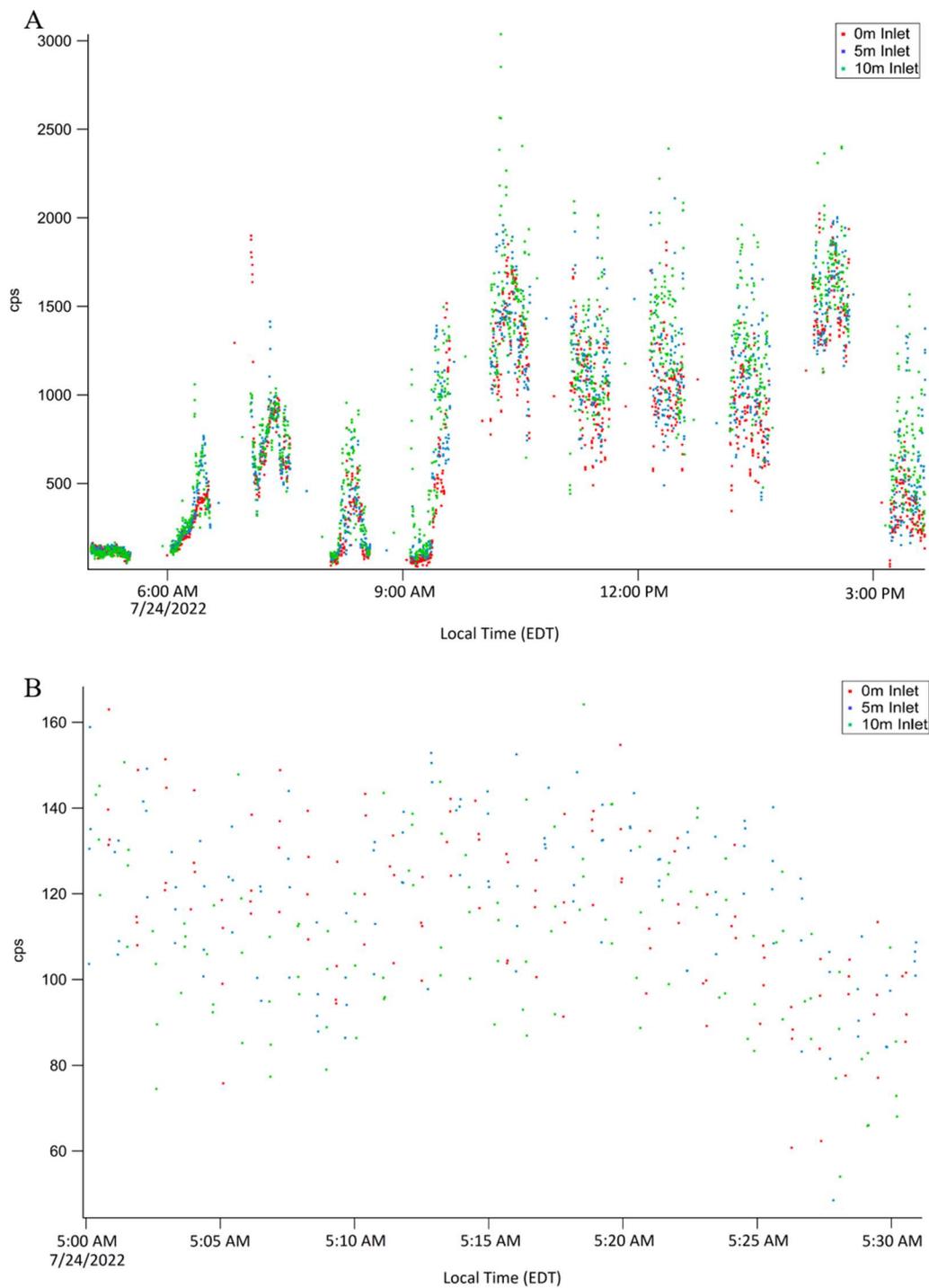


Figure 10 Ion abundance of isoprene at the YCFS during July 24, 2022, sampling period. Panels: (A) Diurnal profile of ion abundance of isoprene (shown as counts per second (cps) on y-axis). Gaps in data are due to removed eddy covariance data sampling. (B) Representative 30-minute sampling period (5:00 AM – 5:30 AM) during onshore wind flow.

Next Steps/Further Research

The data used in this project is from only one day over the full summer of 2022. The rest of the data will be preliminarily analyzed in a similar fashion to identify any recurring daily trends as well as looking at spatial and temporal differences over the course of the full data collection period. Acetone shows a diurnal trend, which if this is recurring throughout the summer, it will be interesting to investigate if it is due to change in wind direction, causing a terrestrial urban influenced air mass to be sampled, or due to oceanic emission patterns.

More compounds will be analyzed, particularly nitrogen containing species, as a previous study at this site has established the presence of amine compounds (Ditto et al., 2022). The full extent of the effects of nitrogen containing compounds—particularly reactive compounds (ie. NO_x , NH_3 , NO_3)—on climate and human health are unknown, however their contribution to ozone production and brown carbon formation has been established (Ditto et al., 2022). Thus, determining potential fluxes of amine compounds from the ocean will inform regional atmospheric chemistry occurring. Nitrogen containing compounds have been found to be higher in our study location when compared to inland sites without marine influence. The nitrogen-containing species found at the site (ex. CHON ($\text{O/N} < 3$) and CHON ($\text{O/N} \geq 3$)) have polarity and Henry's law coefficients that suggest that partitioning into and out of the aqueous phase is possible (Ditto et al. 2020).

While this project focuses on the air-water surface interactions of the Long Island Sound, the observations made of ocean VOC emissions at this site will likely be informative at other coastal locations.

Conclusion

Through the investigation of air-sea exchange of acetone, dimethyl sulfide, and isoprene, it has become increasingly clear that the ocean plays a role in global budgeting of VOCs. The results of existing literature coupled with the preliminary results from the YCFS show the ocean plays an active role in controlling the emissions of these three compounds that have influence over climate and atmospheric chemistry. However, there is still discrepancy in the controls on air-sea fluxes of acetone, isoprene, and to a lesser degree DMS—a discrepancy that likely extends to a wider range of VOCs in active air-sea exchange. This highlights a need for further research on the drivers behind emissions and deposition of VOCs in order to gain a more complete understanding of the ocean's role in VOC exchange with the environment.

References

- Andreae, M. O., & Crutzen, P. J. (1997). Atmospheric Aerosols: Biogeochemical Sources and Role in Atmospheric Chemistry. *Science*, 276(5315), 1052–1058.
<https://doi.org/10.1126/science.276.5315.1052>
- Andreae, M. O., Ferek, R. J., Bermond, F., Byrd, K. P., Engstrom, R. T., Hardin, S., Houmère, P. D., LeMarrec, F., Raemdonck, H., & Chatfield, R. B. (1985). Dimethyl sulfide in the marine atmosphere. *Journal of Geophysical Research: Atmospheres*, 90(D7), 12891–12900.
<https://doi.org/10.1029/JD090iD07p12891>
- Atkinson, R. (2000). Atmospheric chemistry of VOCs and NOx. *Atmospheric Environment*, 34(12), 2063–2101. [https://doi.org/10.1016/S1352-2310\(99\)00460-4](https://doi.org/10.1016/S1352-2310(99)00460-4)
- Atkinson, R., & Arey, J. (2003). Atmospheric Degradation of Volatile Organic Compounds. *Chemical Reviews*, 103(12), 4605–4638. <https://doi.org/10.1021/cr0206420>
- Charlson, R. J., Lovelock, J. E., Andreae, M. O., & Warren, S. G. (1987). Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate. *Nature*, 326(6114), Article 6114. <https://doi.org/10.1038/326655a0>
- Ditto, J. C., Machesky, J., & Gentner, D. R. (2022). Analysis of reduced and oxidized nitrogen containing organic compounds at a coastal site in summer and winter. *Atmospheric Chemistry and Physics*, 22(5), 3045–3065. <https://doi.org/10.5194/acp-22-3045-2022>
- Dixon, J. L., Beale, R., Sargeant, S. L., Tarran, G. A., & Nightingale, P. D. (2014). Microbial acetone oxidation in coastal seawater. *Frontiers in Microbiology*, 5.
<https://www.frontiersin.org/articles/10.3389/fmicb.2014.00243>
- Fares, S., Park, J.-H., Gentner, D., Weber, R., Ormeño, E., Karlik, J., & Goldstein, A. (2012). Seasonal cycles of biogenic volatile organic compound fluxes and concentrations in a California Citrus orchard. *Atmospheric Chemistry & Physics*, 12, 9865–9880.
<https://doi.org/10.5194/acp-12-9865-2012>
- Fischer, E. V., Jacob, D. J., Millet, D. B., Yantosca, R. M., & Mao, J. (2012). The role of the ocean in the global atmospheric budget of acetone. *Geophysical Research Letters*, 39(1).
<https://doi.org/10.1029/2011GL050086>
- Goldstein, A. H., & Galbally, I. E. (2007). Known and Unexplored Organic Constituents in the Earth's Atmosphere. *Environmental Science & Technology*, 8.
- Google Earth. (n.d.). Retrieved December 13, 2022, from
<https://earth.google.com/web/@41.48743867,-72.80867428,29.98639804a,378899.78169736d,35y,-0.00000081h,1.92788756t,0r>

- Guenther, A., Hewitt, C. N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., Mckay, W. A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J., & Zimmerman, P. (1995). A global model of natural volatile organic compound emissions. *Journal of Geophysical Research: Atmospheres*, *100*(D5), 8873–8892. <https://doi.org/10.1029/94JD02950>
- Hackenberg, S. C., Andrews, S. J., Airs, R., Arnold, S. R., Bouman, H. A., Brewin, R. J. W., Chance, R. J., Cummings, D., Dall’Olmo, G., Lewis, A. C., Minaeian, J. K., Reifel, K. M., Small, A., Tarran, G. A., Tilstone, G. H., & Carpenter, L. J. (2017). Potential controls of isoprene in the surface ocean. *Global Biogeochemical Cycles*, *31*(4), 644–662. <https://doi.org/10.1002/2016GB005531>
- Jacob, D. J., Field, B. D., Jin, E. M., Bey, I., Li, Q., Logan, J. A., Yantosca, R. M., & Singh, H. B. (2002). Atmospheric budget of acetone. *Journal of Geophysical Research: Atmospheres*, *107*(D10), ACH 5-1-ACH 5-17. <https://doi.org/10.1029/2001JD000694>
- Jung, D., de la Paz, D., Notario, A., & Borge, R. (2022). Analysis of emissions-driven changes in the oxidation capacity of the atmosphere in Europe. *Science of The Total Environment*, *827*, 154126. <https://doi.org/10.1016/j.scitotenv.2022.154126>
- Kampa, M., & Castanas, E. (2008). Human health effects of air pollution. *Environmental Pollution*, *151*(2), 362–367. <https://doi.org/10.1016/j.envpol.2007.06.012>
- Laboratory (CSL), N. C. S. (n.d.). *AEROMMA Goals*. Retrieved December 19, 2022, from <https://csl.noaa.gov/projects/aeromma/science/goals.html>
- Lewis, A. C., Bartle, K. D., Heard, D. E., McQuaid, J. B., Pilling, M. J., & Seakins, P. W. (1997). In situ , gas chromatographic measurements of non-methane hydrocarbons and dimethylsulfide at a remote coastal location (Mace Head, Eire) July–August 1996. *Journal of the Chemical Society, Faraday Transactions*, *93*(16), 2921–2927. <https://doi.org/10.1039/A701566F>
- Lewis, A. C., Carpenter, L. J., & Pilling, M. J. (2001). Nonmethane hydrocarbons in Southern Ocean boundary layer air. *Journal of Geophysical Research: Atmospheres*, *106*(D5), 4987–4994. <https://doi.org/10.1029/2000JD900634>
- Lewis, A. C., McQuaid, J. B., Carslaw, N., & Pilling, M. J. (1999). Diurnal cycles of short-lived tropospheric alkenes at a north Atlantic coastal site. *Atmospheric Environment*, *33*(15), 2417–2422. [https://doi.org/10.1016/S1352-2310\(98\)00429-4](https://doi.org/10.1016/S1352-2310(98)00429-4)
- Lindinger, W., & Jordan, A. (1998). Proton-transfer-reaction mass spectrometry (PTR–MS): Online monitoring of volatile organic compounds at pptv levels. *Chemical Society Reviews*, *27*(5), 347–375. <https://doi.org/10.1039/A827347Z>

- Marandino, C. A., De Bruyn, W. J., Miller, S. D., Prather, M. J., & Saltzman, E. S. (2005). Oceanic uptake and the global atmospheric acetone budget. *Geophysical Research Letters*, 32(15). <https://doi.org/10.1029/2005GL023285>
- Mayer, K. J., Wang, X., Santander, M. V., Mitts, B. A., Sauer, J. S., Sultana, C. M., Cappa, C. D., & Prather, K. A. (2020). Secondary Marine Aerosol Plays a Dominant Role over Primary Sea Spray Aerosol in Cloud Formation. *ACS Central Science*, 6(12), 2259–2266. <https://doi.org/10.1021/acscentsci.0c00793>
- Monson, R. K., & Holland, E. A. (2001). Biospheric Trace Gas Fluxes and Their Control over Tropospheric Chemistry. *Annual Review of Ecology and Systematics*, 32, 547–576.
- Novak, G. A., & Bertram, T. H. (2020). Reactive VOC Production from Photochemical and Heterogeneous Reactions Occurring at the Air–Ocean Interface. *Accounts of Chemical Research*, 53(5), 1014–1023. <https://doi.org/10.1021/acs.accounts.0c00095>
- Pacifico, F., Harrison, S. P., Jones, C. D., & Sitch, S. (2009). Isoprene emissions and climate. *Atmospheric Environment*, 43(39), 6121–6135. <https://doi.org/10.1016/j.atmosenv.2009.09.002>
- Park, J.-H., Goldstein, A. H., Timkovsky, J., Fares, S., Weber, R., Karlik, J., & Holzinger, R. (2013). Active Atmosphere-Ecosystem Exchange of the Vast Majority of Detected Volatile Organic Compounds. *Science*, 341(6146), 643–647. <https://doi.org/10.1126/science.1235053>
- Phillips, D. P., Hopkins, F. E., Bell, T. G., Liss, P. S., Nightingale, P. D., Reeves, C. E., Wohl, C., & Yang, M. (2021). Air–sea exchange of acetone, acetaldehyde, DMS and isoprene at a UK coastal site. *Atmospheric Chemistry and Physics*, 21(13), 10111–10132. <https://doi.org/10.5194/acp-21-10111-2021>
- Rogers, H. M., Ditto, J. C., & Gentner, D. R. (2020). Evidence for impacts on surface-level air quality in the northeastern US from long-distance transport of smoke from North American fires during the Long Island Sound Tropospheric Ozone Study (LISTOS) 2018. *Atmospheric Chemistry and Physics*, 20(2), 671–682. <https://doi.org/10.5194/acp-20-671-2020>
- Sander, R. (2015). Compilation of Henry’s law constants (version 4.0) for water as solvent. *Atmospheric Chemistry & Physics*, 15(8), 4399–4981. <https://doi.org/10.5194/acp-15-4399-2015>
- Shaw, S. L., Gantt, B., & Meskhidze, N. (2010). Production and Emissions of Marine Isoprene and Monoterpenes: A Review. *Advances in Meteorology*, 2010, e408696. <https://doi.org/10.1155/2010/408696>

- Sinha, V., Williams, J., Meyerhofer, M., Riebesell, U., Paulino, A. I., & Larsen, A. (2007). Air sea fluxes of methanol, acetone, acetaldehyde, isoprene and DMS from a Norwegian fjord following a phytoplankton bloom in a mesocosm experiment. *Atmos. Chem. Phys.*
- Soni, V., Singh, P., Shree, V., & Goel, V. (2018). Effects of VOCs on Human Health. In N. Sharma, A. K. Agarwal, P. Eastwood, T. Gupta, & A. P. Singh (Eds.), *Air Pollution and Control* (pp. 119–142). Springer. https://doi.org/10.1007/978-981-10-7185-0_8
- Taddei, S., Toscano, P., Gioli, B., Matese, A., Miglietta, F., Vaccari, F. P., Zaldei, A., Custer, T., & Williams, J. (2009). Carbon Dioxide and Acetone Air–Sea Fluxes over the Southern Atlantic. *Environmental Science & Technology*, 43(14), 5218–5222. <https://doi.org/10.1021/es8032617>
- Uning, R., Latif, M. T., Hamid, H. H. A., Mohd Nadzir, M. S., Khan, M. F., & Suratman, S. (2021). Sea-to-Air Fluxes of Isoprene and Monoterpenes in the Coastal Upwelling Region of Peninsular Malaysia. *ACS Earth and Space Chemistry*, 5(12), 3429–3436. <https://doi.org/10.1021/acsearthspacechem.1c00270>
- Upstill-Goddard, R. C. (2006). Air–sea gas exchange in the coastal zone. *Estuarine, Coastal and Shelf Science*, 70(3), 388–404. <https://doi.org/10.1016/j.ecss.2006.05.043>
- Yang, M., Beale, R., Liss, P., Johnson, M., Blomquist, B., & Nightingale, P. (2014). Air–sea fluxes of oxygenated volatile organic compounds across the Atlantic Ocean. *Atmospheric Chemistry and Physics*, 14(14), 7499–7517. <https://doi.org/10.5194/acp-14-7499-2014>
- Yu, Z., & Li, Y. (2021). Marine volatile organic compounds and their impacts on marine aerosol—A review. *Science of The Total Environment*, 768, 145054. <https://doi.org/10.1016/j.scitotenv.2021.145054>