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Anthropogenic and Biogenic Contributions to the Organic Composition of Coastal Submicron Sea Spray Aerosol

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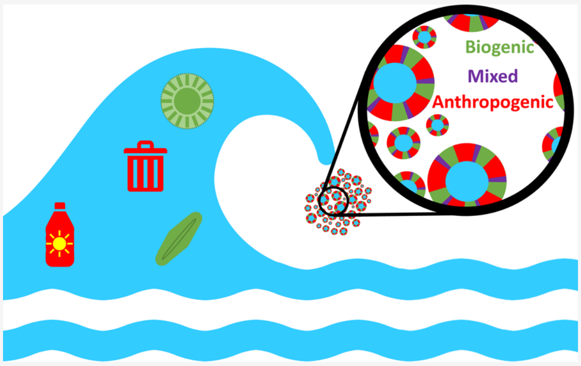

ABSTRACT: The organic composition of coastal sea spray aerosol is important for both atmospheric chemistry and public health but remains poorly characterized. Coastal waters contain an organic material derived from both anthropogenic processes, such as wastewater discharge, and biological processes, including biological blooms. Here, we probe the chemical composition of the organic fraction of sea spray aerosol over the course of the 2019 SeaSCAPE mesocosm experiment, in which a phytoplankton bloom was facilitated in natural coastal water from La Jolla, California. We apply untargeted two-dimensional gas chromatography to characterize submicron nascent sea spray aerosol samples, reporting ∼750 unique organic species traced over a 19 day phytoplankton bloom experiment. Categorization and quantitative compositional analysis reveal three major findings. First, anthropogenic species made up 30% of total submicron nascent sea spray aerosol organic mass under the pre-bloom condition. Second, biological activity drove large changes within the aerosolized carbon pool, decreasing the anthropogenic mass fraction by 89% and increasing the biogenic and biologically transformed fraction by a factor of 5.6. Third, biogenic marine organics are underrepresented in mass spectral databases in comparison to marine organic pollutants, with more than twice as much biogenic aerosol mass attributable to unlisted compounds.

KEYWORDS: *sea spray aerosol, marine, anthropogenic, contaminants, algae bloom, organic pollution*

■ INTRODUCTION

Sea spray aerosols (SSAs), the salty particles and droplets emitted from waves and bubble bursting at the ocean's surface, play an important role in atmospheric chemistry and climate over the ocean and in coastal areas. The SSA organic content increases with decreasing aerosol size below an aerodynamic radius of 2.5 μm. Observations from field studies report values of the total submicron organic mass fraction ranging from 6[1] to 23%[2] of submicron aerosol mass. The SSA organic content plays a critical role in marine atmospheric chemistry as the organic content forms a film on the exterior of the salt crystal cores in salt-organic carbon-type aerosols, which dominate submicron SSA.[3−5] The hygroscopicity, solubility, and ice nucleation-relevant properties of the organic material differ substantially from those of NaCl crystals, thus the organic content of SSAs influences their atmospheric chemistry and climate impacts over the ocean.[4,5] Also, the organic content of SSA is important in coastal areas, where coastal communities can be exposed to toxins such as those produced by harmful algal blooms[6,7] and hazardous marine pollutants.[8]

Coastal ocean water becomes enriched with the organic material through both natural biological processes and anthropogenic pollution. Biogenic sources of the organic material include ocean micro algae, which convert CO_2 to biomass that is either grazed by larger organisms or dies and is degraded by heterotrophic bacteria.[9] Anthropogenic sources of organic compounds include urban runoff, personal care products including sunscreen, wastewater discharge, trash, and shipping pollution.[10−13] In addition to directly producing a new organic material through photosynthesis, marine microbes also produce biologically transformed products from the biodegradation of terrestrial and anthropogenic organic precursors.[14−16] The organic material is not evenly distributed throughout the ocean water column; surfactants, hydrophobic organics, and other organic constituents collect at the ocean's surface to form a thin layer known as the sea surface microlayer

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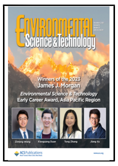

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(SSML).[17−19] Both biogenic and anthropogenic organics can be significantly enriched in the SSML, and enrichment factors of common anthropogenic pollutants including phthalates, polycyclic aromatic hydrocarbons, and heavy metals, can be as high as multiple orders of magnitude.[19−22] The organic composition of SSAs, and in particular submicron film drops, is significantly influenced by the composition of the SSML, making the enrichment of some chemical classes in the SSML important in determining the organic composition of SSAs and the transfer of organic pollutants from ocean to atmosphere.[9,22,23]

There has been a significant recent progress in characterizing the organic content of SSAs, including multiple methods of functional group analysis.[9,24−26] However, a large fraction remains uncharacterized, particularly at the compound-specific level. Two-dimensional gas chromatography (GC × GC), a technique which separates organic constituents across multiple dimensions of chemical properties to yield clean, isomer-specific separation of individual chemical constituents,[27] represents a unique opportunity to probe the organic composition of SSA at a structure-specific level. Analyses of organic aerosol composition by GC × GC regularly catalogue 100's−1000's of unique constituents and offer insights into the sources, properties, and production mechanisms of ambient aerosol across a range of environments.[28−31] This work leverages a mesocosm experiment in which the real coastal water was used to facilitate a bloom of naturally occurring phytoplanktons and bacteria species to investigate how anthropogenic pollution and marine microbes influence the organic composition of submicron SSAs in a coastal context.

MATERIALS AND METHODS

Experimental Campaign and Sample Collection. Samples analyzed in this work originate from the 2019 SeaSCAPE (Sea Spray Chemistry And Particle Evolution) experimental campaign organized by CAICE (the Center for Aerosol Impacts on Chemistry of the Environment) based at UCSD. This campaign, including the unique site features and applicability of findings to other environments, is described in Sauer et al., 2022.[32] Briefly, water collected at Ellen Browning Scripps Memorial Pier (hereafter Scripps Pier) in La Jolla, California, was transported into the Scripps Institute of Oceanography Hydraulics Laboratory wave channel facility (hereafter called the wave channel) which uses mechanically generated breaking waves to generate realistic SSA. Scripps Pier is located close to multiple potential sources of coastal pollution including a high-use beach, multiple stormwater discharge points, and municipal wastewater treatment outflow; a map of the site with local pollution sources indicated can be found in Franklin et al., 2021.[33] Nutrients were added to the natural costal water to induce a micro algae bloom and subsequent bacterial and viral blooms of the species naturally present within the coastal water. The chemical and biological properties of the water, including chlorophyll-*a* concentrations and abundance of phytoplankton, bacteria, and viruses, were monitored both before and throughout the bloom, as documented in Sauer et al., 2022.[32] These indicators are visualized in Figure S6. Phytoplankton enumeration methods are summarized in Supporting Information 5.

Collection of submicron aerosol samples for speciated organic analysis at this campaign has been previously described in Franklin et al., 2021.[33] Briefly, submicron aerosols were collected on 47 mm quartz fiber filters (Pallflex Tissuquartz) using a custom-designed humidity-controlled sequential sampler at a frequency of two samples per day (light synchronized, one “day” and one “night” sample per day). Samples were frozen (−18 °C) for offline compositional analysis as described below. Quality assurance measures for identifying any potential contamination of the water during transport to the wave channel are described in Sauer et al., 2022,[32] and analysis of blanks for the identification of potential contamination of the aerosol filter material is described in Franklin et al., 2021.[33] A brief summary of these measures is provided in Supporting Information 1.

Offline Sample Analysis. Submicron aerosol samples collected at SeaSCAPE were analyzed for speciated organic composition by thermal desorption two-dimensional gas chromatography coupled with electron ionization high-resolution time of flight mass spectrometry (TD-GC × GC−EI-HR-MS, hereafter abbreviated to GC × GC−MS). This instrument separates and detects organic constituents collected on the filter material as follows: organic constituents are thermally desorbed from the filter material, separated by both volatility and polarity by two gas chromatography columns in sequence, and detected by an electron ionization (70 eV) high-resolution time of flight mass spectrometer. This instrument is described in detail in Worton et al., 2017.[27]

Data Analysis. From the 38 samples collected, ∼750 unique organic compounds were compiled into a custom library of mass spectra and retention indices (position relative to the deuterated alkane series in the internal standard, linearly related but not equivalent to a Kovats index). Nearly, all of these organics were identified in either the first sample or the sample corresponding with peak chlorophyll-*a* concentrations in the bulk water (see Figure 1 for chlorophyll-*a* trace). Inclusion in the custom library was predicated upon each compound exhibiting a clearly resolved chromatographic peak, a clean mass spectrum with total ion signal above a consistent threshold, and lack of overlap with peaks observed in field blanks. Using the custom mass spectral library, all ∼750 catalogued species were traced over the entire bloom. Each observation of each compound was normalized by the mean of the three nearest internal standard components to correct for drifts in instrument sensitivity over the analysis period and matrix effects using the methodology described in detail in Franklin et al., 2022.[34] Finally, the mass spectrum of each compound was searched against the NIST-14 mass spectral database. Of the ∼750 compounds catalogued, 14% were identifiable by database match. Compounds were defined as “identifiable” if they produced a match factor >750 with an entry in the NIST14 mass spectral database and an approximate match with a retention index for that compound published in the database or the literature.[27]

Quantification of detected and separated organic species is described in detail in the Supporting Information Section S2 (SI.2). A representative external standard containing ∼130 known components was analyzed in 6-point calibration curves immediately preceding and following sample analysis. Compounds present in both the sample and standard or with clear chemical proxies in the standard were directly quantified by the calibration curves of the external standard, while the quantification factors of all other species were predicted using Ch3MS-RF.[34] Model performance and uncertainties of both modeled and directly calculated quantification factors are described and illustrated in Supporting Information SI.2.

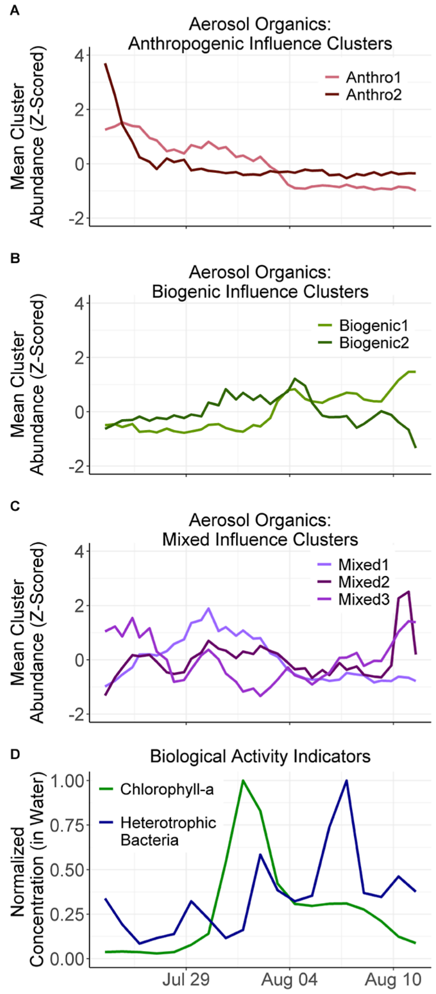

Figure 1. Mean temporal profiles of nascent SSA organic material clusters over the course of the 2019 SeaSCAPE mesocosm experiment. (A) Clusters attributed to anthropogenic influences, (B) clusters attributed to biogenically influenced production processes, (C) clusters attributed to mixed influences, and (D) contextual biological activity markers measured in the wave channel water, specifically chlorophyll-*a* concentrations and heterotrophic bacteria cell concentrations. The aerosol organic concentration time series of each compound is smoothed by 3-point moving average and *z*-scored, and all constituents assigned to an influence group are averaged to yield mean factor profiles.

Segments of the filter samples utilized for speciated organic analysis were also analyzed for total organic carbon to determine the fraction of the collected organic material to which GC × GC−MS analysis is sensitive to. Results indicate that 40 ± 15% of collected submicron organic mass was recovered and quantified by GC × GC−MS analysis, consistent with prior applications of this methodology to organic aerosol collected in other contexts.[30] Examples of previously characterized contributors to submicron SSA organic composition to which this technique is not sensitive include polysaccharides and proteinaceous material.[35,36] Methodological details and validation by complementary measurements are described in Supporting Information SI.3.

Compounds were grouped into clusters of similar temporal variability by dynamic time warping hierarchical clustering,[37] as described in Supporting Information SI.4. The 100 most abundant organics were grouped by cluster analysis, with results optimized by a 7-group solution as illustrated in Figures S4 and S5. All other compounds detected with sufficient frequency for time series construction, defined as present at above detection limit levels in >20% of samples, were assigned to the cluster with which they exhibited the highest Pearson correlation. Only 22 compounds, less than 4% of the number of compounds that met the detection frequency threshold, were assigned to clusters based on a Pearson correlation of less than 0.5. Clusters were then categorized as anthropogenic (resulting from human emissions and not enhanced by biological activity), biogenic (enhanced by biological activity, either through direct production or biotransformation of previously existing species which could be anthropogenic in nature), or mixed (some combination of the two or undetermined) influence through two methods: first, comparison of their mean cluster temporal profiles to indicators of biological activity, including chlorophyll-*a* concentrations and the abundances (cell/L) of microbes including phytoplankton phenotypes, heterotrophic bacteria, and viruses; second, through a literature review of characteristic identifiable constituents within each cluster (Table 1). Justifications for these assignments are addressed in "Results and Discussion" below. Characteristic compounds were selected based on the three criteria. Each was positively identifiable by a database match, demonstrated temporal variability that was close to that of the average of the cluster to which it was assigned, and had been previously referenced in literature that could point to a potential source. The average temporal variability of each cluster relative to chlorophyll-*a* and heterotrophic bacteria concentrations is illustrated in Figure 1, while Figure 2 illustrates the mean Pearson correlation coefficient between each individual aerosol-phase organic and each biological activity or biomass indicator grouped by the aerosol organic cluster. Note that Figure 1 illustrates the relative temporal variability characteristic of each cluster and is not representative of mass contributions, which are illustrated in Figure 3. Given the complexity of the connections between biological activity in the water and transfer of the organic material to SSA, no single indicator was used to determine an anthropogenic or biogenic/biologically transformed source for the aerosol-phase organics. The previous literature describing positively identifiable constituents and temporal variability are equally considered and generally indicated that compound populations that began at high abundance and declined over time had an anthropogenic source while those that increased in abundance after the bloom began were biogenic or biologically transformed. Compound populations exhibiting more complicated temporal variability or containing compounds with conflicting source groups described in the literature were defined as mixed influence. Finally, the chemical properties of unidentifiable compounds, specifically average carbon oxidation state ($\overline{\mathrm{OS}}_{\mathrm{c}}$) and carbon number ($n_{\mathrm{c}}$), were predicted using Ch3MS-RF,[34] as described in detail in Supporting Information SI.7. Visualizations of complex organic mixtures in the $n_{\mathrm{c}}-\overline{\mathrm{OS}}_{\mathrm{c}}$ space are commonly utilized in organic aerosol analysis.[38−41] As both metrics are calculable from the chemical formula, orientation of GC × GC−MS results in $n_{\mathrm{c}}-\overline{\mathrm{OS}}_{\mathrm{c}}$ space facilitates comparison with analyses by techniques that identify compounds by the chemical formula such as high-resolution chemical ionization mass spectrometry. Real and predicted n_{c} and $\overline{\mathrm{OS}}_{\mathrm{c}}$ values for each traced organic are presented in Appendix B.

Table 1. Identities, Potential Sources, and References Describing Representative Identifiable Constituents of Temporal Variability Clusters Used to Group Submicron Nascent SSA Organic Compounds Catalogued and Traced by GC × GC from Samples Collected at the SeaSCAPE Mesocosm Experiment

cluster	representative compound	compound type/potential source(s)	references
anthropogenic 1	7-methyl-benzanthracene	PAH, incomplete combustion	Manodori, 2006[52] Wu, 2011[53] Cross, 1987[54]
	4-methyl-pyrene[b]	PAH, incomplete combustion	
	diethyl phthalate	plasticizer	Polidoro, 2017[48]
anthropogenic 2	homosalate	sunscreen	Tovar-Sanchez, 2013;[55] Bargar, 2015[47]
	2-ethylhexyl salicylate	sunscreen	Mitchelmore, 2019[46]
	dibutyl phthalate	plasticizer	Giam, 1978;[56] Cincinelli, 2001[22]
Biogenic1	dimethyl quinolone	marine biooil component[a]	Madsen, 2017[57]
Biogenic2	phthalic anhydride	bacterial degradation of phthalates	Wright, 2020[58]
Mixed1	benzothiazole	urban effluents	Franklin, 2021[33]
	palmitic acid	marine microbiology (including diatoms)	Tervahattu 2002,[3] Kates 1966[59]
	2,2,4-trimethyl-1,3-pentanediol diisobutyrate	plasticizer, commonly used in food packaging	Kempf, 200960
Mixed2	trimethyl quinolone	marine biooil component[a]	Madsen, 2017[57]
Mixed3	butylphthalimide	plasticizer, personal care product component	Dionisio, 2018[61]

[a] Note that reference refers to the products observed in biocrudes rather than direct products, and as such, observed species could potentially be instrument thermal decomposition products of chemically distinct original bioproducts. [b] Note that references identify the prevalence and sources of the compound class PAH to which this compound belongs rather than identifying this species specifically. This compound has been reported in urban air pollution[62] but has not been explicitly referenced in marine pollution literature to our knowledge.

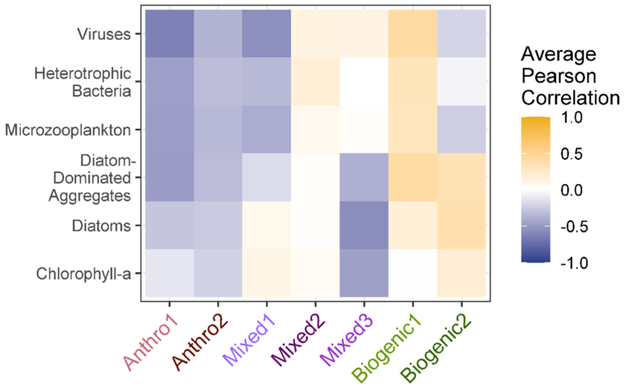

Figure 2. Average Pearson correlation coefficients between constituents in aerosol-phase clusters and water-side biological activity indicators during the SeaSCAPE mesocosm experiment.

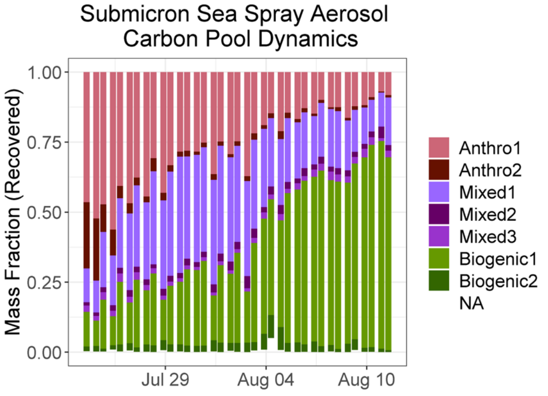

Figure 3. Submicron SSA carbon pool mass attribution to anthropogenic, mixed, and biogenic influence groupings from SSA samples collected over the course of the 2019 SeaSCAPE mesocosm experiment. NA indicates mass attributable to compounds that were too infrequently observed for assignment to time series grouping.

■ RESULTS AND DISCUSSION

Pre-Bloom Contributions of Anthropogenic Compounds to Submicron Aerosol Mass. Over the first full day of analysis, 73% of the recovered organic carbon mass pool was attributed to compounds from anthropogenic clusters (Figure 3). Given the approximate organic material recovery rate of 40% (discussed in Supporting Information SI.3), this implies that at least 30% of the submicron organic material collected during this period is attributable to the anthropogenic source material. Importantly, another 15% of the recovered carbon pool is attributed to mixed cluster categories that include anthropogenic compounds, as summarized in Table 1, meaning that the total recovered mass fraction attributable to anthropogenic organics is greater than 73%. This anthropogenic material was highly diverse, consisting of over 400 individual organic species. Identities and dynamics of specific groups of interest are described below.

One compound class within the anthropogenic fraction that substantially contributed to total recovered mass was a complex mixture of the aliphatic material. This population can be seen in Figure 4A as the tightly grouped distribution of low carbon oxidation state species in the n_c range between 18 and 22 annotated with a black box and included n-alkanes in addition to a variety of branched hydrocarbons. While the aliphatic material in marine environments can have both biogenic and anthropogenic sources, the aliphatic signature identified in the SSA samples was identified as a petrochemical rather than biogenic for three reasons. First, the oil signature was identified as a petrochemical by comparison to ambient marine oil identified in the analysis of the Deep Water Horizon

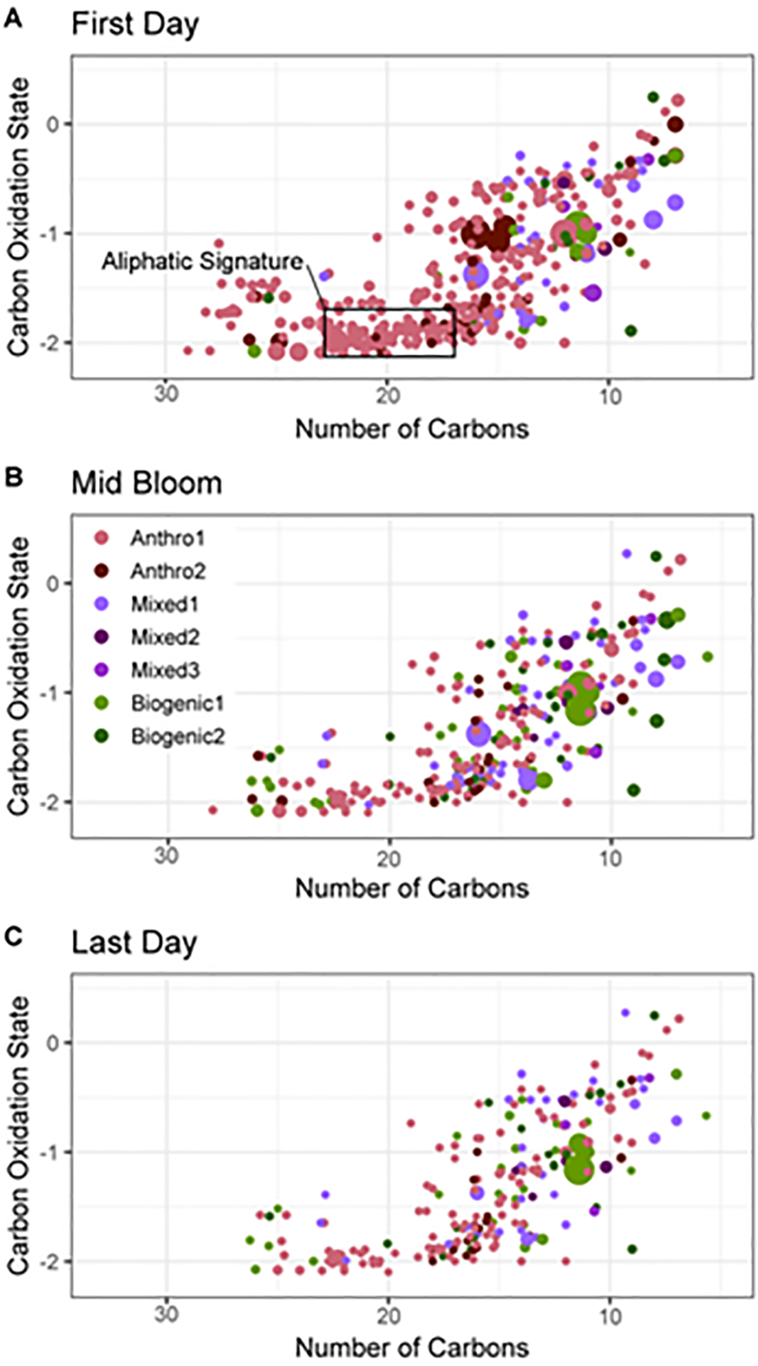

Figure 4. Chemical property distributions in OS_c-n_c space and cluster assignments of speciated aerosol-phase organics detected on the first day (A), the middle of the bloom [(B), daytime on August 4th], and the last day of sample collection (C). Marker size indicates mass concentration in ng/m^3 scaled to the most abundant compound detected in the sample. Unidentifiable compounds' properties are predicted by Ch3MS-RF on a continuous scale, and predicted carbon numbers are therefore not restricted to the integer values. A complex aliphatic signature is annotated with a black box in (A).

oil spill, which was previously analyzed on the instrument utilized in this work and reported in Drozd et al., 2015.[42] As described in the methodology of Tran et al., 1997, the biogenic aliphatic material typically presents as distinct products while oils from fossilized sources present as an incompletely resolved complex mixture, as was identified in this case.[12] It should be noted that Tran et al., 1997, identified the aliphatic material in effluent into the ocean off the coast of San Diego as primarily terrestrial biogenic in origin, but this was due to a distinct product signature (clear individual peaks distinctly separated by gas chromatography) not observed in the SSA samples collected in this study.[12] Finally, as described in Crocker et al., 2022, the carbon stable isotope ($\delta^{13}C$) values of the submicron SSA samples collected at SeaSCAPE (−24 to −29‰) were significantly more negative than the typical seawater $\delta^{13}C$ values for marine biogenic organic matter (−20 to −23‰),[43] which they attributed to a likelihood of anthropogenic influence.[44] While these more negative $\delta^{13}C$ values cannot be attributed to any single compound or group of compounds, they rule out marine biological activity as likely source material and lend credence to an anthropogenic/petrochemical source attribution for the aliphatic product class. Potential sources of petrochemical aliphatic organics at the sampling location include wastewater discharge, urban runoff, and shipping, including from small research vessels launched from Scripps Pier.[12,13] A map of pollution sources surrounding Scripps Pier can be found in Franklin et al., 2021.[33] The potential of an influence from the natural petrochemical seeps at Coal Oil Point and Redondo Beach cannot be entirely ruled out, but they are unlikely to have contributed to the observed signal due to the location of the seeps relative to the sampling location (both seeps North of Scripps Pier, while the Southern California Eddy runs predominantly South to North along the shoreline) and the distance of approximately 120 miles between Scripps Pier and the nearest seep.[13] The petrochemical organic mass contributed approximately 20% of the total recovered anthropogenic organic mass and was almost entirely attributed to cluster Anthro1. Following the behavior of this cluster, the petrochemical aliphatic signal decreased rapidly in the transition period lagging peak chlorophyll, likely indicating that these species were consumed and/or transformed by one or more of the bacterial species which increased in concentration over the bloom.[45]

Other identified and quantified organic compounds that contributed to the anthropogenic mass fraction included compounds attributable to personal care products, as well as phthalates and polycyclic aromatic hydrocarbons (PAHs). Both of these have been previously reported in SSA originating from polluted ocean water.[22] Sunscreen, in particular, stood out as an important potential source; 2-ethylhexyl salicylate and a mixture of homosalate isomers, both compounds that have been attributed to sunscreen pollution when identified in coastal waters,[10,46,47] accounted for >80% of the Antro2 cluster mass during the first day of analysis, which equated to 26% of the total anthropogenic organic mass and 19% of total recovered organic mass over the first day. While these compounds disappeared rapidly, decreasing in abundance by >3 standard deviations over 1−2 days (illustrated in Figures 1 and 3), their abundance at the beginning of the bloom is notable. The loss mechanisms of these products cannot be definitively identified based on the available evidence but are likely attributable to volatilization and loss to surfaces in the wave channel. While the presence of sunscreen products in water collected adjacent to a popular surf beach is not surprising, to our knowledge, their aerosolized emissions from the coastal ocean have not been previously reported.

Contributions of PAHs to pollution in coastal regions, and in particular to SSML organic composition, have been described in a range of environments including Italy, American Samoa, Southern California, and even Antarctica,[22,48−50] and enrichment of PAHs in SSA compared to both dissolved and SSML phases has also been previously described.[22] In this work, 8 PAHs were isolated and identified in nascent SSA, all of which were assigned to group Anthro1, meaning that they were observed in relatively high concentrations at the beginning of the experiment before rapidly declining during the transition period between peak chlorophyll-*a* and peak heterotrophic bacteria in the wave channel water. A full list of the PAH compounds observed in SSA at SeaSCAPE is provided in Supporting Information Table S4. These compounds contributed relatively little to the total anthropogenic carbon pool, making up 1.5% of the anthropogenic attributed mass collected over the first full day of analysis.

In addition to those included in the previously described clustering and quantitative analysis, the following important anthropogenic compounds were observed. Benzophenone, another commonly reported sunscreen pollutant, was identified in the aerosol phase samples through selective ion chromatography comparison to authentic standards, but due to coelution with a contaminant was not able to be accurately traced and quantified. Five siloxanes were observed with temporal variability that would have placed them in either anthropogenic or mixed clusters, but they were not included in the standard and were too chemically distinct for their quantification factors to be currently predicted by Ch3MS-RF and were therefore excluded from quantitative analysis.

Evidence for Biological Transformation of Submicron Aerosol Organic Carbon Pool. Over the course of the SeaSCAPE experimental bloom, the submicron organic composition underwent changes from mostly anthropogenic to mostly biogenic. On the first day of analysis, recovered aerosol mass was 73% anthropogenic compared to 15% mixed influence and 13% biogenic. By the final day of the experiment, however, the recovered carbon pool compositional breakdown had completely changed and was composed of 73% biogenic material, 19% mixed influence material, and only 8% primary anthropogenic material. This transformation is illustrated in Figure 3. While the rapid loss of compounds in the Anthro2 cluster cannot be directly attributed to biological activity and contributes to the significance of differences between compositional indicators at the beginning and end of the bloom, the cumulative growth of the biogenic/biologically transformed compounds, in both absolute (Figure S7) and relative (Figure 3) terms, demonstrates strong temporal connections to the progression of the biological bloom.

The period of most rapid turnover corresponds to the window between August 3rd and August 5th, directly between the peaks in chlorophyll-*a* and heterotrophic bacteria concentrations and a predatory dinoflagellate grazing event (*Podolampas bipes*) on diatoms. Although the correlations between the bulk water chlorophyll-*a* concentration and increases in both biogenic organic clusters are weak, as illustrated in Figure 2, there are stronger associations between the two clusters and the microbial abundances. Cluster Biogenic1 contains constituents that are positively correlated with concentrations of viruses, heterotrophic bacteria, microzooplankton, and diatom-dominated aggregates, while cluster Biogenic2 contains constituents that are positively correlated with diatoms and diatom-dominated aggregates. Although negative correlations between bulk water cell concentrations and biogenic organic constituents in SSAs could reasonably occur for biogenic species released from cellular matrices, which would necessarily rise only as cells were destroyed, both assigned anthropogenic clusters and the primary mixed cluster, Mixed1, peak before all major microbiological subspecies and are therefore not experiencing this phenomenon. The timings and averaging periods of the biological cell/L and SSA samples are also relevant. Water was collected for biological activity analysis in the mornings at approximately 8:00, while the aerosol "day" samples that were compared to the water-side measurements were collected continuously from 7:00 to 21:00. As a result, any lagging within a 14 h time scale would be averaged out and present as a positive unlagged Pearson's correlation. Given the complexities in the evolution of the phytoplankton, bacterial, and viral communities, the covariance between the temporal variability of different species, and the sensitivities of the aerosol-based measurements to variables including pressure and temperature, positive correlations cannot be used to definitively propose the causal relationships between individual microbial species and individual compounds. That said, the presence of relatively strong average correlation coefficients between compounds assigned to the biogenic source groups and negative or very weak correlations between the other source groups and species-specific biomass concentrations supports the assignments of the two biogenic/biologically produced clusters.

There is additional molecular-level evidence for biological transformation of the submicron carbon pool. One identifiable constituent in cluster Biogenic1, phthalic anhydride, has been previously identified as a product of bacterial degradation of phthalates, which were observed in the anthropogenic clusters (Table 1). Additional identity-based analysis of the biogenic fraction is made difficult by the high proportion of biogenic compounds that are not identifiable by database match, as discussed below. Importantly, more commonly reported biogenic products including straight chain fatty acids were observed, but as summarized in Table 1, they followed temporal variability that more closely matched that of compounds with anthropogenic sources and were therefore assigned to a mixed influence cluster. The effects of the biological turnover on the distribution of mass in chemical properties space are visualized in Figure 4. Between the beginning of the bloom and the primary transition period between peak chlorophyll and peak heterotrophic bacteria (Figure 4A,B), changes in property distribution can be observed, as anthropogenic aliphatic compounds with high n_c and low $\overline{\mathrm{OS}}_c$ are lost, while lower carbon number and more oxidized mixed influence and biogenic species appear or increase in importance. There is some evidence of the production of high carbon number slightly more oxidized products in the high carbon number biogenic compounds visible in Figure 4B, some of which could be indicative of the biotransformation products of the aliphatic signature, but it is important to note that previous studies have identified that GC × GC analysis is less sensitive to oxidized oil biodegradation products than to unoxidized precursors.[51] Additionally, any increases in the solubility of degradation products relative to that of precursors would likely decrease observed concentrations of degradation products as those compounds would be more likely to mix into the dissolved phase and therefore be less enriched in the SSML and submicron aerosol phases. Finally, on the last day of analysis (depicted in Figure 4C), both anthropogenic and mixed influence compounds are diminished in comparison to two unidentifiable compounds in the cluster Biogenic1, discussed in greater detail below.

Knowledge Bias against Biologically Transformed and Produced Organics. As previously noted, analysis of the biogenic influence clusters is made more difficult by the fact that the biogenic cluster organic mass pool is significantly under characterized compared to the anthropogenic and mixed fractions. As illustrated in Figure 5, over 50% of organic mass attributed to the anthropogenic and mixed influence clusters was attributable to compounds that could be identified by database match compared to less than 15% of the summed biogenic clusters. Given the transition from anthropogenic-dominated to biogenic-dominated organic carbon over the course of the bloom, this led to a consistent decrease in the fraction of the organic material collected in each sample that could be identified, ranging from approximately 60% of the mass in the first sample to 25% in the last (Figure S9). This phenomenon is in part attributable to the large mass of two unidentifiable compounds from cluster Biogenic1, which dominated recovered mass at the end of the bloom. The mass spectra of these two compounds, along with their n-alkane equivalent Kovats indices in a semistandard nonpolar column and predicted n_c and $\overline{\mathrm{OS}}_c$, are discussed in Supporting Information SI.9. The spectra of these compounds are provided in Appendix B along with all other compounds traced over the SeaSCAPE bloom, along with the identities and properties of identifiable compounds and Ch3MS-RF-predicted properties of not identifiable compounds. They will be searchable through UCB-GLOBES (University of California, Berkeley Goldstein Library of Biogenic and Environmental Spectra) for use by the community in comparing field samples and identifying environmentally important species.

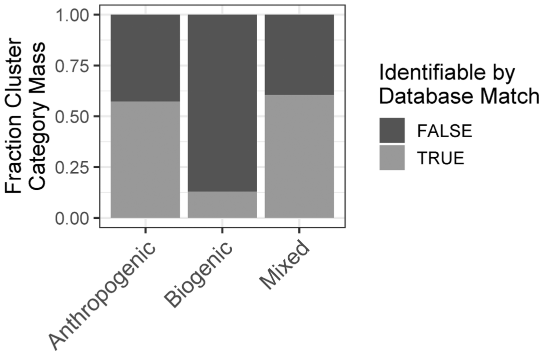

Figure 5. Fraction of nascent SSA organic mass (recovered by GC × GC) attributable to identifiable vs unidentifiable organic compounds averaged over the SeaSCAPE mesocosm experiment.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.2c04848.

Methodological details, including accuracy metrics for quantification and chemical properties' modeling and 70 ev EI mass spectra of unidentifiable compounds of interest (PDF)

Appendix A: Names, Kovats indices, and retention indices of the compounds included in the calibration standard (XLSX)

Appendix B: Unique identifiers, identities, identification methods, calculated or real chemical properties, and mass spectra of the observed and traced seascape organic compounds, both identifiable and not identifiable (XLSX)

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E.B.F. collected aerosol samples, analyzed aerosol samples, analyzed data, and wrote the manuscript. S.M.A. collected and analyzed phytoplankton speciation data. D.C. collected and analyzed chlorophyll-*a* data. C.M. collected and analyzed heterotrophic bacteria data. K.J.M., J.S., and C.L. organized and oversaw the SeaSCAPE experimental campaign. R.J.W. supported aerosol sample analysis. F.M. organized and oversaw biological activity measurements and analysis. C.D.C., T.H.B., and K.A.P. planned and supervised the SeaSCAPE experimental campaign. A.H.G. oversaw sample collection and analysis. S.M.A., D.C., C.M., K.J.M., J.S., C.L., F.M., C.D.C., T.H.B., K.A.P., and A.H.G. reviewed and edited the paper.

Notes

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