Cyanobacterial Emissions of Biogenic Volatile Organic Compounds: Impacts on the Remote Marine Atmosphere

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Abstract

Atmospheric emissions of biogenic volatile organic compounds (BVOCs), including benzene, toluene, and xylene, have implications for climate change through the potential to form secondary organic aerosol (SOA) as well as their ability to impact the oxidative capacity of the atmosphere. Despite the importance of BVOCs, there have been relatively few measurements conducted in remote locations where biogenic sources may dominate, leading to a discrepancy between modeled and observed SOA yields. Recent, albeit sparse, evidence has suggested that marine phytoplankton have the ability to produce measurable quantities of BVOCs, particularly toluene, which may be an unaccounted source in aerosol models.

This work discusses the results of atmospheric VOC measurements over the remote North Atlantic Ocean during the May 2017 Phosphorus, Hydrocarbons, and Transcriptomics cruise aboard the *R/V Neil Armstrong*. Whole air canister samples (n = 160) were collected along a transect through the North Atlantic from Woods Hole, MA to Bermuda and back with 24 hour stops at nine stations encompassing different cyanobacterial populations. At each station, a diurnal time series of samples was collected, and samples were analyzed on a five-detector gas chromatography system.

Analysis of selected BVOCs indicated an additional biogenic source of toluene and other BVOCs such as isoprene, with high mixing ratios correlating with a *Synechococcus* bloom event encountered at station 9. The elevated mixing ratios identified at station 9 were found to increase both hydroxyl reactivities and potential SOA yields compared to the dataset, indicating marine cyanobacteria emissions of VOCs may have a large impact on marine environments.

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1.0 Introduction

The purpose of this study was to determine the magnitude of biogenic emissions in the North Atlantic marine atmosphere through measurements of traditional biogenic volatile organic compounds (BVOCs) such as isoprene and dimethyl sulfide, as well as less widely studied BVOCs including the aromatic hydrocarbons (AH) benzene, toluene, and xylene. Concurrent measurements of abiotic oceanic parameters and phytoplankton cell counts were also collected. A secondary aim was to calculate the secondary organic aerosol (SOA) formation potential of these observed BVOCs, as well as their impact on the oxidative capacity of the atmosphere; both of which are important implications for global climate.

1.1 Biogenic Volatile Organic Compounds

1.1.1 Definitions and Types

Volatile organic compounds (VOCs) are any organic compound with a high enough vapor pressure to exist in the gas phase in appreciable amounts. They are emitted by both biogenic and anthropogenic sources and play a dominant role in atmospheric chemistry. Emissions of VOCs from biological sources are classified as BVOCs, and globally, biogenic sources are the largest known producer, with biogenic emissions equating to approximately 90% of total emissions.[1,2]

BVOCs are separated into several groupings based on their structure and chemical properties (Figure 1). Globally, the most abundant BVOC in the atmosphere and the building block of AH is the hemiterpene isoprene (2-methyl-1,3-butadiene), a five-carbon chain whose function in the synthesis of other BVOCs is comparable to that of amino acids in protein synthesis; both are relatively simple molecules used to create quite complex compounds.[1] Two

isoprene units create a monoterpene ($C_{10}H_{16}$) while three isoprene units create a sesquiterpene ($C_{15}H_{24}$). Monoterpenes and sesquiterpenes may be either linear or cyclic, and are well-known for their aromatic properties, with compounds such as α-pinene and limonene contributing to the familiar scents of pine and citrus.[3] These terpenoid compounds are the most widely studied BVOCs.

Lesser studied BVOCs include non-aromatic BVOCs such as short chain alkanes, collectively known as green leaf volatiles, long chained alkanes such as heptadecane, and AH such as toluene.[4,5] This work will focus on AH, hydrocarbons with a conjugated pi-system that increases the stability of a molecule and subsequently decreases reactivity. Aromatic compounds can be identified by their alternating single and double bonds, depicting the ability of delocalized electrons to form resonance structures.

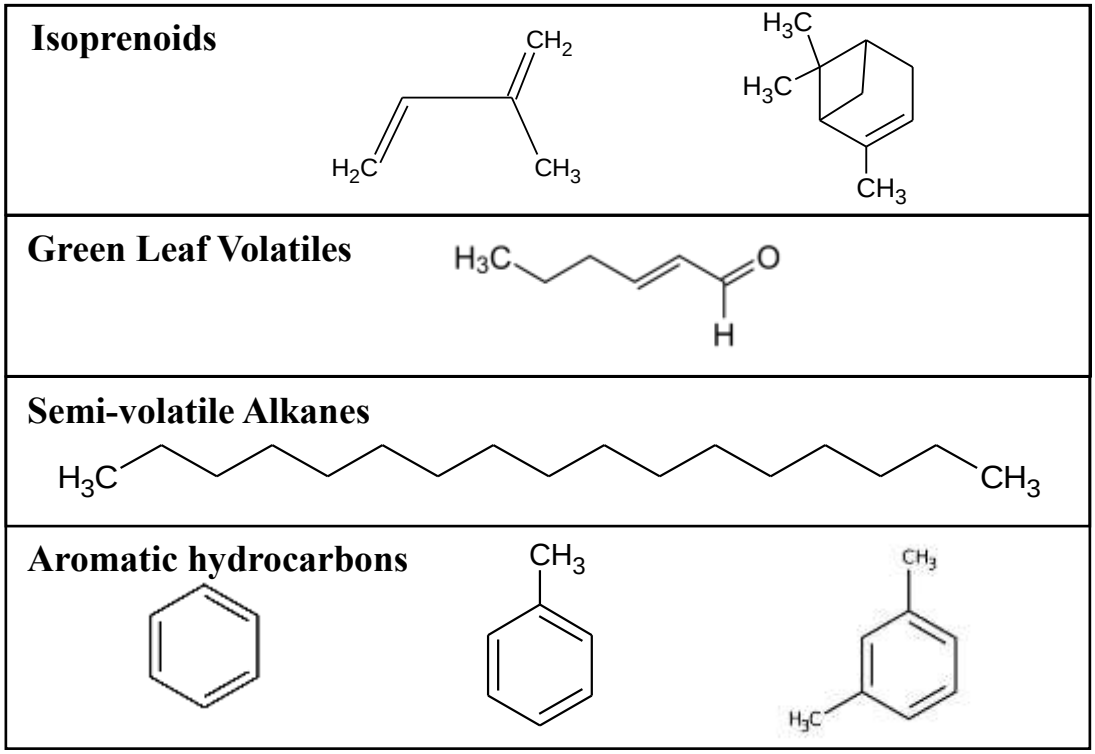


Figure 1- Various BVOC compounds

1.1.2 General Biosynthesis Mechanisms

Terrestrial plants release BVOCs as a byproduct of metabolism; Figure 2 shows a generalized diagram for the formation pathways of different BVOC classes. However, the exact mechanisms for the formation of many individual BVOC molecules are mostly unknown.[2,3]

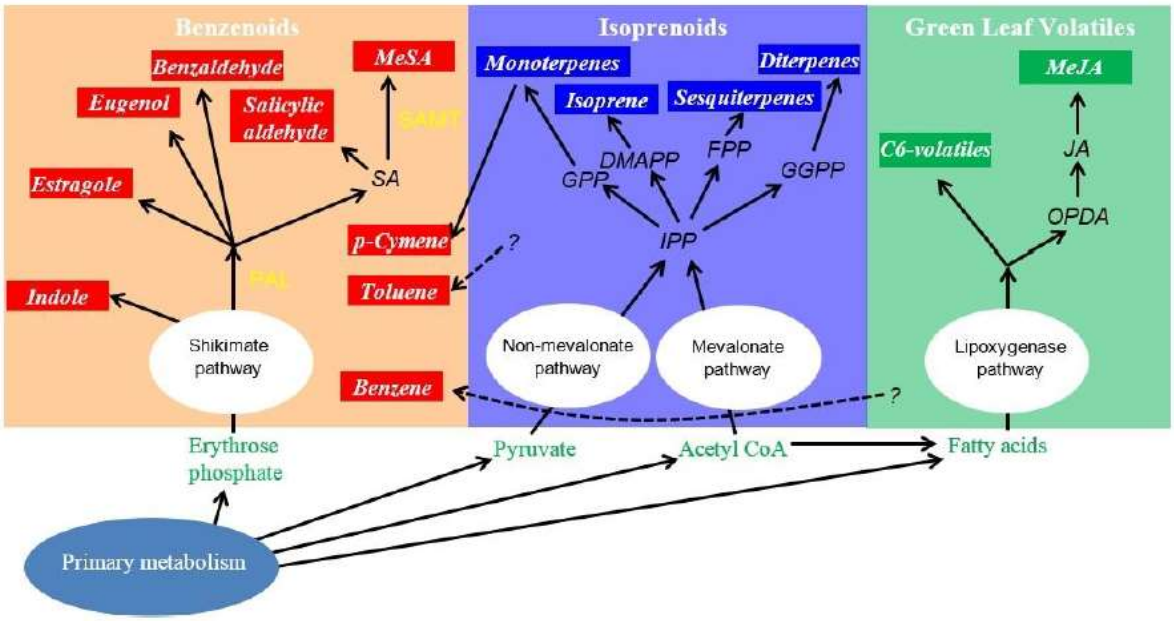


Figure 2 - Primary metabolic pathways for various BVOCs [2]

The biosynthetic pathway of isoprene and other isoprenoid compounds (Figure 3) are a result of two major metabolic pathways; the cytosolic mevalonate pathway and the plastidic methylerythritol phosphate pathway.[3,5] Both will produce isopentenyl pyrophosphate (IPP) and its isomer dimethylallyl pyrophosphate (DMAPP). The two main precursor molecules also contain five carbons and are condensed and modified to create other predecessor compounds. For example, the combination of an IPP with an DMAPP by a plastidic prenyltransferase will create geranyl pyrophosphate (GPP). The production of many monoterpene compounds is the result of enzymes known as terpene synthases (TPSs), which modify precursor molecules such as

DMAPP and GPP to produce isoprene and monoterpenes, respectively.[3] For production of all isoprenoid compounds through these pathways, the first step will be the removal of the pyrophosphate group through catalyzation with terpene synthases (TPSs). This will create a carbocation, which is an unstable intermediate available for a multitude of other reaction steps.[3]

Biogenic synthesis of long-chain alkanes and alkenes, another category of BVOCs, have been identified as the result of another two major metabolic pathways. The first involves acyl-ACP reductase and aldehyde deformylating oxygenase enzymes to produce alkanes such as pentadecane and heptadecane, while the production of biosynthetic alkenes like nonadecene is due to polyketide synthase enzymes.[6] Other BVOCs may be synthesized from coenzyme-A using type III polyketide synthases.[3]

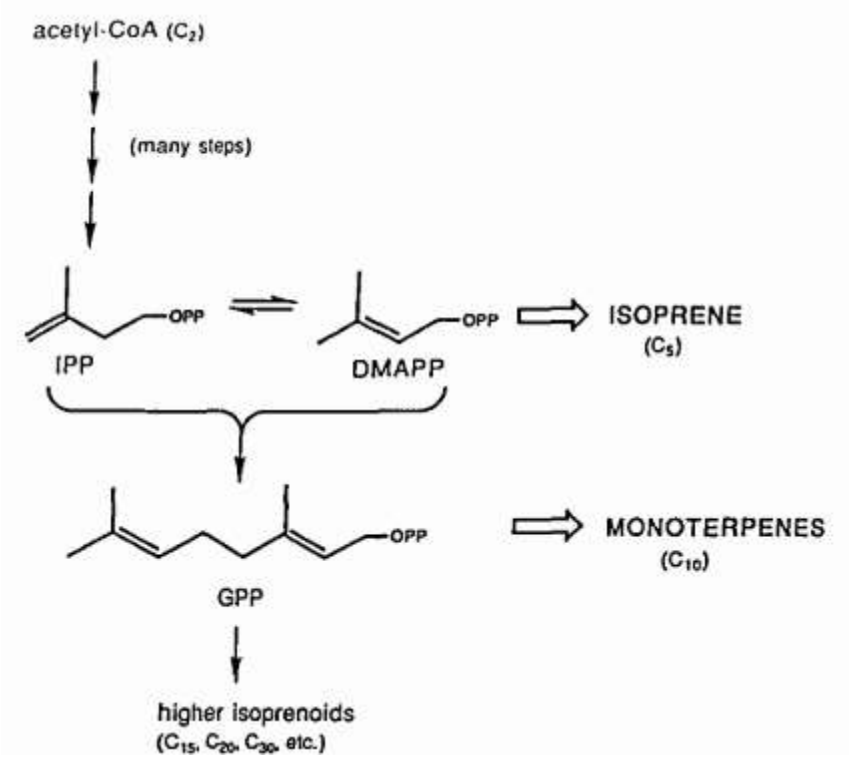


Figure 3 – Summary schematic of isoprene biosynthesis [7]

The majority of metabolic pathways leading to the formation of other aromatic BVOCs, such as benzene, toluene, and xylene, are less well understood.[8] Labeling experiments have shown that plants transform carbon into toluene, xylene, phenol, and a variety of other compounds.[2] For the majority of benzenoid compounds, the Shikimate pathway is an early metabolic step in production, with over 20% of carbon estimated to flow through this pathway.[2] This seven-step pathway has been nicknamed the "common aromatic biosynthetic pathway" in previous literature; however, not all biogenic AH are synthesized through this pathway.[9] The Shikimate pathway is used to produce amino acids in plants, but high stress can activate other secondary metabolic pathways and cause production of different BVOCs. The initial precursor molecule for production of AH is phenylalanine. The enzyme phenylalanine ammonia lyase will catalyze phenylalanine, forming ammonia and cinnamate.[2,5]

The emissions of BVOCs from many plants and other photosynthetic organisms may be the result of stress, which can cause enhanced production of secondary metabolites. For example, increased ozone concentrations can lead to an increase the emissions of certain isoflavonoids. Plants may also emit compounds as a signaling mechanism or as a biochemical defense method. For instance, in some grasses increased grazing can lead to a higher production of indole and/or estragole, which will attract wasps to drive off the herbivores. The biological purpose of many emitted BVOCs, such as toluene, is still unknown. [2]

1.1.3 Terrestrial and Marine BVOC Sources

Natural sources of VOCs include soil and water emissions, with terrestrial sources including trees, crops, grasses, marches, and microbial decomposition responsible for many BVOC emissions. Anthropogenic sources of VOCs include evaporation of solvents, burning of biomass and combustion of fossil fuels.[4,10] Biological sources represent a far greater source of

atmospheric VOCs than anthropogenic sources, with terrestrial vegetation the largest of the biogenic sources.[7] Anthropogenic emission rates of VOCs are approximated at 100 Tg per year of carbon, while biological sources are estimated to emit 1150 Tg per year of BVOCs.[10,11] The composition of global VOC emissions has been estimated at 44% isoprene, 11% monoterpenes, 22.5% VOC, and 22.5% other reactive compounds.[4,10]

Previously, it had been believed that atmospheric AH were primarily emitted by anthropogenic sources from the incomplete combustion of fossil fuels. Studies by Misztal et. al (2015) found that biological emissions of AH are much higher than formerly thought and may be a large contribution source to global VOC concentrations, with evidence of both terrestrial and marine biogenic sources.

Another possible source of BVOCs are marine phytoplankton, primary producers that have been approximated to produce up to 50% of global net primary production.[12] Two of the most abundant marine phytoplankton are the cyanobacteria genera *Prochlorococcus* and *Synechococcus*, which have approximate population sizes of 2.9×10^{27} and 7.0×10^{26} cells, respectively.[6] Together, they have been estimated to be responsible for over one fourth of net marine primary production, with *Prochlorococcus* producing around 8.5 % and *Synechococcus* producing approximately 16.7 %.[12]

Prochlorococcus and *Synechococcus* are both found in different habitats within the ocean. *Synechococcus* tends to dominate in cold, nutrient rich waters but requires high sunlight input and is found closer to the surface in the photic zone. *Prochlorococcus* is more prominent in warmer, low light, low nutrient waters. *Prochlorococcus* is the most abundant group of marine cyanobacteria species found in the lower latitudes (between 40° north and south), oligotrophic

oceans and can survive in water columns down to 200 m that receive less than 0.1% of surface irradiance.[12,13]

Much of the BVOC work on these two cyanobacteria has focused on production of long-chain hydrocarbons. *Prochlorococcus* and *Synechococcus* were determined to emit between 269 to 539 and 39 to 323 million tons of nC_{15} and nC_{17} alkanes a year, respectively.[6] A laboratory study identified pentadecane as the most abundant hydrocarbon emitted by *Prochlorococcus* and *Synechococcus* at 96% of total emissions, with heptadecane making up the other 4%. [6] Multiple studies identified heptadecane as the most abundant hydrocarbon emitted, with *Prochlorococcus* found to produce mainly heptadecane and pentadecane while *Synechococcus* was not found to produce any alkanes.[14,15]

Elevated concentrations of long-chain hydrocarbons have been quantified in tropical areas of the Pacific Ocean, where marine cyanobacteria thrive due to high sunlight and warm waters. Branched alkanes and other hydrocarbons were mainly identified in the North Atlantic oceans, where eukaryotic bacteria dominate.[16] Lea-Smith et. al (2015) attempted to quantify the amount of nC_{15} and nC_{17} hydrocarbon production from *Prochlorococcus* and *Synechococcus* over the open ocean, and extrapolated that production may range from 308 to 771 million tons of these two hydrocarbons every year.[6]

Dimethyl sulfide (DMS) and isoprene are the two other BVOCs that are known to be emitted by marine phytoplankton, which are accredited with being the largest biological producer of DMS. [17] A few laboratory studies have examined the ability of marine phytoplankton to emit isoprene and other monoterpenes, with some success. Shaw et al. (2003) identified both *Prochlorococcus* and *Synechococcus* as emitting isoprene, and Yassaa et al. (2008) actually observed high monoterpene levels above a phytoplankton bloom in the Southern

Atlantic Ocean. [18,19] However, the potential for these cyanobacteria to produce other BVOCs including AH such as toluene or the xylenes is practically unknown.

1.1.4 Marine Cyanobacterial Emissions of VOCs

Researchers have determined that marine phytoplankton have the ability to emit certain BVOCs as secondary metabolites, such as DMS, isoprene, and long-chain alkanes.[6,18,19] As noted above, the production of long chain alkanes, specifically n-C_{15} and n-C_{17}, by cyanobacteria has been reported by a first order estimate and represents a globally significant source of hydrocarbons. Multiple other field studies and laboratory experiments have examined alkane and alkene emissions by cyanobacteria, and two specific metabolic pathways have been identified. One pathway uses the deformylaion of fatty aldehydes, while the other involves decarboxylation of fatty acids to synthesize n-C_{15} and n-$C_{17.}$ [14,20] However, marine phytoplankton are capable of emissions of other compounds such as isoprene and dimethyl sulfide (DMS), all though these data represent an area of study that is not well understood. [21,22]

1.2 Atmospheric Impacts of VOCs

1.2.1 Oxidation Capacity: Hydroxyl Reactivity

The hydrocarbons released by marine phytoplankton are classified as trace gases due their low atmospheric concentrations, usually in the parts per billion or trillion range.[23] They also have short lifespans due to high atmospheric reactivity.[23,24] VOCs are susceptible to oxidation by reactions with hydroxyl radicals (OH), the products of which have the ability to form ozone and SOA.[23] Hydroxyl radicals are the “dominant tropospheric oxidizer” and remove most trace gases from the atmosphere. The term “oxidizing capacity of the atmosphere” refers to the ability of atmospheric oxidants to oxidize trace pollutants and is largely a function of OH availability.[25]

The primary source of OH is the reaction of singlet oxygen with water vapor.[25] This pathway is started by the photolysis of ozone gas by UV light (that is less than 0.32 μm), resulting in the creation of a diatomic oxygen molecule and an electronically excited singlet oxygen atom. The singlet oxygen atom will then go on to react with water vapor to form two OH.[24,26] This pathway is illustrated in the reaction scheme below:

$$O_{3\,(g)} + h\nu \rightarrow O_{2\,(g)} + O(^1D)$$

$$O(^1D) + H_2O_{\,(g)} \rightarrow 2\ OH$$

There are two possible pathways available for an oxidation reaction between a hydrocarbon and a hydroxyl radical; the first involves an addition of the radical to a multiple bond, while the other involves the abstraction of a hydrogen atom. Both oxidation pathways will eventually result in the production of a hydroperoxy radical (HO_2), which can then react with nitric oxide (NO, generated by the photodissociation of nitrogen dioxide) to regenerate the hydroxyl radical and complete the HO_x cycle, according to the reaction scheme below.

$$OH + CO \rightarrow CO_2 + H$$

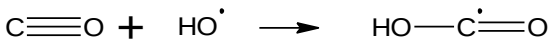
$$H + O_{2\,(g)} \rightarrow HO_2$$

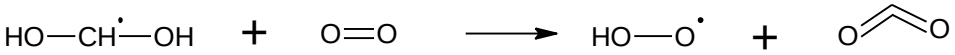
$$HO_2 + NO \rightarrow NO_2 + OH$$

The addition of a hydroxyl radical across a multiple bond results in a carboxyl radical, due to the addition of the hydroxyl group to a carbon atom, which can then bond with an additional oxygen molecule to create the hydroperoxy radical (along with carbon dioxide). The alternative pathway involves the replacement of the hydroxyl radical with a hydrogen atom,

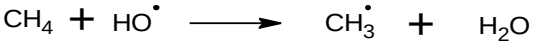
creating water and a carbocation. The carbocation can react with an oxygen molecule, and eventually will also result in a hydroperoxy radical. Both pathways are shown below.

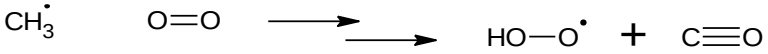
Addition across a bond:





Hydrogen Abstraction:





Atmospheric oxidation of VOCs can lead to the formation of new compounds, such as aldehydes and organic radicals. The new molecules formed can oxidize nitric oxide and lead to the production of tropospheric ozone due to the formation and dissociation of nitrogen dioxide (see Figure 4).[27]

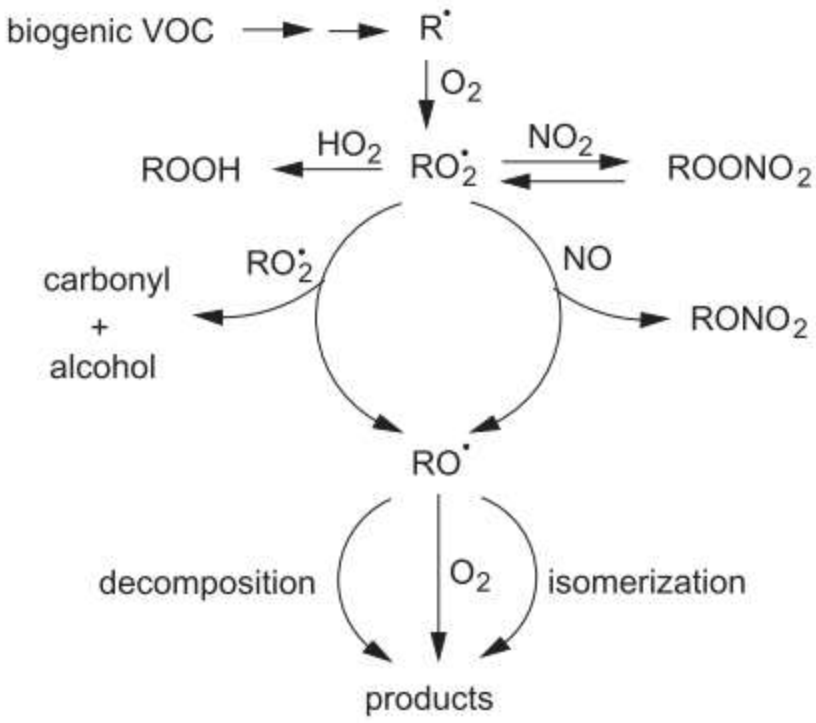


Figure 4- Simplified scheme of atmospheric processes involving BVOCs [28]

Hydroxyl radicals have been found to be significant in the determination of the chemical composition of the atmosphere. A majority of studies have focused on carbon monoxide and methane because of their high atmospheric concentrations; however, other VOCs may be of equal or greater value in the creation or consumption of hydroxyl radicals because, while they have lower concentrations, they undergo a faster reaction rate with hydroxyl radicals (Table 1).[29] The hydroxyl radical reactivity of an air mass is found by summing the concentrations of VOCs (C_i) multiplied by the hydroxyl rate constant (k_i), as defined by equation 1, and does not consider any secondary reactions that may occur.[30]

$$OH\ reactivity\ = \sum k_i C_i \qquad [eq.1]$$

Table 1- k_{OH} values for various VOCs

Parent Compound	k_{OH} x 10^{12} (cm^3 $molecules^{-1}$ s^{-1})	Source
Benzene	1.2	Shaw, 1995
DMS	4.7	Pszenny et al, 1999
Toluene	6.4	Greenman & Zimmerman, 1984
o-xylene	13.6	Atkinson & Arey, 2003
p-xylene	14.3	
m-xylene	23.1	
α-Pinene	53.7	Griffin et al., 1999
β-Pinene	78.9	
Isoprene	92.6	Shaw, 1995

The presence of VOCs can also prolong the lifetime of important greenhouse gases such as methane. This is due to the decrease of hydroxyl radicals from reactions with the VOCs instead of gases such as methane, as some non-methane trace gases are over a hundred time more reactive than methane.[31] Poisson et al. (2000) estimated that the impact of these chemical reactions can increase the lifetime of methane by approximately 15%, from an original lifetime of 6.5 to 7.4 years.[32] In spite of the importance of marine emissions on reactive VOCs on greenhouse gas lifetimes, relatively few measurements have been reported and more data are needed to better constrain these impacts.

1.2.2 SOA Formation

An aerosol is a solid or liquid particle suspended in a gaseous substrate. Aerosols can cause a variety of climatic effects, such as directly reflecting or absorbing solar radiation or indirectly reflecting solar radiation by acting as cloud condensation nuclei.[23] The presence of such fine particulate matter in the atmosphere has been linked to negative health effects such as pulmonary inflammation, suppression of certain immune defenses, and excess stimulation of the airways.[30]

Primary aerosols are directly emitted from a source (such as the black carbon particles from the combustion of fossil fuels or sea salt particles suspended by wave action), while secondary aerosols are created from condensation of gas phase molecules. If the secondary aerosol was initially formed by an organic compound, it is classified as SOA. There are a number of ways SOA can form in the marine boundary layer (MBL), the defined layer of the atmosphere with a height between 100 to 1000m that is direct contact with the ocean surface and thus allows for air-sea exchange of species.[30,33] One possibility is the oxidation of VOCs, leading to the creation of new compounds through the nucleation of small clumps of particles, which can be enlarged through condensation or coagulation. VOCs and their respective oxidation products can also collect and condense on other preexisting particles, allowing for the accumulation of mass.[34]

Aromatic compounds such as benzene, toluene, and traditional BVOCs such as isoprene and monoterpenes are all compounds with a high potential to form SOA, because of the ease in which they can be oxidized and the relatively low volatility of their oxidation products. A previous study by Misztal et al. (2015) found that AH have a high potential for production of both SOA and tropospheric ozone, with a first order estimate of formation potential at approximately 10 Tg per year.[2]

Table 2 gives SOA yields from oxidation chamber studies for specific BVOC and AH compounds. SOA formation can vary depending on the NO_x conditions and relative humidity (RH) of the atmosphere; in order to mimic marine atmospheres, SOA values under low NO_x and high RH conditions were examined. The wide range of SOA yields shown in the table below is due to the discrepancies in the laboratory experiments used. There are a number of variables that can differ when examining SOA yields, such as source of the hydroxyl radical, the seed particle used, the nitric oxide and nitrogen dioxide concentrations, and the type of chamber used. For example, Stirnweis et al. (2017) used a variation of seed particles in their work, including acidic, neutralizing, and hydrophobic particles, while Zhang et al. (2001) used only ammonium sulfate.[35,36]

The BVOCs released by marine phytoplankton have been suggested to be important precursor molecules for SOA formation. Measurements over the North Atlantic Ocean during phytoplankton blooms determined that marine organic matter contributes 63% to the sub-micrometer aerosol mass.[37] However, current models are thought to underestimate biogenic (AH) emissions, thus potentially underestimating the contribution of BVOCs to SOA formation, especially in remote marine environments where measurements are sparse.[2,4]

Table 2 – SOA yields for certain aromatic hydrocarbons under low NO_x conditions

Compound	SOA yield (%)	References
Isoprene	11.5	Zhang et al., 2001
α-Pinene	1.5	Stirnweis et al., 2017
Benzene	36.9 (± 0.9)	Ng et al., 2007
Toluene	30.2 (± 0.7) – 30.8 (± 1.7)	Ng et al., 2007
m-xylene	35.7 (± 1.0) – 37.7 (± 0.8)	Ng et al., 2007
MVK	3.9 – 9.9	Liu et al., 2012
MACR	1.6 – 11.7	Liu et al., 2012

1.3 Underprediction of SOA and Measurement - Model Discrepancies

1.3.1 Uncertainty in SOA Modeling

Overall, there is a high uncertainty in global SOA approximations, with global estimates ranging from 120 to 1820 Tg/year.[38] Numerous factors contribute to this uncertainty, as modeling hydroxyl concentrations is difficult due to complex reaction pathways that govern atmospheric processes. It can also be difficult to determine VOC concentrations due to a high diversity of compounds, differences in sampling and analysis techniques between studies, and a lack of source-specific emission factors.[4] This is particularly relevant for biological sources of VOCs, as models must take into account compound-specific emission estimates for each source, as well as how different factors such as temperature or light affect each source individually and their corresponding reactivity with other atmospheric compounds.[10]

The difficulty with measurements and high uncertainties in VOCs parallels complications in modeling SOA yields, as there are severe discrepancies in the modeled concentrations for SOA when compared to the observed concentrations, especially within the MBL. For example, Gantt et al. (2015) notes an underprediction of approximately 36% (normalized mean bias) by the GEOS-CHEM model when compared to observed marine organic aerosols. Gantt concludes that additional information involving organic aerosol precursor emissions is needed into order to improve futures marine models.[39] Another modeling experiment performed by Myriokefalitakis et al. (2010) found that simulated SOA values in the MBL, estimated by the TM4-ECPL model with marine VOC sources included, showed a clear underprediction of marine SOA compared to measurements. The simulated values showed even higher discrepancies when marine sources were not included (Figure 5).[40] These studies clearly demonstrate that a better understanding of marine sources of SOA is vital to improving the accuracy of our current climate models.

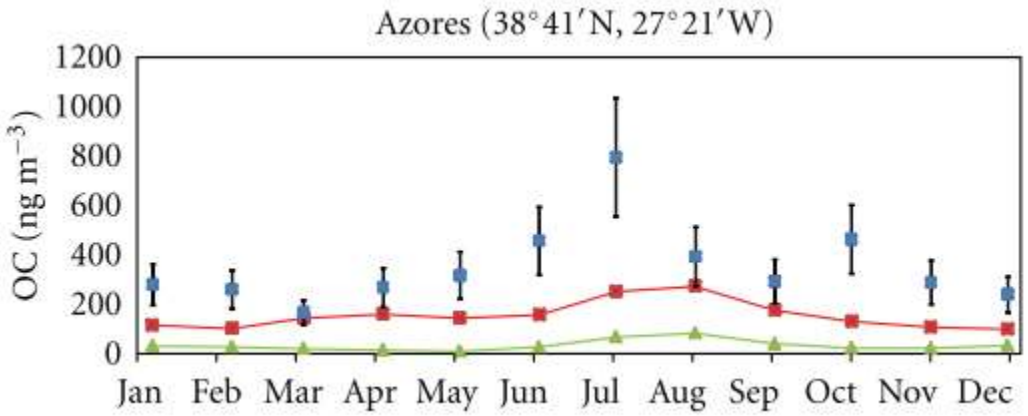


Figure 5- Modeled versus observed values of methanesulphonate at Finokalia Research Station (35° 19'N, 25° 40'E and particular Organic Carbon at Azores Research Station (38° 41'N, 27° 21'W). The red line represents the simulated values estimated by the TM4-ECPL model with marine sources included, the green line represents modeled values without marine sources, and the blue squares represent observed values for marine organic aerosols. [40]

1.3.2 Missing Source of VOCs

One possibility for the underprediction of modeled SOA concentrations in the MBL may be the result of one or more missing VOC sources. Previous reports of VOCs in the remote MBL are scarce and typically lack either spatial or temporal resolution. This lack of measurements, particularly a lack of concurrent measurements in phytoplankton communities, is a major hurdle in improving marine VOC emissions estimates. This is especially relevant given that models have predicted changes in phytoplankton abundances due to increasing surface temperatures of seawater from climate change, with predicted increases of *Prochlorococcus* and *Synechococcus* of 28.7% and 13.9%, respectively.[12] Given their current and future predicted abundance, understanding the roles of cyanobacterial populations on VOC emissions from the ocean is critical to understanding the future oxidative capacity of the remote marine atmosphere and climate feedback cycles involving SOA.

To address uncertainties related to VOC concentrations and impacts in the remote MBL and their relationships to phytoplankton communities, this thesis uses concurrent atmospheric VOC and phytoplankton abundance data collected aboard a May 2017 research cruise in the Northern Atlantic Ocean. Specifically, this work addresses two questions:

1) What is the impact of the observed VOCs on OH reactivity and SOA formation?

2) What are the sources of the observed VOCs and is there a relationship with phytoplankton cell counts?

This study adds to the sparse dataset of VOC observations over oceans and is one of the first to include concurrent in-situ measurements of phytoplankton community composition.

2.0 Methods

2.1 VOC Sampling and Collection

In May of 2017, the Phosphorous, Hydrocarbons, and Transcriptions cruise aboard the *R/V Neil Armstrong* conducted a round-trip transect from Woods Hole, MA to Bermuda (Figure 6). The cruise sampled at a total of nine stations, each for 24-hours, along the transect that encompassed various cyanobacteria populations and different nutrient regimes. Whole-air samples (n = 160 total) were collected en route and at each station with 2-liter electropolished stainless steel canisters for collection of OVOC's and VOC's. The canisters were flushed before field sampling by being evacuated to 0.01 torr, refilled to 760 torr with ultrapure helium passed through an activated charcoal/molecular sieve and then re-evacuated to 0.01 torr. Before collection of the field samples, the canisters were flushed five times with ambient air from a 100-ft stainless steel sample line on the bow of the ship pulled by a metal bellows pump. All canisters were pressurized to 26 psi over approximately five minutes.

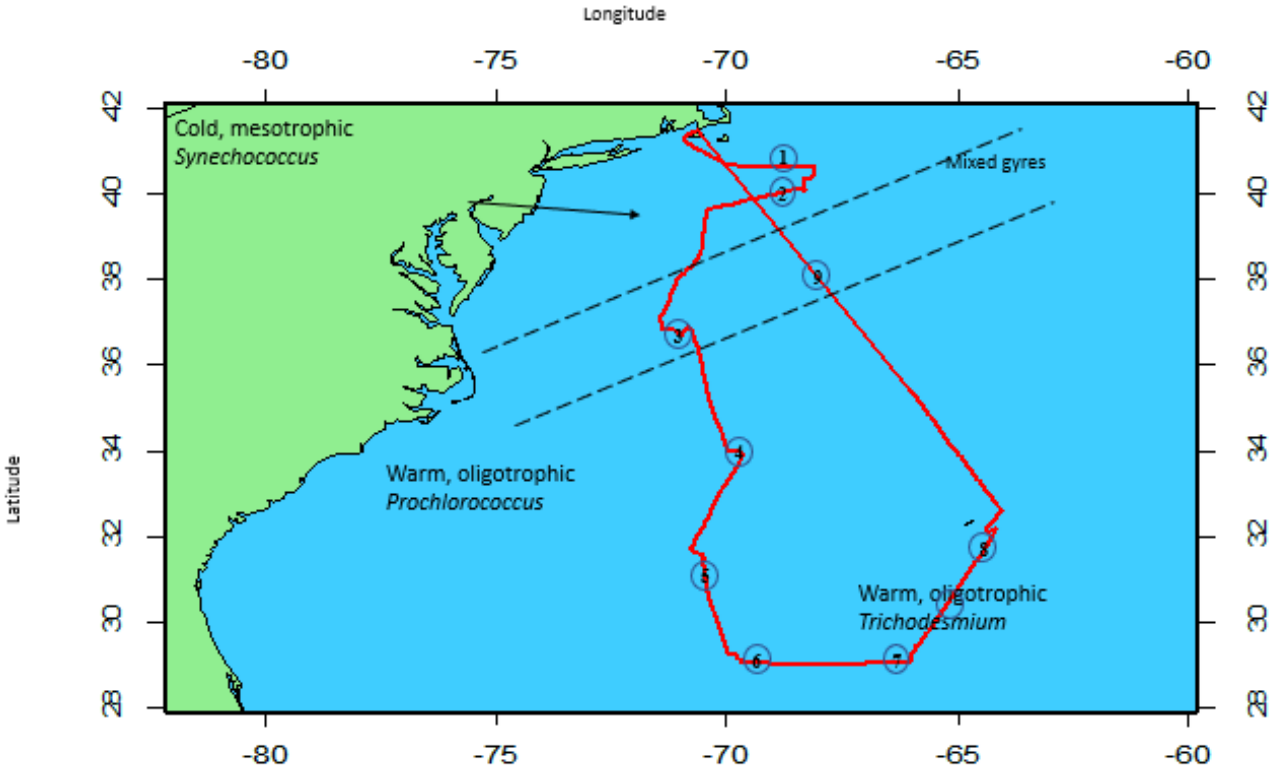


Figure 6- Cruise transect for the *R/V Armstrong*, with sampling stations marked

The ship's crew made an effort to constantly orient the ship into the prevailing wind, and care was taken to not sample when the wind was blowing from the stern of the ship to avoid sampling ship exhaust. Additional source samples of ship exhaust and fuel tank venting were collected, and no evidence of either source was indicated in any samples through the presence of higher hydrocarbons or high acetylene values. Samples were collected roughly every four hours with higher frequency sampling at some stations and during Gulf Stream wall transits. No samples were collected from May 5th to May 7th due to inclement weather.

2.2 Instrumental Analysis and Data Processing

Canister samples were analyzed on a five-detector gas chromatograph equipped with two flame ion detectors (FID), two electron capture detectors (ECD), and a quadrupole mass

spectrometer (MS), and is depicted in Figure 7. The FID channel used a VF-1ms column with dimensions of 60 m x 0.32 mm x 1µm thick film and the EDC used a CP-PoraBond-Q column at 25 m x 0.25 mm x 3 µm thick film coupled to a Restek XTI-5 column with dimensions of 30 m x 0.25 mm x 0.25 µm thick film. A 700 torr aliquot (approximately 1500 cm^3) of each sample was cryogenically trapped using liquid nitrogen on a 5 cm^3 sample loop filled with glass beads and then desorbed by immersing the loop in boiling water and injected onto the instrument.

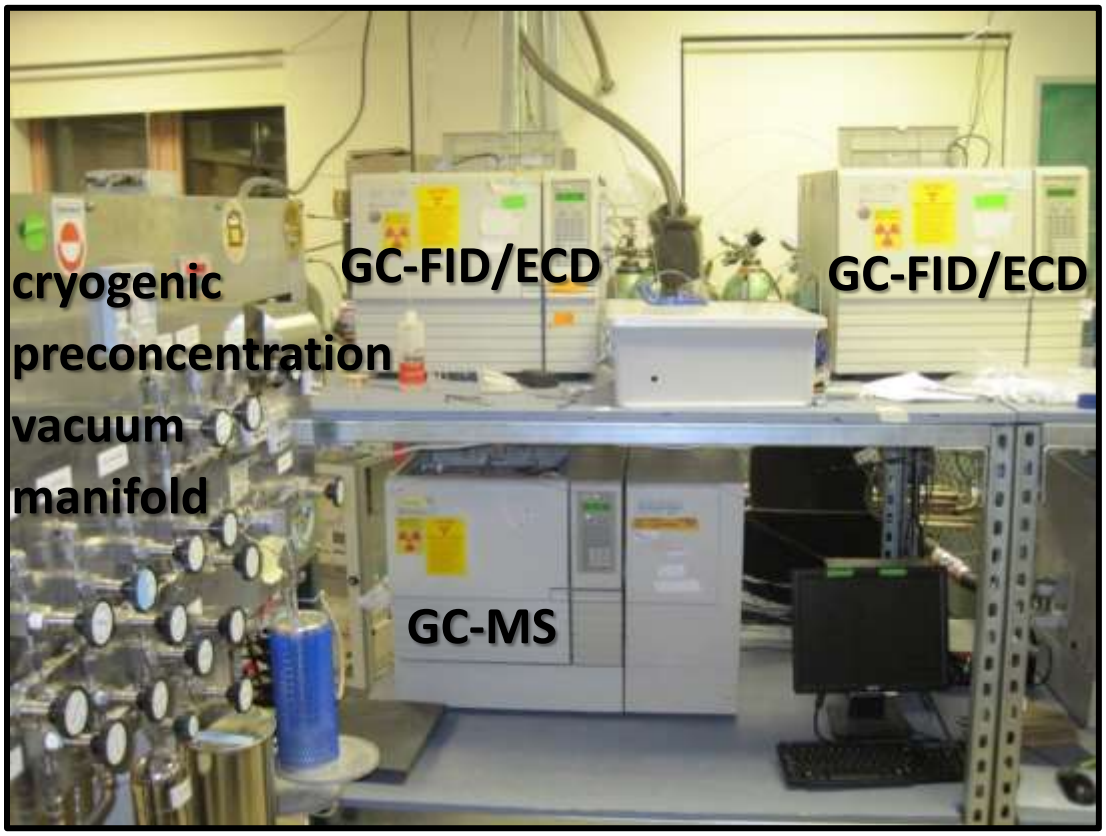


Figure 7- Photograph of the five-detector GC/ECD/ECD/FID/FID/MS system

Generated chromatograms were examined for over 80 VOC's, including $C_2 - C_{10}$ alkanes, $C_2 - C_5$ alkenes, $C_1 - C_2$ halocarbons, $C_6 - C_9$ aromatic hydrocarbons, traditional BVOCs, and oxygenated VOCs (OVOCs).

For each compound to be quantified, multiple NIST-tracable standard cylinders were used to calculate response factors. The concentrations of the standard cylinders covered a broad range of concentration values in order to cover a variety of possible sample mixing ratios. Equation 2 outlines how mixing ratios for specific compounds [X] were calculated from the standard response factor (RF) and the chromatogram peak area (A):

$$[X] = A / RF \qquad [eq.\ 2]$$

While over 80 VOCs were analyzed, many were consistently below the detection limits of the instrument, including the majority of the alkenes. This analysis will focus primarily on the compounds known or suspected to have biogenic sources and a high potential to contribute to SOA formation: the traditional BVOCs, OVOCs, and AH.

2.3 Biological Ancillary Data

2.3.1 Phytoplankton Cell Counts

Water samples were collected at each of the nine stations to examine phytoplakton populations present. At each station, samples were taken at various depths throughout the photic zone ranging from 10 – 90 m to cover a range in photosynthetically active radiation values. These samples were analyzed for cell counts including *Prochlorococcus*, *Synechococcus*, and other eukaryotic species using flow cytometry by the Chisholm Lab at the Massachusetts Institute of Technology. No cell count data was available for station 2 due to a lack of sampling caused by inclement weather. Table 3 gives the mean cell counts for both species of cyanobacteria.

Table 3- Mean cell counts for *Prochlorococcus* and *Synechococcus* at each sampling station, with the range for each value indicated in parentheses

Station	*Prochlorococcus (cells/mL)*	*Synechococcus (cells/mL)*
1	0.00	344 (369 – 308)
3	76554 (15192 - 120252)	5824 (590 - 12910)
4	43558 (21111 - 81362)	14150 (10331 – 19006)
5	35458 (4913 – 83021)	12347 (10533 – 15766)
6	33235 (2325 – 73949)	7953 (9630 – 6857)
7	19564 (5162 – 33966)	6829 (6441 – 7218)
8	37895 (11017 – 59346)	9789 (4145 – 13557)
9	0	186090 (155554 – 199858)

Note: No cell count data was collected at station 2

2.3.2 Oceanographic and Meteorological Variables

Throughout the research cruise, various meteorological and oceanographical data was collected. Seawater variables measured by a real-time flow through system including sea surface temperature (SST), fluorescence (FLR), and nitrate and phosphate concentrations. Meteorological variables measured by two Visala weather stations located at the forward mast of the ship included wind speed and direction, photosynthetically active radiation (PAR), relative humidity, and air temperature. These data were compiled at one-minute sampling frequency and data were averaged over the five-minute interval during which each canister collected.

3.0 Results

3.1 Comparisons to Previous Values

Table 4 gives the average mixing ratios for selected VOCs that may contribute to SOA formation sampled during the R/V Armstrong research cruise, compared to previously measured values. Samples showed a large range of concentration values and most compounds displayed high variability within their individual data.

Examination of the small dataset available of previous observations of VOCs over marine atmospheres led to the values given in Table 4. Isoprene, α-Pinene, β-Pinene, MEK, methanol, OCS, methacrolein, acetonitrile, and ethanol fell within the previously reported concentration ranges by Lewis et al. (2001), Yassaa et al. (2008), Montzka et al. (2007), Gilman et al. (2008) and Singh et al. (2004), with MEK and β-Pinene technically within the range.[19,33,41–43]

Acetone, benzene, toluene, and all the xylenes observed during this study were lower than values reported by other researchers. Greenberg & Zimmerman (1984) gave ranges for these compounds in units of parts per billion (ppb); however, we report mixing ratios with values in the parts per trillion (ppt) range.[27] The variation in concentration may be a consequence of sampling location, as Greenberg & Zimmerman (1984) reported values of samples collected in the South Pacific Ocean along the coast of Peru, while our sampling took place in the North Atlantic. These low values indicate that this study sampled clean air masses with little anthropogenic influence. Both studies used GC/FID-MS for analysis and used similar mechanisms for sample collection, making it unlikely that the discrepancies are a result of differences in methodology.

Table 4- Previously measured concentrations from aromatic BVOCs in marine atmospheres compared to previously measured values

Compound	Average Mixing Ratio (pptv) ± standard deviation	Range (pptv)	Previously Reported Values
Methanol	1010 (± 699)	0 – 6150	1096 (± 1246) pptv (Singh et al., 2004)
Ethanol	311 (± 659)	0.12 - 5105	165 (± 246) pptv (Singh et al., 2004)
Isoprene	4 (± 6)	0 – 57	26 (0 - 48) pptv (Yassaa et al., 2008)
Acetone	1558 (± 946)	0 – 9081	4 (± 354) pptv (Singh et al., 2004)
DMS	272 (± 274)	0 – 1229	2 -7 pptv (Carslaw et al., 1999)
Acetonitrile	42 (± 14)	0.18 – 75	---
Methacrolein	8 (± 8)	0.29 – 64	0.008 (Gilman et al., 2008)
Methyl vinyl ketone	24 (± 8)	0 – 144	---
Methyl ethyl ketone	29 (± 32)	0 – 260	74 (± 90) pptv (Singh et al., 2004)
Benzene	42 (± 18)	0 – 116	0.04 – 2.96 ppbv (Greenberg & Zimmerman, 1984)
Toluene	28 (± 123)	0 – 1104	0.05 – 1.49 ppbv (Greenberg & Zimmerman, 1984)
m + p xylene	9 (± 29)	0 – 213	0 – 0.31 ppbv (Greenberg & Zimmerman, 1984)
o-xylene	5 (± 16)	0 – 119	0.04 – 0.77 ppbv (Greenberg & Zimmerman, 1984)
α-Pinene	3 (± 7)	0 – 70	5 (0 – 15) pptv (Yassaa et al., 2008)
β-Pinene	1 (± 1)	0 – 10	Not detected (Gilman et al., 2008)
OCS	221 (± 38)	77.31 – 391	478 (± 8) ppt (Montzka et al., 2007)
MBO	4 (± 4)	0 - 39	---

3.2 Temporal and Spatial Variation

Figure 8 shows time series created for each of the selected VOCs sampled, with mixing ratios of each compound plotted against the entire transect. The red bar shown in the figure indicates station 2, where no sampling took place. All of the compounds (excluding benzene) show a similar trend, with elevated concentrations appearing towards the end of the transect (shown highlighted in green). While there is a bump in the acetone concentrations at those same dates (approximately May 22nd), the acetone concentrations actually dip slightly at the end of the series, a singularity not demonstrated in the other samples shown below.

While benzene, toluene, and DMS show the elevated mixing ratios towards the end of the research cruise, the concentrations are more variable; toluene only has three points that really differ from the baseline and benzene concentrations drop after the initial peak in concentration. The DMS time series shows the most variability within these three compounds, with several large spikes in concentration followed by a sharp drop. DMS also shows a wide peak around the middle of May, a trend that is not shown in the other compounds. Marine sources of DMS are thought to be the largest in the world, with multiple species of phytoplankton known for producing and emitting DMS, which may explain some of the variability and higher concentrations shown in the time series below.[17]

The high mixing ratios shown at the end of the cruise transect may correspond to a *Synechococcus* bloom that was sampled at the end of the research cruise at station 9. Diurnal variability was examined but showed no consistent trends.

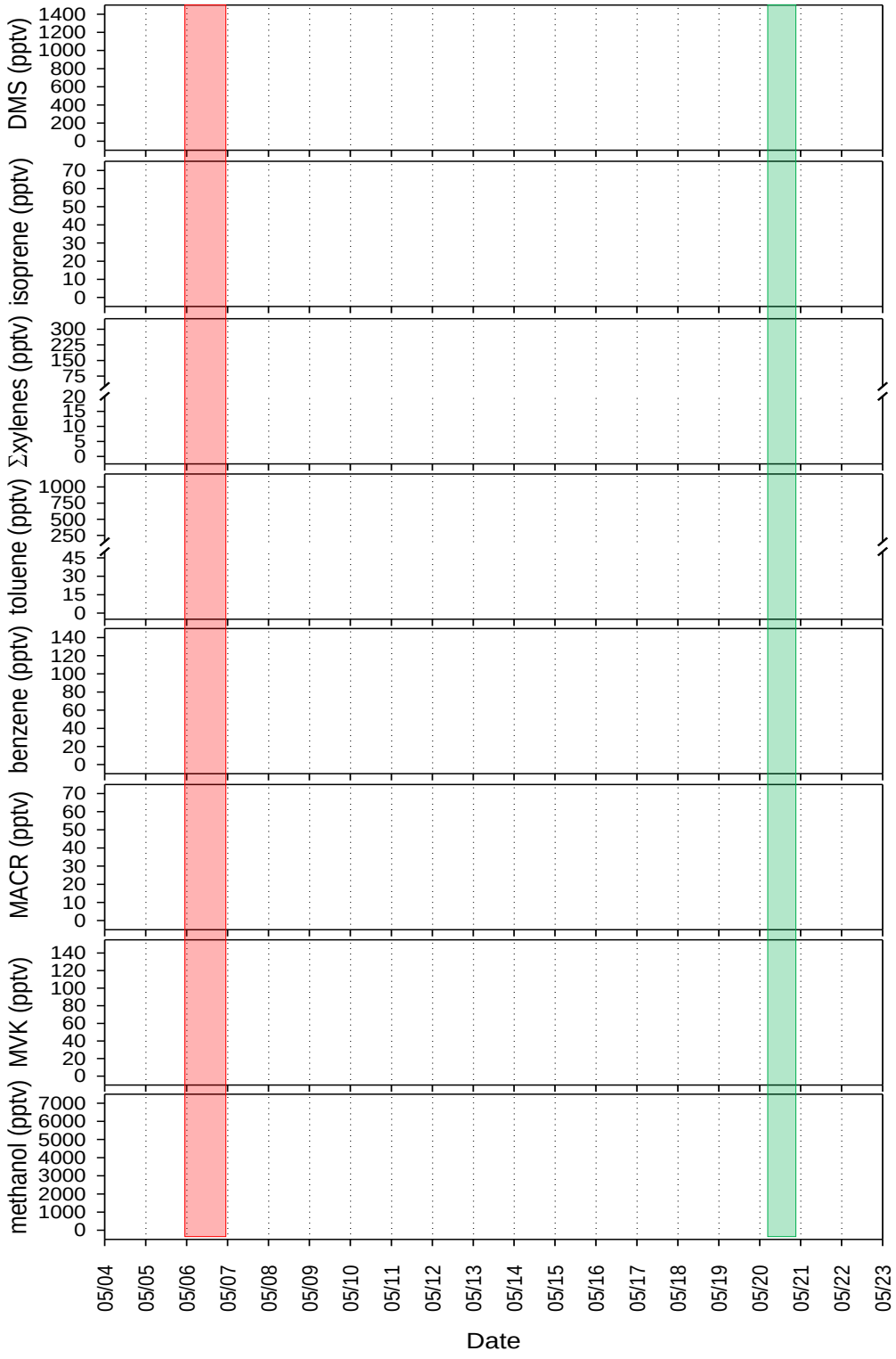


Figure 8- Time series for selected VOCs. Red bar indicates no sampling, green bar indicates elevated mixing ratios at station nine

3.3 Evidence for Biogenic Production of Toluene

3.3.1 Correlations to Tracer Compounds

Various organic compounds are emitted from similar sources together, and thus will be found in similar ratios together. For example, the ratio of benzene and toluene is often used as a tracer for anthropogenic emissions, due to their presence in gasoline compounds.[44] Figure 9 shows the linear correlation plot between the concentrations of measured toluene and benzene, with the green line representing the background ratio present in the samples. The red line indicates a theoretical additional source of toluene, as the high toluene values correspond to lower benzene concentrations.

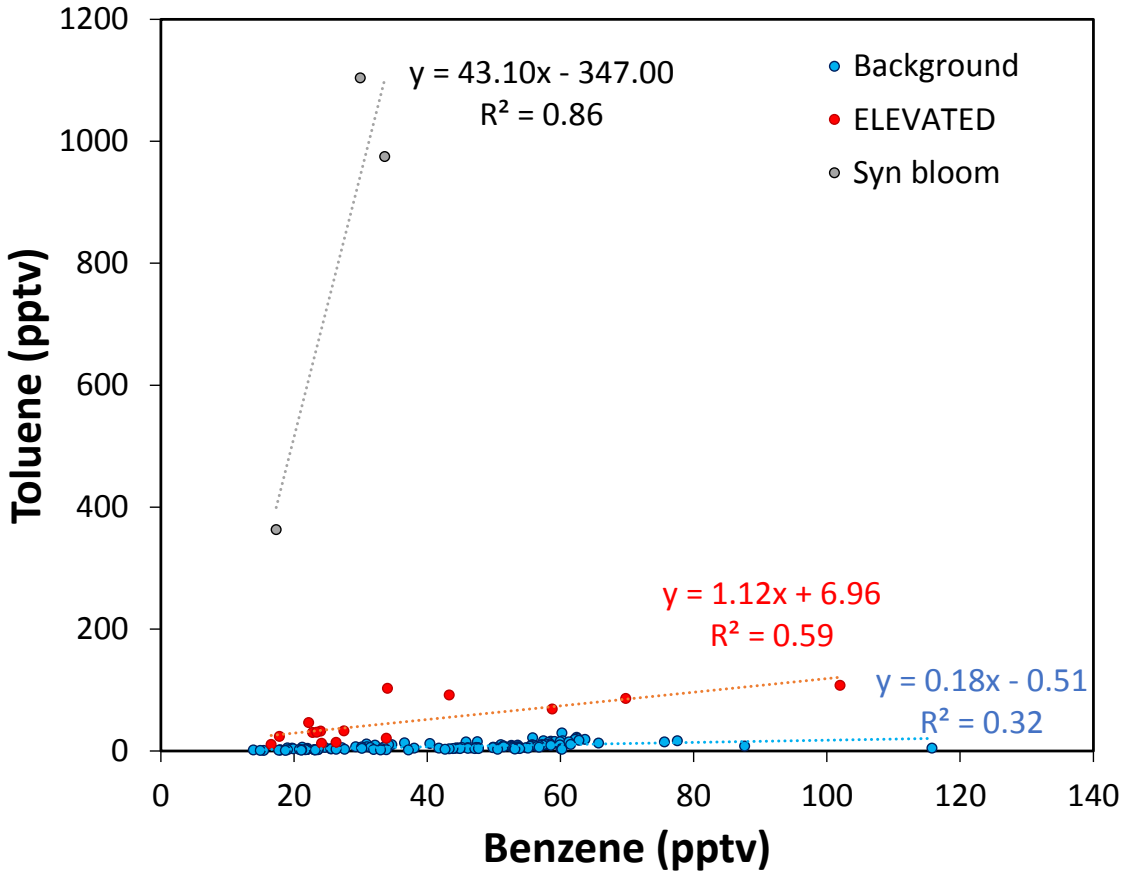


Figure 9- Comparison of toluene and benzene mixing ratios

Chlorinated hydrocarbons are another organic compound that are often used as tracer molecules. Tetrachloroethylene (C_2Cl_4) is often used, as it is an extremely long-lived compound that is commonly used in industrial solvents. Figure 10 displays correlation plots created to compare the concentrations of toluene and benzene to tetrachloroethylene. Benzene shows a high correlation to the tracer compound, indicating an anthropogenic source of benzene. Again, toluene seems to display two possible trendlines; one corresponding to a background ratio of toluene to the tracer and a second indicating an additional, biogenic source of toluene.

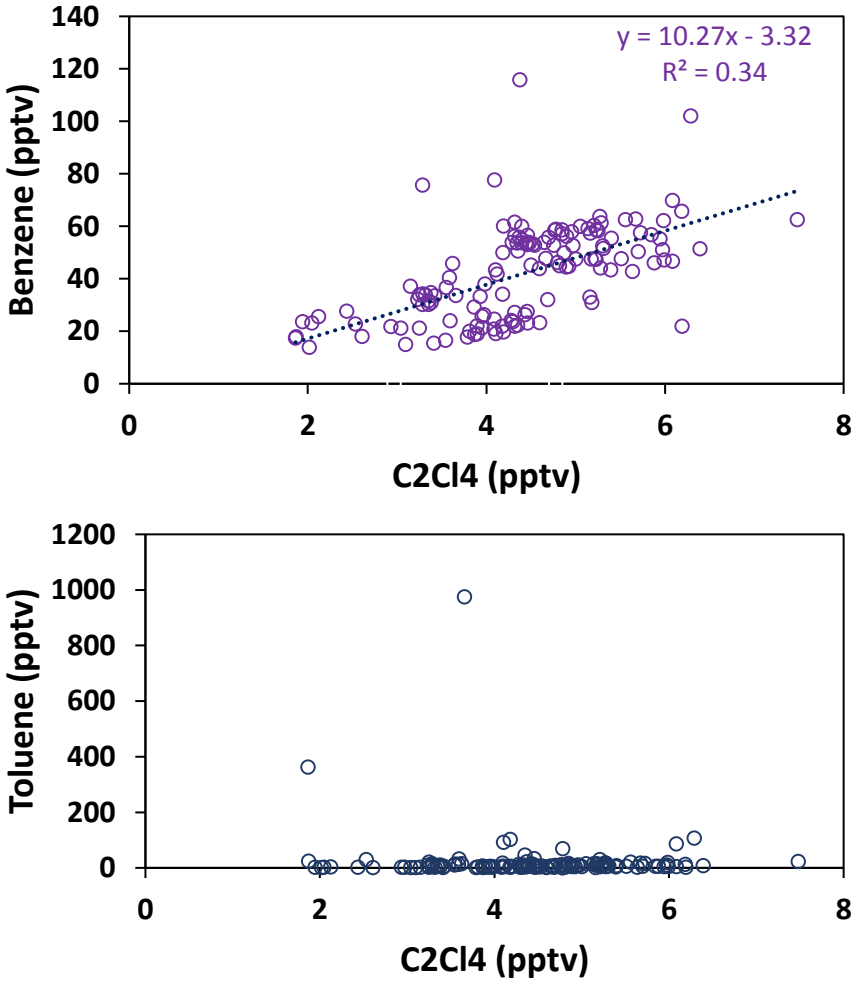


Figure 10- Comparison of toluene and benzene to tetrachloroethylene

Back-trajectories were calculated for station 9, in order to confirm that the elevation in mixing ratios is not due to a source other than the *Synechococcus* bloom, the results of which are shown in Figure 11 below.

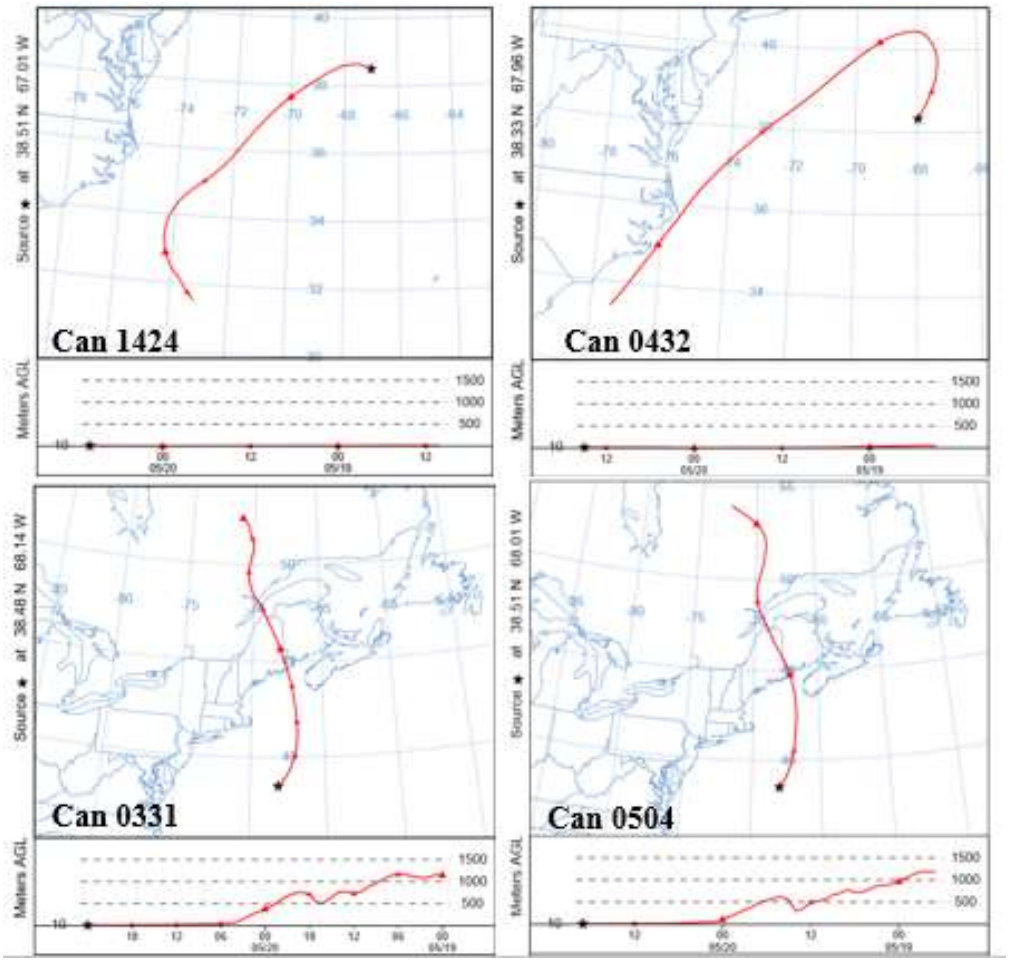


Figure 11- Results of the back trajectories at station 9, created using the NOAA HYSPLIT Model and NAM meteorological data with a final altitude of 10 m

The trajectories shown above show two patterns of air mass movement. Canisters 1424 and 0432 both show air masses originating in the south west before reaching the sampling point, with both masses containing little to no toluene. Canisters 0331 and 0504 sampled air masses starting in the north over land, both of which contained higher mixing ratios of toluene. The

variability in the mixing ratios of the samples may indicate that the ship moved within the bloom, despite best efforts to remain stationary. However, prior to the 24-hour sampling period, none of the four air masses spent a large amount of time over land masses, and thus the toluene values are most likely not due to anthropogenic sources.

Isoprene and DMS are both compounds known known to be emitted by phytoplankton and cyanobacteria, and thus can be used for biological tracers of phytoplankton emissions, as there should be a constant background ratio present in atmospheric samples.[17,18] The plots shown in Figures 12 and 13 compare toluene to both compounds, with the background ratio shown by the blue trendline and higher toluene values shown by the red trendline. Figure 12 indicates that the additional source of toluene is shared by isoprene, due to the correlation between the two with the higher toluene values. This is corroborated by the correlations examined previously with anthropogenic tracers, all of which showed a supplementary source beyond the background ratios. Meanwhile, figure 13 shows no such correlation of toluene to DMS, indicating they do not share a similar source at station 9.

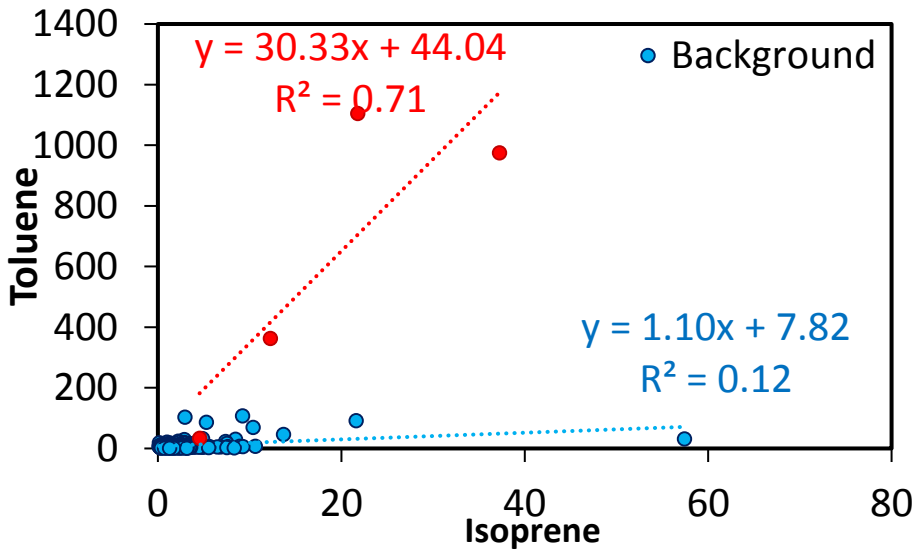


Figure 12- Comparison of toluene to isoprene as a tracer compound

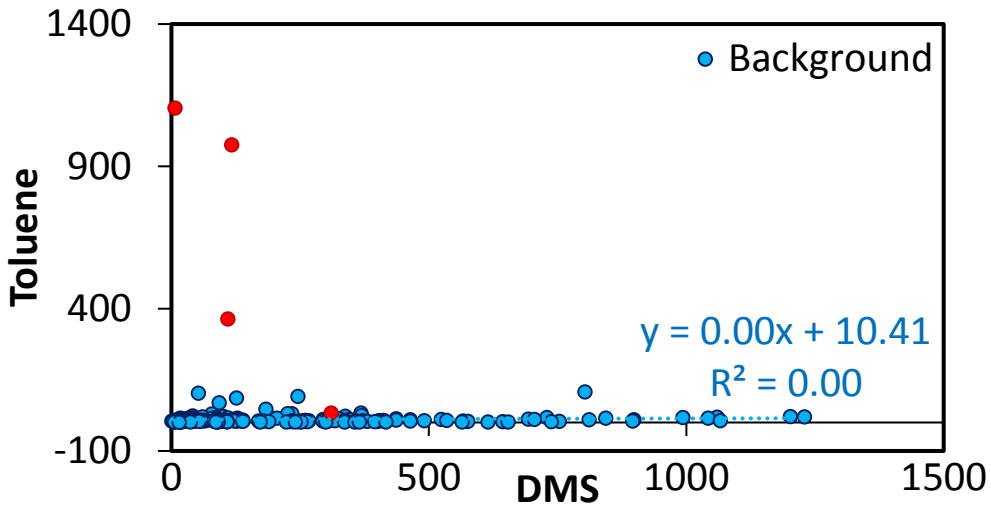


Figure 13- Comparison of toluene to DMS as a tracer compound

3.3.2 Correlations with Cell Count Data

Both *Prochlorococcus* and *Synechococcus* have been previously studied by other researchers to gain a deeper understanding of their biosynthetic mechanisms and their ability to produce both aromatic and linear hydrocarbons. Studies by Lea-Smith (2015) and Shaw et al. (2003) identified both species of cyanobacteria as emitting isoprene, n-pentadecane, and n-heptadecane.[6,18] Specific cell count numbers for *Synechococcus* and *Prochlorococcus* are given in Table 3, section 2.3.1. At station 9, the research cruise encountered a large *Synechococcus* bloom.

Prochlorococcus cell counts differ slightly from those of *Synechococcus*; while *Synechococcus* had its highest cell counts at station 9 and its lowest at station 1, no *Prochlorococcus* cells were quantified at either station 9 or 1. Rather, *Prochlorococcus* tends to be clustered around the middle stations, which is seen in Figure 14 below. This is due to the cruise path as stations 1 and 9 were sampled during the first and last leg, both of which were colder waters where *Synechococcus* tends to dominate. The middle stations were sampled in the

lower latitudes where *Prochlorococcus* thrive, due to the lower nutrient content of the waters and higher temperatures.

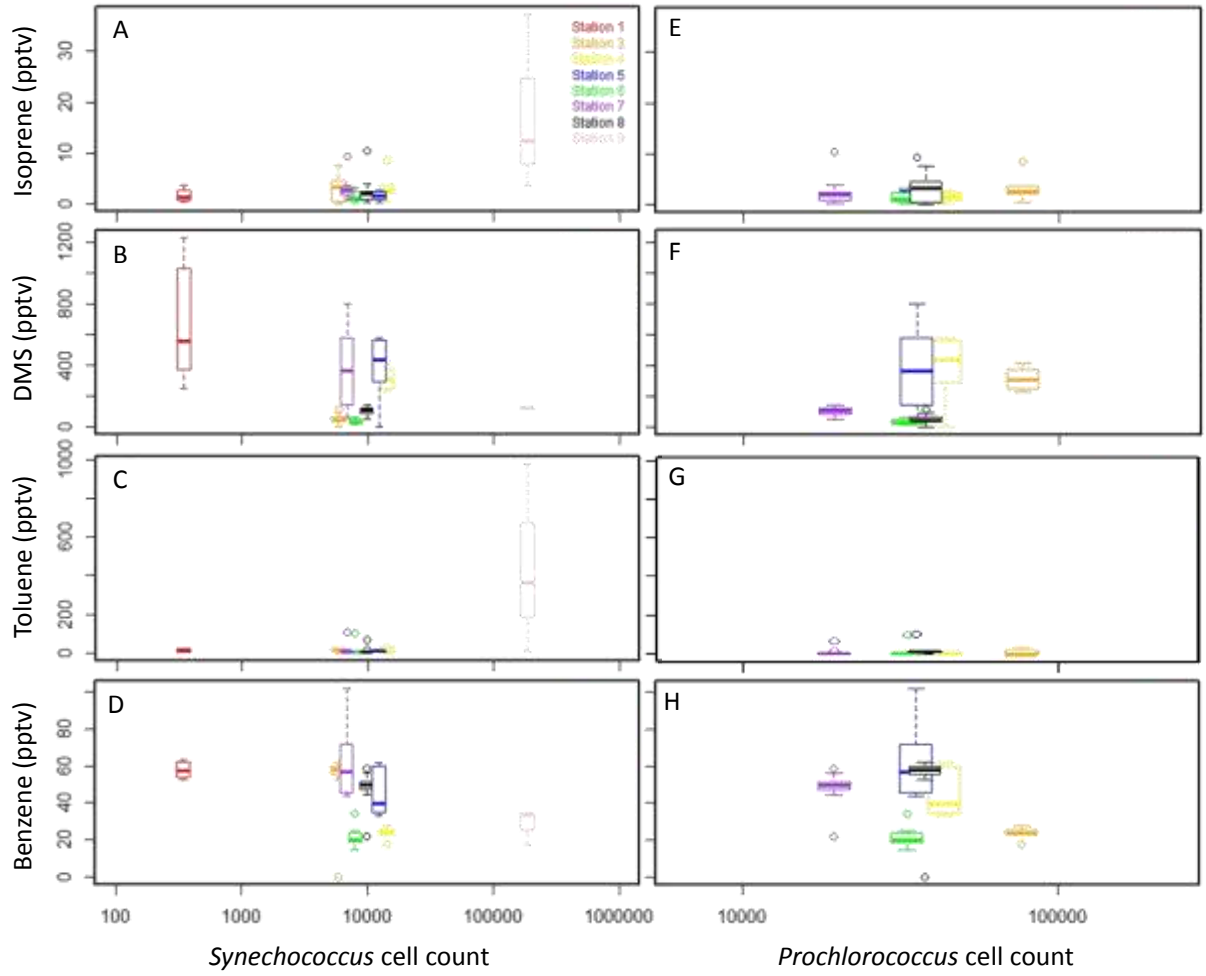


Figure 14- Correlations between mixing ratios and cell counts for isoprene, DMS, toluene, and benzene.

As seen in Figure 14, isoprene and toluene show the highest concentration (and largest variability) at station nine for the *Synechococcus* data. This is compatible to the time series examined above in section 3.2 (Figure 8), which showed the largest peak in mixing ratios occurring at the end of the transect. Station 9 also corresponds the largest cell count for

Synechococcus, which is due to a large *Synechococcus* bloom that was encountered during the last leg of the research cruise. This bloom may be responsible for the elevated mixing ratios seen in many of the compounds at station 9.

Stations 3 and 4 contain the highest *Prochlorococcus* cell counts yet tend to associate with lower mixing ratios for isoprene and toluene. Within these two compounds, there is variety in the range of concentrations for the different stations. Station 7 was the south most station sampled, and waters may have been either too warm due to higher PAR levels (which might explain the lower cell counts). However, several of the boxplots show high outliers for the mixing ratios at station 7, which may be the result of an added source of isoprene and toluene.

Benzene and DMS show elevated mixing ratios at station 1, which also happened to contain the lowest *Synechococcus* and *Prochlorococcus* cell counts. Due to the proximity of station 1 to land, these higher concentrations may be a result of terrestrial air masses contaminating the sampled air. DMS shows a large range of values at station 1 as well, which may be a result of terrestrial and marine air mixing. The time series for DMS also shows only a few outliers at higher concentrations, which may explain the larger variability seen for DMS. Benzene and DMS also show more variety with the variability of the mixing ratios than isoprene and toluene. For example, benzene and DMS show a wide spread for station 5 while isoprene shows none. The variability in benzene values may be associated with anthropogenic sources as well as biogenic ones, as benzene is known to enter the atmosphere through combustion of fossil fuels.[2]

Overall, the mixing ratios for toluene and isoprene seem to be positively correlated to *Synechococcus* cell counts, with the highest mixing ratios associated with the *Synechococcus* bloom at station 9. There seems to be no visible correlation with the *Prochlorococcus* cell data,

with the highest mixing ratios occurring from stations 5 to 7. This data seems to indicate increased production of isoprene and toluene from *Synechococcus*.

3.4 Implications of Biogenic Production

3.4.1 Impacts on Hydroxyl Reactivity

Emissions of VOCs by biogenic sources have the potential to extend the life of various greenhouse gases such as methane. Given the elevated mixing ratios of various VOCs in the *Synechococcus* bloom, calculations were performed to identify the relative contribution of these higher mixing ratios compared to the transect values as a whole. Figure 15 compares the differences in hydroxyl reactivities for selected VOCs for the regional mean values and the *Synechococcus* bloom. The potential for phytoplankton blooms to increase relative hydroxyl reactivities by increased emissions of VOCs may be small, but the calculated differences between the average reactivity and that of the *Synechococcus* bloom demonstrates the ability of these blooms to affect global reactivity values.

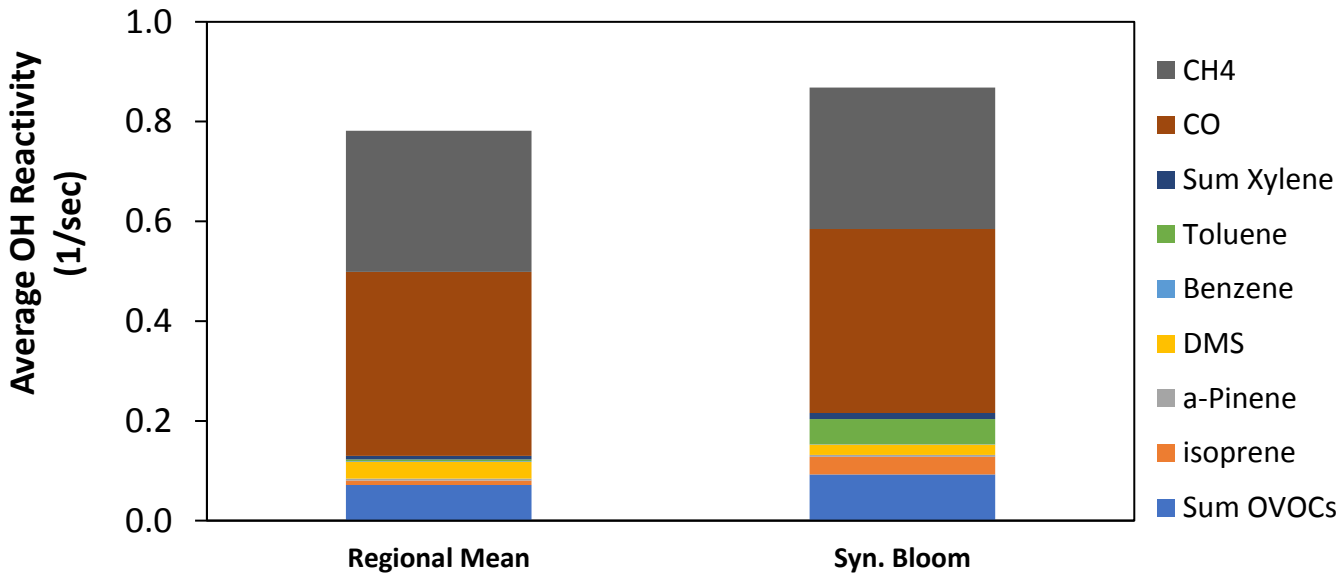


Figure 15- Comparison of VOC hydroxyl reactivities to the *Synechococcus bloom*

As seen in Figure 15 above, the majority of the hydroxyl reactivity comes from methane and carbon monoxide, which is expected in areas without large point sources of VOCs such as urban areas. Compounds such as toluene, isoprene, and the OVOCs in the *Synechococcus* bloom demonstrated increased hydroxyl reactivities compared to the regional bloom, with differences in relative contribution at 0.047, 0.260, and 0.021%, respectively. However, the relative contribution of DMS hydroxyl reactivities decreased between the two groups by 0.013%; which corresponds to the low DMS mixing ratios sampled at station 9, as seen in the time series shown above in section 3.2. The relative contribution of compounds such as α-Pinene and the xylenes also increased by a minimal amount in the bloom, with a difference of 0.0007 and 0.0053 %, respectively.

3.4.2 Impacts on Potential SOA Formation

The ability of marine cyanobacteria to emit VOCs and thus undergo attacks by hydroxyl radicals will have a corresponding effect on the potential for SOA formation. Previous SOA yields for specific VOCs measured by other researchers are given in Table 2 in section 1.2.2. These yields were used to calculate the potential for SOA formation above marine atmospheres, given the observed mixing ratios of various VOCs sampled by this research cruise. In order to examine the effect that emissions from marine phytoplankton may have on SOA formation, the potential maximum for SOA yields was calculated for only the *Synechococcus* bloom, to compare to the dataset as a whole. Figure 16 visually demonstrates this comparison.

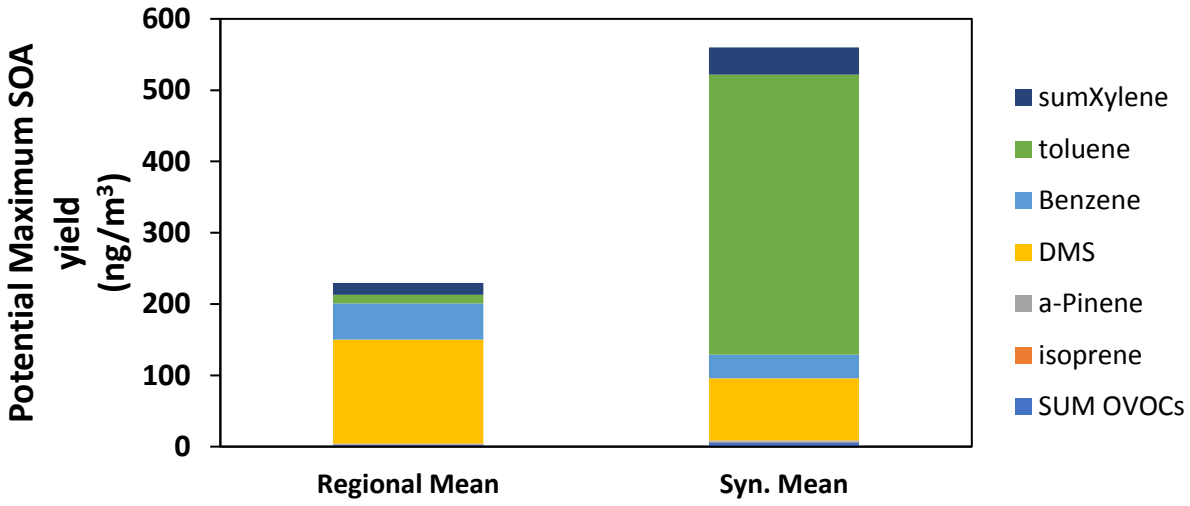


Figure 16- Calculated potential maximum SOA yields for various VOCs

Comparison of the average SOA yields of the entire dataset to just the average from the *Synechococcus*, there is an obvious increase in SOA formation as a whole. Specifically, the largest increase in SOA yield is associated with the massive increase in toluene values seen in the figure above. Along with toluene, there is also a visible increase in SOA yield from the xylenes and the OVOCs, all of which are reflected in the elevated mixing ratios observed during the bloom. DMS and benzene both show a decrease in SOA yields, which could be expected from the lower mixing ratios found at station 9.

4.0 Conclusions and Implications for Future Work

Biological sources represent the largest source of VOCs to the atmosphere; however, our current understanding of the biosynthesis mechanisms behind BVOCs is severely lacking. BVOCs have a high potential for oxidation by hydroxyl radicals, and thus are a large source for SOA formation. Current climate models underpredict the amount of marine SOA formation, possibly due to a missing BVOC source. Marine cyanobacteria are known to emit various BVOC compounds such as isoprene, yet there is a deficiency of observed BVOC concentrations over marine atmospheres This work attempted to quantify certain BVOC concentrations and examine possible correlations to various marine cyanobacterial populations.

Overall, increased emissions of BVOCs from marine cyanobacteria likely play an influential role in marine atmospheres, due to the increase in both hydroxyl reactivities and potential SOA yields during a *Synechococcus* bloom event. The VOCs sampled during this study are predicted to have biogenic origins due to relationships with tracer compounds, and were shown to be strongly associated with *Synechococcus*, with elevated mixing ratios corresponding to high cell counts around station 9.

The VOCs analyzed by this study will add to a scarce dataset of trace gases over marine atmospheres, as well as provide some insight into the possibility of marine cyanobacteria acting as a missing source for SOA formation. Future work will include more accurate source identification and apportionment, as well as eventual inclusion of these data into modeling systems.

References

(1) Sindelarova, K.; Granier, C.; Bouarar, I.; Guenther, A.; Tilmes, S.; Stavrakou, T.; Müller, J. F.; Kuhn, U.; Stefani, P.; Knorr, W. Global Data Set of Biogenic VOC Emissions Calculated by the MEGAN Model over the Last 30 Years. *Atmos. Chem. Phys.* **2014**, *14* (17), 9317–9341.

(2) Misztal, P. K.; Hewitt, C. N.; Wildt, J.; Blande, J. D.; Eller, A. S. D.; Fares, S.; Gentner, D. R.; Gilman, J. B.; Graus, M.; Greenberg, J.; et al. Atmospheric Benzenoid Emissions from Plants Rival Those from Fossil Fuels. *Sci. Rep.* **2015**, *5* (June), 1–10.

(3) Pichersky, E.; Noel, J. P.; Dudareva, N. Biosynthesis of Plant Volatiles: Nature's Diversity and Ingenuity. *Science (80-.).* **2006**, *311* (5762), 808–811.

(4) Kesselmeier, J.; Staudt, M. Biogenic Volatile Organic Compunds (VOC): An Overview on Emission, Physiology and Ecology. *J.Atmos.Chem.* **1999**, *33*, 23–88.

(5) Dudareva, N.; Klempien, A.; Muhlemann, J. K.; Kaplan, I. Biosynthesis, Function and Metabolic Engineering of Plant Volatile Organic Compounds. *New Phytol.* **2013**, *198* (1), 16–32.

(6) Lea-Smith, D. J.; Biller, S. J.; Davey, M. P.; Cotton, C. A. R.; Perez Sepulveda, B. M.; Turchyn, A. V.; Scanlan, D. J.; Smith, A. G.; Chisholm, S. W.; Howe, C. J. Contribution of Cyanobacterial Alkane Production to the Ocean Hydrocarbon Cycle. *Proc. Natl. Acad. Sci.* **2015**, *112* (44), 13591–13596.

(7) Fehsenfeld, F.; Calvert, J.; Fall, R.; Goldan, P.; Guenther, A. B.; Hewitt, N. . C.; Lamb, B.; Shaw, L.; Trainer, M.; Westberg, H.; et al. Emissions of Volatile Organic Compounds

from Vegetation and the Implications for Atmospheric Chemistry. Globabl Biogeochemical cycles 1992, pp 389–430.

(8) Cieslik, S.; Omasa, K.; Paoletti, E. Why and How Terrestrial Plants Exchange Gases with Air. *Plant Biol.* **2009**, *11* (SUPPL.1), 24–34.

(9) Herrmann, K. M. The Shikimate Pathway: Early Steps in the Biosynthesis of Aromatic Compounds. *Plant Cell* **2007**, *7* (7), 907.

(10) Guenther, A. A Global Model of Natural Volatile Organic Compound Emissions. *J. Geophys. Res.* **1995**, *100* (D5), 8873–8892.

(11) Liakakou, E.; Vrekoussis, M.; Bonsang, B.; Donousis, C.; Kanakidou, M.; Mihalopoulos, N. Isoprene above the Eastern Mediterranean: Seasonal Variation and Contribution to the Oxidation Capacity of the Atmosphere. *Atmos. Environ.* **2007**, *41* (5), 1002–1010.

(12) Flombaum, P.; Gallegos, J. L.; Gordillo, R. a; Rincón, J.; Zabala, L. L.; Jiao, N.; Karl, D.; Li, W.; Lomas, M.; Veneziano, D.; et al. Present and Future Global Distributions of the Marine Cyanobacteria Prochlrococcus and Synechococcus. *Pnas* **2013**, *110* (24), 9824–9829.

(13) Partensky, F.; Hess, W. R.; Vaulot, D. Prochlorococcus, a Marine Photosynthetic Prokaryote of Global Significance. *Microbiol. Mol. Biol. Rev.* **1999**, *63* (1), 106–127.

(14) Schirmer, A.; Rude, M.A.; Li, X.; Popova, E.; Cardayre, S. B. Microbial Biosynthesis of Alkanes. *Science (80-.).* **2010**, *329* (July), 559–562.

(15) Han, J.; McCarthy, E.D.; Calvin, M.; Benn, M. H. Hydrocarbons Constituents of the Blue-Green Algae Nostoc Muscorum, Anacystis Nidulans, Phormidium Luridium, and

Chlorogloea Fritschii. *J. Chem. Soc. C Org.* **1968**, No. 0.

(16) Reddy, C.; Valentine, D. L.; Swarthout, R. F. Collaborative Research : Do Cyanobacteria Drive Marine Hydrocarbon Biogeochemistry ? 2016, pp 1–19.

(17) Keller, M. D. Dimethyl Sulfide Production and Marine Phytoplankton: The Importance of Species Composition and Cell Size. *Biol. Oceanogr.* **1989**, *6*, 375–383.

(18) Shaw, S. L.; Chisholm, S. W.; Prinn, R. G. Isoprene Production by Prochlorococcus, a Marine Cyanobacterium, and Other Phytoplankton. *Mar. Chem.* **2003**, *80* (4), 227–245.

(19) Yassaa, N.; Peeken, I.; Zllner, E.; Bluhm, K.; Arnold, S.; Spracklen, D.; Williams, J. Evidence for Marine Production of Monoterpenes. *Environ. Chem.* **2008**, *5* (6), 391–401.

(20) Coates, R. C.; Podell, S.; Korobeynikov, A.; Lapidus, A.; Pevzner, P.; Sherman, D. H.; Allen, E. E.; Gerwick, L.; Gerwick, W. H. Characterization of Cyanobacterial Hydrocarbon Composition and Distribution of Biosynthetic Pathways. *PLoS One* **2014**, *9* (1).

(21) Shaw, S. L.; Gantt, B.; Meskhidze, N. Production and Emissions of Marine Isoprene and Monoterpenes: A Review. *Adv. Meteorol.* **2010**, *2010* (1), 1–24.

(22) Charlson, R. J.; Lovelock, J. E.; Andreae, M. O.; Warren, S. G. Ocean Phytoplankton, Atmospheric Sulfur, Cloud Albdeo, and Climate. *Nature* **1987**, *326*, 655–661.

(23) Shaw, S. L. The Production of Non-Methane Hydrocarbons by Marine Plankton. Massachusetts Institute of Technology 1995, pp 1–169.

(24) Pszenny, A. A. P.; Prinn, R. G.; Kleiman, G.; Shi, X.; Bates, T. S. Nonmethane Hydrocarbons in Surface Waters, Their Sea-Air Fluxes and Impact on OH in the Marine

Boundary Layer during the First Aerosol Characterization Experiment (ACE 1). *J. Geophys. Res. Atmos.* **1999**, *104* (D17), 21785–21801.

(25) Prinn, R. G. The Cleansing Capacity of the Atmosphere. *Annu. Rev. Environ. Resour.* **2003**, *28*, 29–57.

(26) Hewitt, C. N.; Harrison, R. M. Tropospheric Concentrations of the Hydroxyl Radical-a Review. *Atmos. Environ.* **1985**, *19* (4), 545–554.

(27) Greenberg, J. P.; Zimmerman, P. R. Nonmethane Hydrocarbons in Remote Tropical , Continental , and Marine Atmospheres. *J. Geophys. Res.* **1984**, *89* (D3), 4767–4778.

(28) Atkinson, R.; Arey, J. Atmospheric Degradation of Volatile Organic Compounds. *Chem. Rev.* **2003**, *103* (12), 4605–4638.

(29) Zimmerman, P. R.; Greenberg, J. P.; Westberg, C. E. Measurements of Atmospheric Hydrocarbons and Biogenic Emission Fluxes in the Amazon Boundary Layer. *J. Geophys. Res.* **1988**, *93* (D2), 1407–1416.

(30) Pöschl, U. Atmospheric Aerosols: Composition, Transformation, Climate and Health Effects. *Angew. Chemie - Int. Ed.* **2005**, *44* (46), 7520–7540.

(31) Bonsang, B.; Kanakidou, M.; Lambert, G. NMHC in the Marine Atmosphere: Preliminary Results of Monitoring at Amsterdam Island. *J. Atmos. Chem.* **1990**, *11* (1–2), 169–178.

(32) Poisson, N.; Kanakidou, M.; Crutzen, P. J. Impact of Non-Methane Hydrocarbons on Tropospheric Chemistry and the Oxidizing Power of the Global Troposphere: 3-Dimensional Modeling Results. *J. Atmos. Chem.* **2000**, *36*, 157–230.

(33) Lewis, A. C.; Carpenter, L. J.; Pilling, M. J. Nonmethane Hydrocarbons in Southern

Ocean Boundary Layer Air. *J. Geophys. Res. Atmos.* **2001**, *106* (D5), 4987–4994.

(34) Rinaldi, M.; Decesari, S.; Finessi, E.; Giulianelli, L.; Carbone, C.; Fuzzi, S.; O'Dowd, C. D.; Ceburnis, D.; Facchini, M. C. Primary and Secondary Organic Marine Aerosol and Oceanic Biological Activity: Recent Results and New Perspectives for Future Studies. *Adv. Meteorol.* **2010**, *2010*, 1–10.

(35) Stirnweis, L.; Marcolli, C.; Dommen, J.; Barmet, P.; Frege, C.; Platt, S. M.; Bruns, E. A.; Krapf, M.; Slowik, J. G.; Wolf, R.; et al. Assessing the Influence of NOx Concentrations and Relative Humidity on Secondary Organic Aerosol Yields from α-Pinene Photo-Oxidation through Smog Chamber Experiments and Modelling Calculations. *Atmos. Chem. Phys.* **2017**, *17* (8), 5035–5061.

(36) Zhang, H.; Surratt, J. D.; Lin, Y. H.; Bapat, J.; Kamens, R. M. Effect of Relative Humidity on SOA Formation from Isoprene/NO Photooxidation: Enhancement of 2-Methylglyceric Acid and Its Corresponding Oligoesters under Dry Conditions. *Atmos. Chem. Phys.* **2011**, *11* (13), 6411–6424.

(37) O'Dowd, C. D.; Facchini, M. C.; Cavalli, F.; Ceburnis, D.; Mircea, M.; Decesari, S.; Fuzzi, S.; Young, J. Y.; Putaud, J. P. Biogenically Driven Organic Contribution to Marine Aerosol. *Nature* **2004**, *431* (7009), 676–680.

(38) Zhao, D. F.; Kaminski, M.; Schlag, P.; Fuchs, H.; Acir, I. H.; Bohn, B.; Häseler, R.; Kiendler-Scharr, A.; Rohrer, F.; Tillmann, R.; et al. Secondary Organic Aerosol Formation from Hydroxyl Radical Oxidation and Ozonolysis of Monoterpenes. *Atmos. Chem. Phys.* **2015**, *15* (2), 991–1012.

(39) Gantt, B.; Johnson, M. S.; Crippa, M.; Prévôt, A. S. H.; Meskhidze, N. Implementing

Marine Organic Aerosols into the GEOS-Chem Model. *Geosci. Model Dev.* **2015**, *8* (3), 619–629.

(40) Myriokefalitakis, S.; Vignati, E.; Tsigaridis, K.; Papadimas, C.; Sciare, J.; Mihalopoulos, N.; Facchini, M. C.; Rinaldi, M.; Dentener, F. J.; Ceburnis, D.; et al. Global Modeling of the Oceanic Source of Organic Aerosols. *Adv. Meteorol.* **2010**, *2010*, 1–16.

(41) Singh, H. B.; Salas, L. J.; Chatfield, R. B.; Czech, E.; Fried, A.; Walega, J.; Evans, M. J.; Field, B. D.; Jacob, D. J.; Blake, D.; et al. Analysis of the Atmospheric Distribution, Sources, and Sinks of Oxygenated Volatile Organic Chemicals Based on Measurements over the Pacific during TRACE-P. *J. Geophys. Res. D Atmos.* **2004**, *109* (15).

(42) Gilman, J. B.; Kuster, W. C.; Goldan, P. D.; Herndon, S. C.; Zahniser, M. S.; Tucker, S. C.; Brewer, W. A.; Lerner, B. M.; Williams, E. J.; Harley, R. A.; et al. Measurements of Volatile Organic Compounds during the 2006 TexAQS/GoMACCS Campaign: Industrial Influences, Regional Characteristics, and Diurnal Dependencies of the OH Reactivity. *J. Geophys. Res. Atmos.* **2009**, *114* (7), 1–17.

(43) Montzka, S. A.; Calvert, P.; Hall, B. D.; Elkins, J. W.; Conway, T. J.; Tans, P. P.; Sweeney, C. S. On the Global Distribution, Seasonality, and Budget of Atmospheric Carbonyl Sulfide (COS) and Some Similarities to CO2. *J. Geophys. Res. Atmos.* **2007**, *112* (9), 1–15.

(44) Swarthout, R. F.; Russo, R. S.; Zhou, Y.; Hart, A. H.; Sive, B. C. Volatile Organic Compound Distributions during the NACHTT Campaign at the Boulder Atmospheric Observatory: Influence of Urban and Natural Gas Sources. *J. Geophys. Res. Atmos.* **2013**, *118* (18), 10614–10637.