Environmental Science & Technology

pubs.acs.org/est Article

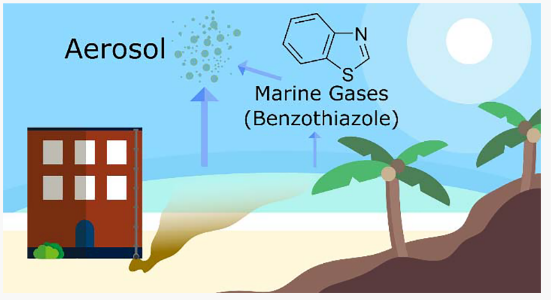
Atmospheric Benzothiazoles in a Coastal Marine Environment

Emily B. Franklin,*,# Michael R. Alves,# Alexia N. Moore, Delaney B. Kilgour, Gordon A. Novak, Kathryn Mayer, Jonathan S. Sauer, Robert J. Weber, Duyen Dang, Margaux Winter, Christopher Lee, Christopher D. Cappa, Timothy H. Bertram, Kimberly A. Prather, Vicki H. Grassian, and Allen H. Goldstein

Cite This: *Environ. Sci. Technol.* 2021, 55, 15705−15714

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information



ABSTRACT: Organic emissions from coastal waters play an important but poorly understood role in atmospheric chemistry in coastal regions. A mesocosm experiment focusing on facilitated biological blooms in coastal seawater, SeaSCAPE (Sea Spray Chemistry and Particle Evolution), was performed to study emission of volatile gases, primary sea spray aerosol, and formation of secondary marine aerosol as a function of ocean biological and chemical processes. Here, we report observations of aerosol-phase benzothiazoles in a marine atmospheric context with complementary measurements of dissolved-phase benzothiazoles. Though previously reported dissolved in polluted coastal waters, we report the first direct evidence of the transfer of these molecules from seawater into the atmosphere. We also report the first gas-phase observations of benzothiazole in the environment absent a direct industrial, urban, or rubber-based source. From the identities and temporal dynamics of the dissolved and aerosol species, we conclude that the presence of benzothiazoles in the coastal water (and thereby their emissions into the atmosphere) is primarily attributable to anthropogenic sources. Oxidation experiments to explore the atmospheric fate of gas-phase benzothiazole show that it produces secondary aerosol and gas-phase SO_2, making it a potential contributor to secondary marine aerosol formation in coastal regions and a participant in atmospheric sulfur chemistry.

KEYWORDS: *benzothiazole, marine, anthropogenic, contaminants, secondary organic aerosol, sea spray aerosol*

■ INTRODUCTION

Coastal oceans are often enriched with organic species from both biogenic and anthropogenic sources. Biogenic sources include phytoplankton, which convert CO_2 to ocean biomass that is then transformed by the microbial loop.[1,2] Direct anthropogenic sources of marine organics in seawater include wastewater discharge and urban runoff (often enriched with personal care products), trash, and shipping pollution.[3−5] Phytoplankton blooms occur naturally but also can be induced by anthropogenic discharges of fertilizer enriched runoff and can be enhanced by climate change induced perturbations to ocean temperatures and chemistry.[6−9] Ocean-derived organic species can be transferred from the ocean to the atmosphere through two major mechanisms, both of which can influence atmospheric chemistry over the ocean. The first of these produces sea spray aerosol (SSA) from bubble bursting and wind shear at the surface.[10] The second method involves the emission of volatile organic compounds (VOCs) from the ocean surface, either through volatilization or interfacial reactions producing volatile products.[11−13]

The composition and properties of organic material emitted from the ocean are important areas of atmospheric research, as they influence marine atmospheric chemistry and public health. Salt and organics have different cloud and ice nucleation properties, meaning that organic enrichment of SSA is important for climate.[14−17] Marine VOCs oxidize in the atmosphere, where they can form secondary marine aerosols (SMA).[18] Recent laboratory and field studies have suggested that SMA may play a significant role in cloud formation over the ocean,[19,20] making the emission and oxidation processes of marine volatile organics a critical area of atmospheric chemistry research. Organic enriched marine aerosols are also a growing area of concern in public health, as they can expose coastal communities to marine toxins and pollutants, including biogenic toxins from harmful algal blooms, pesticides, and phthalates.[21−23]

Production of plasticizers, pharmaceuticals, pesticides, and more, over the course of the last century, has led to a portion of dissolved organic matter (DOM) in marine ecosystems

Received: July 15, 2021
Revised: November 1, 2021
Accepted: November 8, 2021
Published: November 17, 2021

https://doi.org/10.1021/acs.est.1c04422
Environ. Sci. Technol. 2021, 55, 15705−15714

being classified as anthropogenic dissolved organic carbon (ADOC).[24] The 100,000+ commercialized synthetic compounds produced by humans have been continually increasing in both number and concentration in many environments.[25,26] These human-produced compounds tend to be hydrophobic and, for the most part, have completely unknown breakdown byproducts, toxicities, and fates in the environment.[27,28] Though there is no study to our knowledge that has reported total anthropogenic DOM concentrations in coastal waters near populated areas, it is expected that this number will be greater than the <1 uM, or 0.05 to 1% of total DOM, reported for water collected from the open ocean due to the more concentrated coastal inputs and sources.[24,29] The hydrophobic fraction of these species will be highly concentrated at the surface of the ocean, joining biogenically formed molecules in a 1−100 μm thick region known as the sea surface microlayer (SSML).[30] Many studies have shown that the ocean surface is a source of organic material for both SSA and SMA, significantly contributing to the overall chemistry and properties of these aerosols.[31,32,15,33,13,34]

Benzothiazoles are a class of anthropogenic pollutants that have been previously reported and in a variety of freshwater and coastal aquatic environments, including the southern California coast,[35−40] but they are also produced biogenically from select marine microbiological species.[41,42] Benzothiazole (hereafter BT) (C_7H_5NS) is an aromatic heterocyclic organic compound containing both sulfur and nitrogen. Benzothiazoles are here defined as compounds containing a benzothiazole moiety. Benzothiazoles are high production volume chemicals used in a wide range of industrial and consumer products, with significant sources including rubber production, leather and paper production, antifreeze, herbicides, textiles, and plastics.[35] They are found in both urban runoff and wastewater, with urban runoff frequently the more concentrated of the two source groups.[43] A review of the ranges of measured concentrations of dissolved BT and 2-(methylthio)-benzothiazole in stormwater runoff and wastewater effluent at sites along the southern California coast (ranging from 0.05 to 0.5 μg/L for BT and 0.04 to 0.3 μg/L for 2-(methylthio)-benzothiazole) can be found in Zeng et al.[40] Benzothiazoles have been observed in the dissolved-phase in a variety of coastal marine settings and used as tracers of wastewater discharge.[38,40,37,36] This compound class is a growing area of concern in both marine ecosystem and public health; benzothiazole derivatives from rubber leachates are toxins hazardous to marine microbiology, and various benzothiazoles are human dermal sensitizers, endocrine disruptors, carcinogens, and genotoxins.[35,44−46]

In this study, we investigate the transfer of benzothiazoles from coastal water into the atmosphere through a controlled mesocosm study. While dissolved benzothiazoles have been reported in the water in a variety of coastal regions, we report observations of benzothiazoles in sea spray aerosols and emitted VOCs, showing for the first time that polluted coastal oceans likely emit these chemicals to the atmosphere. Furthermore, we explore the atmospheric oxidation and aerosol formation potential of gas-phase BT, which has implications for air quality in both polluted coastal regions and urban or industrial centers in which benzothiazoles are most concentrated (Figure S1).

MATERIALS AND METHODS

Experimental Campaign, Sample Collection, and Online Analysis. The results from this study derive primarily from Sea Spray Chemistry And Particle Evolution (SeaSCAPE) 2019, a collaborative mesocosm experiment described in Sauer, Mayer, and Lee et al..[47] Coastal water (12,000 L) from Ellen Browning Scripps Memorial Pier (hereafter Scripps Pier) in La Jolla, CA, was transported into an indoor wave chamber facility (hereafter referred to as the wave channel), in which mechanically generated waves break on an artificial beach to create realistic primary sea spray aerosols. The natural coastal water was amended with nutrients to initiate an algal bloom of the naturally existing phytoplankton species, including three bloom experiments, replicating methodology described in Wang et al.[48] Water from the wave channel was diverted through an inert glass and Teflon chamber forming an isolated sampling vessel (ISV), allowing analysis of gas-phase marine emissions. This analysis focuses on the third algal bloom experiment, which lasted 20 days from July 24 to August 12, 2019, and is described in detail in Sauer, Mayer, and Lee et al.[47]

Periodically over the course of the bloom, water from the SeaSCAPE channel was collected for offline analysis of headspace gases (described below) and of extracted DOM chemical composition (also described below). One water sample directly from Scripps Pier was collected on July 23 for DOM extraction and analysis of dissolved analytes under ambient conditions. Submicron aerosol samples from the channel were collected on quartz fiber filters (Pallflex Tissuequartz) using a custom designed automated sequential sampler. Additional sample collection and storage details can be found in Supporting Information section 3 (SI.3). ISV VOCs were collected on custom triple bed sorbent tubes (Camsco). Samples (2 L) were collected every 2−3 days during the early stages of the bloom and 1−2 times per day during peak biological activity. Sorbent tube material and sampling details can be found in SI.1 and SI.4. VOCs both within the ISV and in the channel were additionally measured by Vocus proton-transfer-reaction time-of-flight mass spectrometer (Vocus PTR-TOF by Aerodyne/Tofwerk).[47] Following the conclusion of SeaSCAPE, the Vocus was relocated to the end of the Scripps Pier for ambient coastal VOC sampling. A full description of Scripps Pier VOC sampling can be found in SI.5.

Collection and extraction of marine DOM was performed using solid-phase extraction (SPE) by PPL resin (Bond Elut, Agilent), following methods previously characterized in Dittmar et al. and described in detail in SI.6.[49]

Offline Analysis. A high-resolution Orbitrap spectrometer equipped with a modified Atmospheric Pressure Chemical Ionization source (APCI-Orbitrap, ThermoFisher) was used to detect VOCs in the headspace of collected water during the SeaSCAPE campaign in a method adapted from Roveretto and co-workers.[50] Operational details can be found in SI.7.

Aerosol filters, DOM, and VOC sorbent tubes were all analyzed by thermal desorption two-dimensional gas chromatography coupled with electron ionization time-of-flight mass spectrometry (TD-GCxGC-ToF-MS) on two separate instruments covering differing volatility ranges. DOM and aerosol samples were analyzed on GCxGC A, while VOC sorbent tubes were analyzed on GCxGC B (details in SI.2). DOM and aerosol samples were normalized by internal standard and

Table 1. Identities, Solubilities, and Concentrations of Benzothiazoles Observed at SeaSCAPE[a]

compound identity	solubility in water (mg/L)	aerosol-phase mean concentration [s.d.] (ng/m^3)	DOM-phase concentration- 7/23 ambient sample (μg/L)
benzothiazole[b]	1684	13 [4.7]	0.29
phenylbenzothiazole[b,g]	8.804	0.64 [.30]	0.0093
2-(methylthio)benzothiazole[b]	66.61	1.4 [.77]	0.96
butylbenzothiazole[d]	12.8	9.2 [4.8]	0.017
Alk-benzothiazole (1)[c]	12.8[h]	0.59 [.44]	
Alk-benzothiazole (2)[c]	12.8[h]	0.032 [.033]	
Alk-Benzothiazole (3)[c]	12.8[h]	0.028 [.031]	
Alk-benzothiazole (4)[c]	12.8[h]	0.045 [.043]	
Alk-benzothiazole (5)[c]	12.8[h]	0.0067 [.0071]	
2-*o*-tolylbenzothiazole[d]	4.81	0.012 [.0088]	
3-methyl-3*H*-benzothiazol-2-one[d]	1319		0.31
3-ethylbenzothiazolin-2-thione[e]		0.32 [.26]	
N-ethyl-2-benzothiazoleamine[e]	142.2[i]	0.17 [.043]	
R-mercaptobenzothiazole[f]	0.05096[i]	0.030 [.021]	
R-2(3*H*)-benzothiazolone[e]	2354[i]	0.032 [.039]	0.016

[a]Aerosol-phase concentrations are reported as an average and standard deviation of concentrations over the full experimental campaign, while dissolved phase concentrations are reported from the initial pre-experiment sample for comparison to other ambient sampling measurements of benzothiazoles. [b]Isomer specific identification confirmed via an authentic standard. [c]Series of alkyl benzothiazoles, identified via high (>750) match factor with spectrum of butylbenzothiazole and location in GCxGC space. Based on kovats indices, likely C4−C7 straight- and branched-chain alkyl benzothiazoles. [d]Identified via high (>800) match factor with a NIST14 mass spectral database entry along with Kovats index matches from previously published isolation where available. [e]Classified as benzothiazole due to relatively high (>700, <800) NIST match factor with named benzothiazole or by a high match factor but kovats index disagreement; novel compound without published mass spectra, tentatively identified as benzothiazole due to mass spectral indicators. [f]Identity unknown, but based on the mass spectrum assigned the identity of R-mercaptobenzothiazole, with R an unknown group likely containing heteroatom(s). [g]Note that there are two distinct speciations of phenyl benzothiazoles observed between the two phases; 2-phenyl benzothiazole is observed in the aerosol phase, while an undetermined alternate phenyl benzothiazole isomer is observed in the dissolved phase. [h]There were no predicted or experimental solubility values for C5+ Alk-benzothiazoles; therefore, they were assigned solubility of butyl benzothiazole. [i]Note that the exact identities of these species are unknown but the solubilities match those of the identified chemically similar benzothiazoles named in column 1.

derivatized to enhance recovery of polar organics. TD-GCxGC methodology is described in detail in Worton et al. and details specific to this analysis can be found in SI.9.[51]

From SeaSCAPE samples, 754 unique aerosol organics and 991 unique DOM organics were compiled into libraries of mass spectra and retention indices (internal standard normalized position in the volatility dimension) were catalogued. Of these unique organic species, 12 SSA organics and 6 DOM organics were identified as benzothiazoles based on matches and similarities to authentic standards and species catalogues in the NIST-14 mass spectral database according to four classes of identification certainty (see Table 1). Each observed benzothiazole was assigned to a benzothiazole external standard chemical proxy for quantification based on exact match or chemical similarity and proximity in GCxGC space. Proxy assignments and additional details can be found in SI.11.

Benzothiazole Oxidation Study. To complement the mesocosm study and better understand the atmospheric fate of gas-phase BT, we used a Potential Aerosol Mass Oxidation Flow Reactor (PAM-OFR) in a separate laboratory oxidation study to produce BT oxidation products. PAM-OFR operation and calibration details can be found in SI.16. BT was introduced into the PAM-OFR through two methods; in the first, liquid BT dissolved in a methanol carrier was introduced in a plug injection experiment at a constant exposure setting. In the second, a BT permeation tube continuously introduced gas-phase BT at different OH concentrations (2.9, 3.5, and 4.9 days equivalent aging). Particle formation and size distributions, SO_2 production, and HSO_4^- production from the BT oxidation experiments were all monitored (SI.16).

Reported herein we show that BT and benzothiazole-moiety compounds are not just present in sea spray aerosols but also show an ability to form secondary aerosols using an oxidative flow reactor to simulate photochemical aging.

RESULTS AND DISCUSSION

Gas-Phase Benzothiazole Observations. In the early stages of the SeaSCAPE experiment, a significant and unexpected peak was observed to correspond to $C_7H_5NSH^+$ (BT) by APCI-Orbitrap headspace VOC analysis. Gas-phase BT and its isomeric identity was confirmed using the Orbitrap's tandem mass spectrometry capabilities and the clear observation of the benzene and cyclic ring (containing the nitrogen and sulfur) fragments. This peak's identity was later confirmed and quantified by offline TD-GCxGC-ToF-MS analysis of sorbent tube samples collected from the SeaSCAPE ISV (14 ev and 70 ev EI spectra illustrated in Figure S2). Time resolved measurements of the ion corresponding to gas-phase benzothiazole were obtained by the Vocus throughout SeaSCAPE. A quantitative comparison of GCxGC and Vocus benzothiazole and summed monoterpene ISV measurements is shown in the SI (Figure S4), while absolute quantities measured by each instrument differ, variability over the SeaSCAPE bloom and relative abundances of significant observed gases agree, with R^2 of 0.91 and 0.98 for benzothiazole and summed monoterpenes, respectively.

Gas-phase benzothiazole has been reported in atmospheric measurements in the contexts of freshly shredded rubber,[35] urban traffic, and coal burning in a region with plastic production,[52] but emissions of gas-phase benzothiazole from coastal waters are, to our knowledge, a novel finding. As

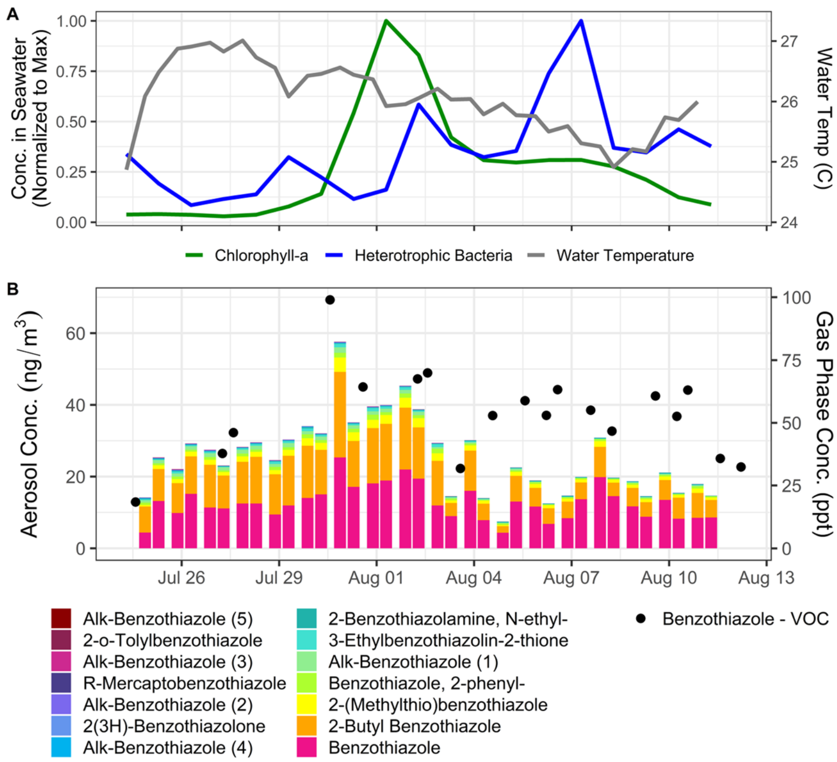


Figure 1. Time series of biological activity indicators and water temperature (A) and atmospheric benzothiazoles (B) at a SeaSCAPE 2019 bloom 3 experiment. Atmospheric benzothiazole concentrations are differentiated into gas-phase BT from the dome (black circles) and submicron nascent sea spray aerosol phase benzothiazoles from the wave chamber (colored bars). A detailed discussion of uncertainties can be found in the Supporting Information.

benzothiazole is a common anthropogenic contaminant that could potentially be added if the water were mishandled, we confirmed the presence of benzothiazoles in the collected coastal water absent perturbations from transport into the SeaSCAPE wave channel. Benzothiazole was consistently found in all monitored phases (dissolved, aerosol, and gas) (Table 1; Figure 1), and dissolved-phase concentrations did not increase between the first sample (collected directly at Scripps Pier) and the next DOM sample, collected from the channel 2 days following transport. Additionally, the ion corresponding to gas-phase BT was observed by the Vocus PTR-MS at the end of Scripps Pier directly following the SeaSCAPE experimental campaign, confirming that gas-phase BT is present in the local coastal marine atmosphere. End-of-pier BT concentrations averaged 2.5 ppt (compared to a detection limit of 0.5 ppt for a 10 s averaging time, averaged over the entire ~1 month measurement period), and SeaSCAPE ISV concentrations (as quantified by GCxGC) averaged 53 ppt. Given the elevated water temperature, enclosed conditions, and low gas-phase flow rate of the SeaSCAPE ISV (described in Sauer, Mayer, and Lee et al.), absolute gas-phase ISV concentrations exceeding ambient concentrations at the end of the pier is indicative of emissions to the gas phase.[47]

Previously reported Henry's law constants for BT ($K_{H'}$, estimated from vapor pressure and solubility in Reddy et al., predicted from structure through various methods as reported in Sander, and predicted from structure based on HENRYWIN v. 3.10, EPA EPI Suite) range from 1.5×10^{-5} to 2.6×10^{-4} (dimensionless gas over liquid, converted assuming 25 °C).[53,54] Under the aqueous concentration (0.29 μg/L at day 1 sampling time, as shown in Table 1) and temperature conditions observed at SeaSCAPE, this would imply a maximum equilibrium gas concentration of BT between 0.7 and 12 ppt, a factor of 75−4.4 below the average concentrations observed in the ISV (53 ppt). A simplified partitioning experiment using benzothiazole and reference species dissolved in simplified simulated seawater in concentrations mirroring those identified in the SeaSCAPE DOM (described in SI.10) did not detect benzothiazole above a detection limit of 10 ppt, supporting the conclusion that observed gas-phase concentrations of benzothiazole in the SeaSCAPE ISV cannot be adequately explained by ideal air water partitioning governed by Henry's law. This implies that some ocean-atmosphere transfer mechanism other than idealized aqueous partitioning plays an important role in gas-phase BT emissions. It should also be noted that the lowest reported Henry's law constant of BT, that reported by HENRYWIN v. 3.10, EPA EPI Suite, is the most commonly referenced value across popular chemical information repositories (such as PubChem and ChemSpider) and has been used to assume negligible volatilization of benzothiazole from organic rich aquatic systems (wastewater), rendering this finding of elevated benzothiazole emissions from real organic-rich aquatic systems particularly important.[55]

Aerosol and DOM Benzothiazole Observations and Comparisons. In addition to BT, a suite of larger compounds containing a benzothiazole moiety were observed in both the aerosol and dissolved phases (Table 1). BT accounts for 50% of the total mean benzothiazole carbon pool in the aerosol phase and is the second most significant contributor to dissolved benzothiazoles at 43% of the mean DOM benzothiazole carbon pool. DOM BT concentrations measured directly at the pier (0.29 ± 0.15 ug/L), reported in Table 1, fall

https://doi.org/10.1021/acs.est.1c04422
Environ. Sci. Technol. 2021, 55, 15705−15714

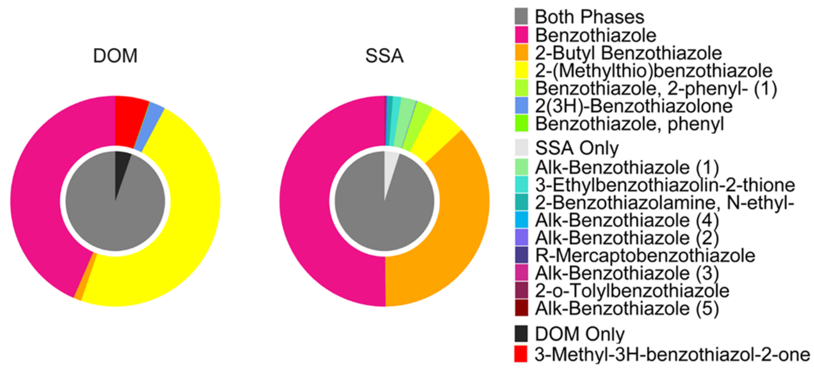


Figure 2. Molecular distributions and molecular overlap (by mass) of benzothiazoles observed in DOM (left) and nascent sea spray aerosol (right) at SeaSCAPE 2019.

within reported ranges of observed BT in freshwater aquatic environments along the southern California coast, which range from 0.05 to 0.5 μg/L.[40] 2-(Methylthio)benzothiazole, a commonly reported tracer species for benzothiazoles originating from wastewater or runoff,[40,43] is the most abundant benzothiazole species observed in the dissolved phase at 47% of mean DOM benzothiazole carbon pool. Butylbenzothiazole, a species not previously reported in environmental measurements and present at near detection limit levels in the dissolved phase, contributes the second highest fraction of the aerosol benzothiazole carbon pool (37%), while 2-(methylthio)benzothiazole contributes the third highest fraction at 6%.

The time series of gas and aerosol-phase benzothiazoles provide valuable insights into likely sources and transfer processes governing marine benzothiazole emissions (Figure 1). Prior to August 5, a key biological transition period between peak chlorophyll and peak heterotrophic bacteria during which many key biogenic gases peak (as illustrated in Figure S3), gas and aerosol-phase BT are highly correlated (R^2 = 0.78). In both phases, BT begins relatively low before increasing (by a factor of 5 in the gas phase and a factor of 3 in the aerosol phase) to a peak in the afternoon through night of July 30, after which it declines, back to initial concentrations for the aerosol phase and to approximately double initial concentrations in the gas phase. There is no clear temperature, biological, or perturbation-based explanation for the July 30 peak, but in the gas phase it is observed for BT across all instruments and sampling strategies (GCxGC, Vocus PTR-ToF, and APCI-Orbitrap) and is common to an array of anthropogenic gases, as illustrated in Figure S3. After August 5, however, the BT traces of the two phases are loosely anticorrelated with an R^2 of 0.11. As previously noted, the composition and thickness of the sea surface microlayer have been observed, modeled, and demonstrated to play an important role in the transfer of marine gases.[11,34] Changes in SSML composition and characteristics during the second half of the bloom, described in Crocker et al.,, could therefore at least partially explain the lack of correlation in this period.[56]

Although there are some similarities between the temporal variability of benzothiazoles and biological indicators (specifically chlorophyll-a concentrations in the bulk water), the time series of both gas and aerosol-phase benzothiazoles are much more similar to anthropogenic species than to any known biogenic products. In the aerosol phase, the total benzothiazole carbon pool time series is strongly correlated across the entire bloom (R^2 = 0.85, see Figure S8) with that of tetradecamethylcycloheptasiloxane (more commonly known as D7), an anthropogenic species attributable to personal care products,[57] wastewater,[58] and sewage and also observed to bioaccumulate in marine ecosystems.[59] In the gas phase, BT also displays similar temporal dynamics to anthropogenic species (Figure S3), specifically benzophenone (a common sunscreen and personal care product component)[60] and naphthalene (a polycyclic aromatic hydrocarbon (PAH), previously identified as a coastal marine contaminant off the Southern California coast and likely originating from some combination of petroleum and combustion sources).[61] While the correlations between BT and benzophenone and naphthalene are not strong (R^2 = 0.25 and 0.35, respectively), they are far stronger than the correlations with any of the known biogenic gases; the R^2 of the correlations between BT and isoprene, DMS, and beta-cyclocitral are all below 0.005. While there may be some degree of biogenic contribution to observed atmospheric benzothiazoles, there is no compelling evidence for such a source in the temporal variability. A full discussion of potential sources and justification for a conclusion of a dominant anthropogenic origin based on additional chemical indicators can be found in the following section.

One observed aerosol-phase species deserving particular attention is butylbenzothiazole. Although butylbenzothiazole sulfenamides are broadly characterized rubber vulcanization agents[62] and butylbenzothiazole has been synthesized in laboratory environments, it has never to our knowledge been reported in the environment. During the bloom, butylbenzothiazole decreases both in terms of absolute mass concentration and as a fraction of the total benzothiazole carbon pool and drives the majority of the decrease in the total aerosol-phase benzothiazole carbon pool. To our knowledge, there are no studies investigating the biodegradation of butylbenzothiazole in marine settings, but this finding in conjunction with the significant observed aerosol levels indicates that butylbenzothiazole biodegradation may be an important environmental process. No identified benzothiazoles are observed to increase significantly as the aerosol benzothiazole carbon pool shrinks (see Figure S7). There are several probable contributions to this phenomenon. The biodegradation of butylbenzothiazole has not been studied in marine contexts, and its products may not have published mass spectra allowing them to be confirmed as benzothiazole biodegradation products. Additionally, benzothiazole degradation products with published mass spectra may fall outside the TD-GCxGC's sensitivity range, as biological degradation often produces highly oxygenated species not amenable to GC analysis, as described

https://doi.org/10.1021/acs.est.1c04422
Environ. Sci. Technol. 2021, 55, 15705−15714

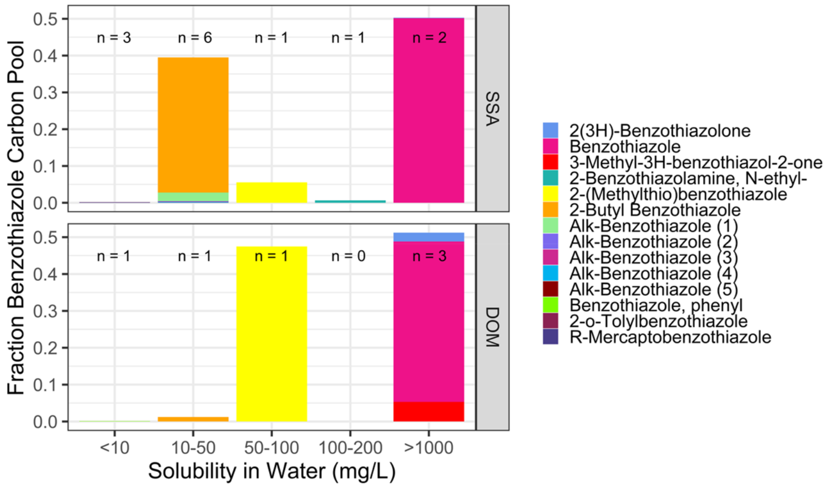


Figure 3. Solubility distributions of benzothiazoles weighted by contribution to cumulative observed benzothiazole carbon pools in the dissolved (DOM) and aerosol (SSA) phases. Number of individual species within each solubility bracket in each phase indicated by *n*. No solubility information for 3-ethylbenzothiazolin-2-thione is available, and it is therefore excluded from visualization.

in Nowak et al., 2018.[63] Benzothiazoles may also bioaccumulate in the biological species within the channel, partition into suspended organic matter, or onto the organic film on the wave channel surfaces or decrease as a relative fraction of submicron organics emitted from bubble-bursting processes due to changes in the structure and composition of the SSML.

While the most abundant benzothiazole species are common to both dissolved and aerosol phases, unique isomers are observed in each and the relative distribution of common species differ (Figure 2), leading to a significant discrepancy between the solubility distributions of the benzothiazole carbon pools in the bulk and aerosol phases; bulk-phase benzothiazoles are more water-soluble and less diverse in low solubility species compared to aerosol-phase benzothiazoles (Figure 3). Of the five species observed in both phases, the low solubility (<15 mg/L) species are significantly enhanced as a fraction of the total benzothiazole carbon pool in SSA (Figure S10). Solubilities in water are estimated from log K_{ow} (WSKOW v. 1.41, EPA EPI Suite) with all alkyl benzothiazoles parametrized as equal in solubility to butylbenzothiazole. The solubility distribution discrepancy is likely due to the concentration of low-solubility organics in the SSML[64] and previously reported film-jet sea spray aerosol formation dynamics, which cause SSML organics to preferentially aerosolize into smaller aerosol particles from film drops.[65−67] The different benzothiazoles' implications for climate and public health relevant properties of sea spray aerosol lie beyond the scope of this publication. However, the differing chemical distributions between dissolved and aerosol phases, in particular the abundance of low solubility benzothiazoles not observed in the bulk water, highlight that measurements of bulk-phase organics in ocean waters are imperfect indicators of which organic species enrich the submicron aerosol particles. This size population has the longest atmospheric lifetime, dominates the marine aerosol surface area distribution, and has the potential to be transported farthest inland. This finding therefore has implications for marine pollutant human exposure in coastal regions; marine pollutant monitoring focuses nearly exclusively on the bulk water, but as this study demonstrates, bulk water and aerosol-phase organic distributions and concentrations differ significantly, meaning that bulk water toxin measurements may not accurately reflect the sea spray aerosol concentrations of hazardous marine pollutants including carcinogens and respiratory irritants not reported in this work.

Evidence for Anthropogenic Origin. While benzothiazoles are high-volume industrial chemicals and are commonly studied as wastewater contaminants in coastal areas, there are also marine biogenic sources of benzothiazoles.[41,42] Coupled with the early bloom increase in gas and aerosol-phase benzothiazole levels that cannot be explained by (do not correlate with) either the rising temperatures or indicators of biological activity (including chlorophyll-a concentrations, heterotrophic bacteria concentrations, and peaks in typical biogenic gases such as DMS and isoprene) (Figure 1), this necessitates a more nuanced investigation of the most probable origins of the benzothiazoles observed at the SeaSCAPE campaign and in ambient air at Scripps Pier. Prominent among benzothiazoles in both dissolved and aerosol phases and observed in particularly high abundance in the dissolved phase was 2-(methylthio)benzothiazole, a known and commonly reported tracer of anthropogenic benzothiazoles originating from runoff or wastewater.[40,68,35] Compared to other anthropogenic benzothiazole tracers, 2-(methylthio)-benzothiazole is relatively resistant to both photochemical and biological degradation, and is itself a biodegradation product of another commonly reported anthropogenic benzothiazole, 2-mercaptobenzothiazole.[69] While multiple naturally occurring benzothiazoles have been characterized and reported, notably including several originating from the marine bacterium species *Micrococcus* sp.,[41] to our knowledge none (with the exception of BT) overlap with those observed in this study. Furthermore, the majority of reported biogenic benzothiazoles contain hydroxy groups, a functional group that is notably absent from all benzothiazole species observed in the dissolved and aerosol phases.[41,70] On the water collection day for SeaSCAPE bloom 3 (July 23, 2019), the coastal current near San Diego ran from north to south at ∼0.3 m/s (SCCOOS HR radar online mapping, documented in Harlan et al.),[71] which would have transported the wastewater from the nearest up-current wastewater discharge point, Oceanside Outfall, to Scripps Pier on a time scale of 36 h (see Figure S5). While enrichment of benzothiazoles from the Oceanside Outfall is certainly a potential contributing factor, given the

https://doi.org/10.1021/acs.est.1c04422
Environ. Sci. Technol. 2021, 55, 15705−15714

distance and dilution more local sources also merit consideration. As illustrated in Figure S6, there are multiple runoff, storm drain, and residential use discharge points along the beach surrounding the Scripps Pier sampling location, all of which could have washed road residues enriched in benzothiazoles into the coastal waters.

Finally, when compared to confidently identified biogenic and anthropogenic gas species, the temporal profile of gas-phase BT is more similar to those of multiple positively identified anthropogenic species than to any positively identified biogenic species or biological indicators, as illustrated in Figure S3 and previously noted in greater detail. The temporal evolution of a suite of anthropogenic gases suggests that some processes related to the establishment of thermal, physical, and chemical equilibrium within the wave channel and ISV caused a lagged peak in some anthropogenic VOCs compared to bulk water temperatures and is not indicative of a significant source of benzothiazole within the wave channel. The identification of known tracers of anthropogenic benzothiazole pollution, multiple logical local sources of anthropogenic benzothiazole runoff, similarity in benzothiazole and some other known anthropogenic VOC temporal profiles, and absence of known biogenic benzothiazoles all lead to the conclusion that the source of benzothiazoles in the SeaSCAPE and Scripps Pier studies is primarily anthropogenic in nature. Scripps Pier lies within the San Diego Scripps State Marine Conservation Area, a relatively clean and protected area of coastline. Given this, the results from this study may be considered a relatively conservative lens into the extent to which these anthropogenic marine contaminants may influence the composition of aerosol and gas-phase emissions in coastal areas.

Benzothiazole Oxidation and Secondary Aerosol Formation. In order to better understand the eventual fate of atmospheric benzothiazole in both coastal marine and urban settings, we investigated the atmospheric oxidation and aerosol formation potential of gas-phase BT in a controlled laboratory oxidation experiment. When a plug of BT (62 ug in 5 uL of MeOH or 1%) was oxidized in the PAM-OFR to an equivalent 5 days of atmospheric aging, secondary aerosol formed, as illustrated by the new particle formation event in Figure 4. From this experiment, we produced a cumulative mass of 7.2 μg of aerosol during the plug injection experiment. Further experiments are necessary to determine the aerosol yield of BT under typical atmospheric conditions, but these results suggest it could be significant. Products formed from this aging, analyzed using previously described HESI Orbitrap mass spectrometry, primarily include reduced nitrogen and CHON species, with aerosol sulfur primarily in the form of sulfuric acid as shown in the identified molecular species listed in SI Table S4. In the second previously described benzothiazole oxidation experiment, in which a constant source of gas-phase benzothiazole from a perm tube diluted to 12.8 ppb was oxidized at three aging equivalents ranging from 2.9 to 4.7 days, both aerosol and SO_2 production were observed to increase with oxidative aging over this range, as illustrated in Figure S11. Aerosol mass concentrations ranged from 9 ± 2 $\mu g/m^3$ at 2.9 days to 19 ± 2 $\mu g/m^3$ at 4.7 days and produced SO_2 concentrations ranged from. 67 ±. 08 ppb at 2.9 days to 1.3 ±.12 ppb at 4.7 days. The aerosol size distributions peak near 20 nm particle diameter for all exposure experiments, indicating new particle formation from benzothiazole oxidation (Figure S11). While conditions in the PAM-OFR do not directly mimic those of the ambient atmosphere, the results of the benzothiazole oxidation study indicate two things: first, gas-phase BT has the capacity to contribute to SMA (or more generally secondary aerosol) formation and second, BT oxidation has the capacity to form sulfur dioxide and sulfuric acid in the atmosphere, possibly suggesting the presence of sulfate aerosol produced during BT oxidation. This finding has relevance for polluted coastal marine environments, in which both benzothiazole and other anthropogenic marine pollutants should be evaluated for their potential influence on the abundance and characteristics of secondary marine aerosol. It also suggests implications for urban environments, in which benzothiazoles are highly abundant and may contribute to secondary organic aerosol formation and urban smog.

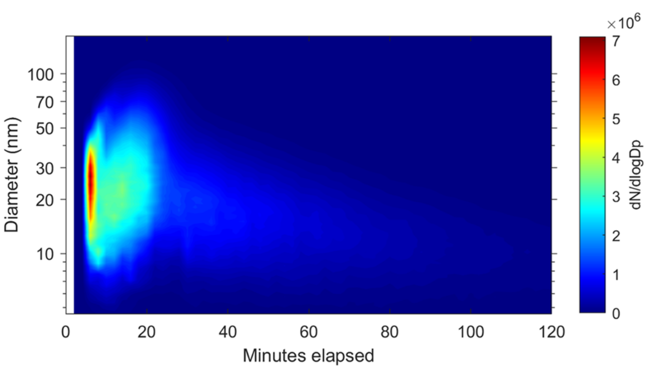


Figure 4. Nucleation of new particles from benzothiazole oxidation in PAM-OFR. Liquid benzothiazole dissolved in a methanol carrier (1% BT) is introduced at 5 min.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.1c04422.

Methodological details and contextual and supporting figures and tables (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Emily B. Franklin − *Department of Civil and Environmental Engineering, University of California, Berkeley, California 94720, United States;* orcid.org/0000-0002-3568-5359; Email: barnes_emily@berkeley.edu

Authors

Michael R. Alves − *Department of Chemistry & Biochemistry, University of California, San Diego, La Jolla, California 92093, United States;* orcid.org/0000-0003-1434-5483

Alexia N. Moore − *Department of Chemistry & Biochemistry, University of California, San Diego, La Jolla, California 92093, United States*

Delaney B. Kilgour − *Department of Chemistry, University of Wisconsin−Madison, Madison, Wisconsin 53706, United States*

Gordon A. Novak − *Department of Chemistry, University of Wisconsin−Madison, Madison, Wisconsin 53706, United States*

Kathryn Mayer − *Department of Chemistry & Biochemistry, University of California, San Diego, La Jolla, California 92093, United States;* orcid.org/0000-0003-1179-9244

Jonathan S. Sauer − *Department of Chemistry & Biochemistry, University of California, San Diego, La Jolla, California 92093, United States;* orcid.org/0000-0001-7527-109X

Robert J. Weber − *Department of Environmental Science, Policy and Management, University of California, Berkeley, California 94720, United States*

Duyen Dang − *Department of Chemistry & Biochemistry, University of California, San Diego, La Jolla, California 92093, United States*

Margaux Winter − *Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts 02138, United States*

Christopher Lee − *Scripps Institution of Oceanography, University of California, San Diego, La Jolla, California 92093, United States*

Christopher D. Cappa − *Department of Civil and Environmental Engineering, University of California, Davis, California 95616, United States;* orcid.org/0000-0002-3528-3368

Timothy H. Bertram − *Department of Chemistry, University of Wisconsin−Madison, Madison, Wisconsin 53706, United States;* orcid.org/0000-0002-3026-7588

Kimberly A. Prather − *Department of Chemistry & Biochemistry, University of California, San Diego, La Jolla, California 92093, United States; Scripps Institution of Oceanography, University of California, San Diego, La Jolla, California 92093, United States*

Vicki H. Grassian − *Department of Chemistry & Biochemistry, University of California, San Diego, La Jolla, California 92093, United States; Scripps Institution of Oceanography, University of California, San Diego, La Jolla, California 92093, United States;* orcid.org/0000-0001-5052-0045

Allen H. Goldstein − *Department of Civil and Environmental Engineering, University of California, Berkeley, California 94720, United States; Department of Environmental Science, Policy and Management, University of California, Berkeley, California 94720, United States;* orcid.org/0000-0003-4014-4896

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.est.1c04422

Author Contributions

[#]E.B.F. and M.R.A contributed equally and are cofirst authors.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank the NSF Center for Aerosol Impacts on Chemistry of the Environment (an NSF Chemical Innovation Center (CHE-1801971)) and the entire experimental campaign team which participated in the SeaSCAPE for their support of this work. We specifically thank Julie Dinasquet, Francesca Malfatti, Clare Morris, and Daniel Crocker for their contribution of biological indicator data in support of this publication. We gratefully acknowledge the support of the National Science Foundation Graduate Research Fellowship Program (DGE-1650112) as well as Neal Arakawa and the use of facilities at the Environment Complex Analysis Laboratory (ECAL) at the University of California San Diego.

REFERENCES

(1) Azam, F.; Fenchel, T.; Field, J. G.; Prog, S.; Gray, J. S.; Meyer-Reil, L. A.; Thingstad, F. The Ecological Role of Water-Column Microbes in the Sea Placing Marine Mixoplankton in Context View Project DOMAINE View Project MARINE ECOLOGY-PROGRESS SERIES The Ecological Role of Water-Column Microbes in the Sea*. *Mar. Ecol.: Prog. Ser.* **1983**, *10*, 257−263.

(2) Cochran, R. E.; Laskina, O.; Trueblood, J. V.; Estillore, A. D.; Morris, H. S.; Jayarathne, T.; Sultana, C. M.; Lee, C.; Lin, P.; Laskin, J.; Laskin, A.; Dowling, J. A.; Qin, Z.; Cappa, C. D.; Bertram, T. H.; Tivanski, A. V.; Stone, E. A.; Prather, K. A.; Grassian, V. H. Molecular Diversity of Sea Spray Aerosol Particles: Impact of Ocean Biology on Particle Composition and Hygroscopicity. *Chem.* **2017**, *2* (5), 655−667.

(3) Tovar-Sánchez, A.; Sánchez-Quiles, D.; Basterretxea, G.; Benedé, J. L.; Chisvert, A.; Salvador, A.; Moreno-Garrido, I.; Blasco, J. Sunscreen Products as Emerging Pollutants to Coastal Waters. *PLoS One* **2013**, *8* (6), e65451.

(4) Zeng, E. Y.; Vista, C. L. Organic Pollutants in the Coastal Environment off San Diego, California. 1. Source Identification and Assessment by Compositional Indices of Polycyclic Aromatic Hydrocarbons. *Environ. Toxicol. Chem.* **1997**, *16* (2), 179−188.

(5) Elliott, J. E.; Elliott, K. H. Tracking Marine Pollution. *Science* **2013**, *340*, 556−558.

(6) Glibert, P. M.; Maranger, R.; Sobota, D. J.; Bouwman, L. The Haber Bosch-Harmful Algal Bloom (HB-HAB) Link. *Environ. Res. Lett.* **2014**, *9* (10), 105001.

(7) Kahru, M.; Mitchell, B. G. Ocean Color Reveals Increased Blooms in Various Parts of the World. *Eos (Washington. DC)*. **2008**, *89* (18), 170.

(8) Dale, B.; Edwards, M.; Reid, P. C. Climate Change and Harmful Algal Blooms. *Ecol. Stud.* **2006**, *189*, 367−378.

(9) Paerl, H.; Huisman, J. Blooms like It Hot. *Science (Washington, DC, U. S.)* **2008**, *320*, 57.

(10) Blanchard, D. C. Bubble Scavenging and the Water-to-Air Transfer of Organic Material in the Sea. *Adv. Chem. Ser.* **1975**, *145*, 360−387.

(11) Carpenter, L. J.; Archer, S. D.; Beale, R. Ocean-Atmosphere Trace Gas Exchange. *Chem. Soc. Rev.* **2012**, *41* (19), 6473−6506.

(12) O'Dowd, C. D.; De Leeuw, G. Marine Aerosol Production: A Review of the Current Knowledge. *Philos. Trans. R. Soc., A* **2007**, *365*, 1753−1774.

(13) Trueblood, J. V.; Wang, X.; Or, V. W.; Alves, M. R.; Santander, M. V.; Prather, K. A.; Grassian, V. H. The Old and the New: Aging of Sea Spray Aerosol and Formation of Secondary Marine Aerosol through OH Oxidation Reactions. *ACS Earth Sp. Chem.* **2019**, *3* (10), 2307−2314.

(14) 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.

(15) Lee, H. D.; Morris, H. S.; Laskina, O.; Sultana, C. M.; Lee, C.; Jayarathne, T.; Cox, J. L.; Wang, X.; Hasenecz, E. S.; Demott, P. J.; Bertram, T. H.; Cappa, C. D.; Stone, E. A.; Prather, K. A.; Grassian, V. H.; Tivanski, A. V. Organic Enrichment, Physical Phase State, and Surface Tension Depression of Nascent Core-Shell Sea Spray Aerosols during Two Phytoplankton Blooms. *ACS Earth Sp. Chem.* **2020**, *4* (4), 650−660.

(16) Hodas, N.; Zuend, A.; Mui, W.; Flagan, R. C.; Seinfeld, J. H. Influence of Particle-Phase State on the Hygroscopic Behavior of Mixed Organic−Inorganic Aerosols. *Atmos. Chem. Phys.* **2015**, *15* (9), 5027−5045.

(17) Fuentes, E.; Coe, H.; Green, D.; McFiggans, G. On the Impacts of Phytoplankton-Derived Organic Matter on the Properties of the Primary Marine Aerosol - Part 2: Composition, Hygroscopicity and

Cloud Condensation Activity. *Atmos. Chem. Phys.* **2011**, *11* (6), 2585−2602.
(18) Myriokefalitakis, S.; Vignati, E.; Tsigaridis, K.; Papadimas, C.; Sciare, J.; Mihalopoulos, N.; Facchini, M. C.; Rinaldi, M.; Dentener, F. J.; Ceburnis, D.; Hatzianastasiou, N.; O'Dowd, C. D.; van Weele, M.; Kanakidou, M. Global Modeling of the Oceanic Source of Organic Aerosols. *Adv. Meteorol.* **2010**, *2010*, 1−16.
(19) Mayer, K. J.; Wang, X.; Santander, M. V.; Mitts, B. A.; Sauer, J. S.; Sultana, C. M.; Cappa, C. D.; Prather, K. A. Secondary Marine Aerosol Plays a Dominant Role over Primary Sea Spray Aerosol in Cloud Formation. *ACS Cent. Sci.* **2020**, *6*, 2259.
(20) Zheng, G.; Kuang, C.; Uin, J.; Watson, T.; Wang, J. Large Contribution of Organics to Condensational Growth and Formation of Cloud Condensation Nuclei (CCN) in the Remote Marine Boundary Layer. *Atmos. Chem. Phys.* **2020**, *20* (21), 12515−12525.
(21) Kirkpatrick, B.; Fleming, L. E.; Squicciarini, D.; Backer, L. C.; Clark, R.; Abraham, W.; Benson, J.; Cheng, Y. S.; Johnson, D.; Pierce, R.; Zaias, J.; Bossart, G. D.; Baden, D. G. Literature Review of Florida Red Tide: Implications for Human Health Effects. *Harmful Algae* **2004**, *3*, 99−115.
(22) Grattan, L. M.; Holobaugh, S.; Morris, J. G. Harmful Algal Blooms and Public Health. *Harmful Algae* **2016**, *57*, 2−8.
(23) Walsh, J. J.; Lenes, J. M.; Weisberg, R. H.; Zheng, L.; Hu, C.; Fanning, K. A.; Snyder, R.; Smith, J. More Surprises in the Global Greenhouse: Human Health Impacts from Recent Toxic Marine Aerosol Formations, Due to Centennial Alterations of World-Wide Coastal Food Webs. *Mar. Pollut. Bull.* **2017**, *116*, 9−40.
(24) Vila-Costa, M.; Cerro-Gálvez, E.; Martínez-Varela, A.; Casas, G.; Dachs, J. Anthropogenic Dissolved Organic Carbon and Marine Microbiomes. *ISME J.* **2020**, *14* (10), 2646−2648.
(25) Wang, Z.; Walker, G. W.; Muir, D. C. G.; Nagatani-Yoshida, K. Toward a Global Understanding of Chemical Pollution: A First Comprehensive Analysis of National and Regional Chemical Inventories. *Environ. Sci. Technol.* **2020**, *54* (5), 2575−2584.
(26) Bernhardt, E. S.; Rosi, E. J.; Gessner, M. O. Synthetic Chemicals as Agents of Global Change. *Front. Ecol. Environ.* **2017**, *15* (2), 84−90.
(27) Ott, A.; Martin, T. J.; Whale, G. F.; Snape, J. R.; Rowles, B.; Galay-Burgos, M.; Davenport, R. J. Improving the Biodegradability in Seawater Test (OECD 306). *Sci. Total Environ.* **2019**, *666*, 399−404.
(28) Cincinelli, A.; Stortini, A. M.; Perugini, M.; Checchini, L.; Lepri, L. Organic Pollutants in Sea-Surface Microlayer and Aerosol in the Coastal Environment of Leghorn - (Tyrrhenian Sea). *Mar. Chem.* **2001**, *76* (1−2), 77−98.
(29) Cerro-Gálvez, E.; Dachs, J.; Lundin, D.; Fernández-Pinos, M. C.; Sebastián, M.; Vila-Costa, M. Responses of Coastal Marine Microbiomes Exposed to Anthropogenic Dissolved Organic Carbon. *Environ. Sci. Technol.* **2021**, *55*, 9609.
(30) Cunliffe, M.; Engel, A.; Frka, S.; Gašparović, B. Ž.; Guitart, C.; Murrell, J. C.; Salter, M.; Stolle, C.; Upstill-Goddard, R.; Wurl, O. Sea Surface Microlayers: A Unified Physicochemical and Biological Perspective of the Air-Ocean Interface. *Prog. Oceanogr.* **2013**, *109*, 104−116.
(31) Tervahattu, H.; Juhanoja, J.; Kupiainen, K. Identification of an Organic Coating on Marine Aerosol Particles by TOF-SIMS. *J. Geophys. Res.* **2002**, *107* (D16), ACH 18.
(32) Vignati, E.; Facchini, M. C.; Rinaldi, M.; Scannell, C.; Ceburnis, D.; Sciare, J.; Kanakidou, M.; Myriokefalitakis, S.; Dentener, F.; O'Dowd, C. D. Global Scale Emission and Distribution of Sea-Spray Aerosol: Sea-Salt and Organic Enrichment. *Atmos. Environ.* **2010**, *44* (5), 670−677.
(33) Prather, K. A.; Bertram, T. H.; Grassian, V. H.; Deane, G. B.; Stokes, M. D.; DeMott, P. J.; Aluwihare, L. I.; Palenik, B. P.; Azam, F.; Seinfeld, J. H.; Moffet, R. C.; Molina, M. J.; Cappa, C. D.; Geiger, F. M.; Roberts, G. C.; Russell, L. M.; Ault, A. P.; Baltrusaitis, J.; Collins, D. B.; Corrigan, C. E.; Cuadra-Rodriguez, L. A.; Ebben, C. J.; Forestieri, S. D.; Guasco, T. L.; Hersey, S. P.; Kim, M. J.; Lambert, W. F.; Modini, R. L.; Mui, W.; Pedler, B. E.; Ruppel, M. J.; Ryder, O. S.; Schoepp, N. G.; Sullivan, R. C.; Zhao, D. Bringing the Ocean into the Laboratory to Probe the Chemical Complexity of Sea Spray Aerosol. *Proc. Natl. Acad. Sci. U. S. A.* **2013**, *110* (19), 7550−7555.
(34) Engel, A.; Bange, H. W.; Cunliffe, M.; Burrows, S. M.; Friedrichs, G.; Galgani, L.; Herrmann, H.; Hertkorn, N.; Johnson, M.; Liss, P. S.; Quinn, P. K.; Schartau, M.; Soloviev, A.; Stolle, C.; Upstill-Goddard, R. C.; van Pinxteren, M.; Zäncker, B. The Ocean's Vital Skin: Toward an Integrated Understanding of the Sea Surface Microlayer. *Front. Mar. Sci.* **2017**, *4*, 165.
(35) Liao, C.; Kim, U. J.; Kannan, K. A Review of Environmental Occurrence, Fate, Exposure, and Toxicity of Benzothiazoles. *Environ. Sci. Technol.* **2018**, *52* (9), 5007−5026.
(36) Halsband, C.; Sørensen, L.; Booth, A. M.; Herzke, D. Car Tire Crumb Rubber: Does Leaching Produce a Toxic Chemical Cocktail in Coastal Marine Systems? *Front. Environ. Sci.* **2020**, *8*, 125.
(37) Wever, H. De; Research, H. V. Biodegradation and Toxicity of Benzothiazoles. *Water Res.* **1997**, *31*, 2673.
(38) Fries, E.; Gocht, T.; Klasmeier, J. Occurrence and Distribution of Benzothiazole in the Schwarzbach Watershed (Germany). *J. Environ. Monit.* **2011**, *13* (10), 2838−2843.
(39) Brownlee, B. G.; Carey, J. H.; Fox, M. E. *A Review of Benzothiazoles in the Aquatic Environment*; Scientific Series No. 126; Inland Waters Directorate, 1981.
(40) Zeng, E. Y.; Tran, K.; Young, D. Evaluation of Potential Molecular Markers for Urban Stormwater Runoff. *Environ. Monit. Assess.* **2004**, *90* (1−3), 23−43.
(41) Stierle, A. A.; Cardellina, J. H.; Singleton, F. L. Benzothiazoles from a Putatitve Bacterial Symbiont of the Marine Sponge Tedania Ignis. *Tetrahedron Lett.* **1991**, *32* (37), 4847−4848.
(42) Chhalodia, A. K.; Rinkel, J.; Konvalinkova, D.; Petersen, J.; Dickschat, J. S. Identification of Volatiles from Six Marine Celeribacter Strains. *Beilstein J. Org. Chem.* **2021**, *17* (1), 420−430.
(43) Kloepfer, A.; Jekel, M.; Reemtsma, T. Occurrence, Sources, and Fate of Benzothiazoles in Municipal Wastewater Treatment Plants. *Environ. Sci. Technol.* **2005**, *39* (10), 3792−3798.
(44) Sorahan, T. Bladder Cancer Risks in Workers Manufacturing Chemicals for the Rubber Industry. *Occup. Med. (Chic. Ill).* **2008**, *58* (7), 496−501.
(45) Sorahan, T. Cancer Risks in Chemical Production Workers Exposed to 2- Mercaptobenzothiazole. *Occup. Environ. Med.* **2008**, *66* (4), 269−273.
(46) Liao, X.; Zou, T.; Chen, M.; Song, Y.; Yang, C.; Qiu, B.; Chen, Z. F.; Tsang, S. Y.; Qi, Z.; Cai, Z. Contamination Profiles and Health Impact of Benzothiazole and Its Derivatives in PM2.5 in Typical Chinese Cities. *Sci. Total Environ.* **2021**, *755*, 142617.
(47) Sauer, J. S.; Mayer, K. J.; Lee, C.; Alves, M. R.; Amiri, S.; Bahaveolos, C.; Barnes, E. B.; Crocker, D. R.; Dinasquet, J.; Garofalo, L. A.; Kaluarachchi, C. P.; Kilgour, D.; Mael, L.; Mitts, B. A.; Moon, D. R.; Morris, C. K.; Moore, A. N.; Ni, C.-M.; Pendergraft, M. A.; Petras, D.; Simpson, R.; Smith, S.; Tumminello, P. R.; Walker, J. L.; DeMott, P. J.; Farmer, D. K.; Goldstein, A. H.; Grassian, V. H.; Jaffe, J. S.; Malfatti, F.; Martz, T. R.; Slade, J.; Tivanski, A. V.; Bertram, T. H.; Cappa, C. D.; Prather, K. A. The Sea Spray Chemistry and Particle Evolution Study (SeaSCAPE): Overview and Experimental Methods. *Environ. Sci. Process. Impacts* **2021**, DOI: 10.33774/CHEMRXIV-2021-SM7VW.
(48) Wang, X.; Sultana, C. M.; Trueblood, J.; Hill, T. C. J.; Malfatti, F.; Lee, C.; Laskina, O.; Moore, K. A.; Beall, C. M.; McCluskey, C. S.; Cornwell, G. C.; Zhou, Y.; Cox, J. L.; Pendergraft, M. A.; Santander, M. V.; Bertram, T. H.; Cappa, C. D.; Azam, F.; DeMott, P. J.; Grassian, V. H.; Prather, K. A. Microbial Control of Sea Spray Aerosol Composition: A Tale of Two Blooms. *ACS Cent. Sci.* **2015**, *1* (3), 124−131.
(49) Dittmar, T.; Koch, B.; Hertkorn, N.; Kattner, G. A Simple and Efficient Method for the Solid-Phase Extraction of Dissolved Organic Matter (SPE-DOM) from Seawater. *Limnol. Oceanogr.: Methods* **2008**, *6* (6), 230−235.
(50) Roveretto, M.; Li, M.; Hayeck, N.; Brüggemann, M.; Emmelin, C.; Perrier, S.; George, C. Real-Time Detection of Gas-Phase

Organohalogens from Aqueous Photochemistry Using Orbitrap Mass Spectrometry. *ACS Earth Sp. Chem.* **2019**, *3* (3), 329−334.

(51) Worton, D. R.; Decker, M.; Isaacman-VanWertz, G.; Chan, A. W. H.; Wilson, K. R.; Goldstein, A. H. Improved Molecular Level Identification of Organic Compounds Using Comprehensive Two-Dimensional Chromatography, Dual Ionization Energies and High Resolution Mass Spectrometry. *Analyst* **2017**, *142* (13), 2395−2403.

(52) Dörter, M.; Odabasi, M.; Yenisoy-Karakaş, S. Source Apportionment of Biogenic and Anthropogenic VOCs in Bolu Plateau. *Sci. Total Environ.* **2020**, *731*, 139201.

(53) Reddy, C. M.; Quinn, J. G. Environmental Chemistry of Benzothiazeles Derived from Rubber. *Environ. Sci. Technol.* **1997**, *31* (10), 2847−2853.

(54) Sander, R. Compilation of Henry's Law Constants (Version 4.0) for Water as Solvent. *Atmos. Chem. Phys.* **2015**, *15* (8), 4399−4981.

(55) Kowalska, K.; Felis, E.; Sochacki, A.; Bajkacz, S. Removal and Transformation Pathways of Benzothiazole and Benzotriazole in Membrane Bioreactors Treating Synthetic Municipal Wastewater. *Chemosphere* **2019**, *227*, 162−171.

(56) Crocker, D.; Kaluarachchi, C.; Cao, R.; Dinasquet, J.; Franklin, E.; Morris, C.; Martz, T.; Malfatti, F.; Goldstein, A.; Tivanski, A.; Prather, K.; Thiemens, M. Isotopic Insights into Organic Composition Differences between Supermicron and Submicron Sea Spray Aerosol. *Environ. Sci. Technol.* **2021**.

(57) Tran, T. M.; Kannan, K. Occurrence of Cyclic and Linear Siloxanes in Indoor Air from Albany, New York, USA, and Its Implications for Inhalation Exposure. *Sci. Total Environ.* **2015**, *511*, 138−144.

(58) Bletsou, A. A.; Asimakopoulos, A. G.; Stasinakis, A. S.; Thomaidis, N. S.; Kannan, K. Mass Loading and Fate of Linear and Cyclic Siloxanes in a Wastewater Treatment Plant in Greece. *Environ. Sci. Technol.* **2013**, *47* (4), 1824−1832.

(59) Hong, W. J.; Jia, H.; Liu, C.; Zhang, Z.; Sun, Y.; Li, Y. F. Distribution, Source, Fate and Bioaccumulation of Methyl Siloxanes in Marine Environment. *Environ. Pollut.* **2014**, *191*, 175−181.

(60) Mao, F.; He, Y.; Gin, K. Y. H. Occurrence and Fate of Benzophenone-Type UV Filters in Aquatic Environments: A Review. *Environmental Science: Water Research and Technology* **2019**, *5*, 209−223.

(61) Zeng, E. Y.; Vista, C. L. Organic Pollutants in the Coastal Environment off San Diego, California. 1. Source Identification and Assessment by Compositional Indices of Polycyclic Aromatic Hydrocarbons. *Environ. Toxicol. Chem.* **1997**, *16* (2), 179−188.

(62) Aprem, A. S.; Joseph, K.; Mathew, T.; Altstaedt, V.; Thomas, S. Studies on Accelerated Sulphur Vulcanization of Natural Rubber Using 1-Phenyl-2, 4-Dithiobiuret/Tertiary Butyl Benzothiazole Sulphenamide. *Eur. Polym. J.* **2003**, *39* (7), 1451−1460.

(63) Nowak, J. A.; Shrestha, P. M.; Weber, R. J.; McKenna, A. M.; Chen, H.; Coates, J. D.; Goldstein, A. H. Comprehensive Analysis of Changes in Crude Oil Chemical Composition during Biosouring and Treatments. *Environ. Sci. Technol.* **2018**, *52* (3), 1290−1300.

(64) Hardy, J. T. The Sea Surface Microlayer: Biology, Chemistry and Anthropogenic Enrichment. *Prog. Oceanogr.* **1982**, *11*, 307−328.

(65) Spiel, D. E.; Leeuw, G. DE Formation and Production of Sea Spray Aerosol. *J. Aerosol Sci.* **1996**, *27*, S65.

(66) Cipriano, R.; Blanchard, D.; Hogan, A.; Lala, G. On the Production of Aitken Nuclei from Breaking Waves and Their Role in the Atmosphere. *J. Atmos. Sci.* **1983**, *40*, 469.

(67) Wang, X.; Deane, G. B.; Moore, K. A.; Ryder, O. S.; Stokes, M. D.; Beall, C. M.; Collins, D. B.; Santander, M. V.; Burrows, S. M.; Sultana, C. M.; Prather, K. A. The Role of Jet and Film Drops in Controlling the Mixing State of Submicron Sea Spray Aerosol Particles. *Proc. Natl. Acad. Sci. U. S. A.* **2017**, *114* (27), 6978−6983.

(68) Fiehn, O.; Reemtsma, T.; Jekel, M. Extraction and Analysis of Various Benzothiazoles from Industrial Wastewater. *Anal. Chim. Acta* **1994**, *295* (3), 297−305.

(69) De Wever, H.; Verachtert, H. Biodegradation and Toxicity of Benzothiazoles. *Water Res.* **1997**, *31* (11), 2673−2684.

(70) Le Bozec, L.; Moody, C. J. Naturally Occurring Nitrogensulfur Compounds. the Benzothiazole Alkaloids. *Aust. J. Chem.* **2009**, *62* (7), 639−647.

(71) Harlan, J.; Terrill, E.; Hazard, L.; Keen, C.; Barrick, D.; Whelan, C.; Howden, S.; Kohut, J. The Integrated Ocean Observing System High-Frequency Radar Network: Status and Local, Regional, and National Applications NOAA IOOS ® Program. *Mar. Technol. Soc. J.* **2010**, *44* (6), 122.