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Article

Sources of Water-Soluble Organic Carbon in Aerosols at the Cape Point GAW Station

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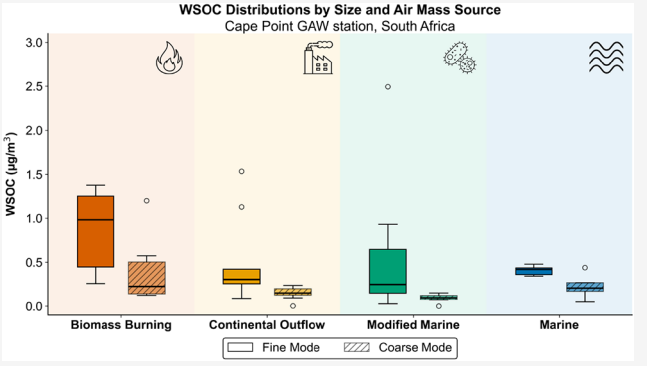
ABSTRACT: Aerosols play a major role in climate by influencing both radiative forcing and cloud condensation nuclei (CCN) formation, with organic aerosols comprising a large fraction of the global natural aerosol burden (~20−70%). Despite this importance, long-term observations of water-soluble organic carbon (WSOC), particularly in size-segregated aerosols from natural sources, remain scarce in the southern hemisphere. Here, we present size-resolved WSOC measurements from an eight-month observational campaign (April to November 2018) at the Cape Point Global Atmosphere Watch (GAW) station, a remote coastal site at the southern tip of Africa, ideally suited for elucidating marine, continental, and mixed aerosol sources. Weekly aerosol samples were classified using air mass back trajectories, radon-222 and carbon monoxide concentrations, wildfire observations, and satellite-derived chlorophyll-*a* to assess source influences. Across all air mass classifications, WSOC concentrations were consistently higher in the fine mode (<1 μm) than in the coarse mode (>1 μm) aerosols (0.58 ± 0.55 $\mu g/m^3$ vs 0.20 ± 0.22 $\mu g/m^3$, respectively). Fine mode WSOC concentrations were highest during periods influenced by biomass burning (0.87 ± 0.49 $\mu g/m^3$) and continental outflow, while marine and modified marine air masses exhibited lower fine mode WSOC concentrations. However, periods of enhanced marine biological activity were associated with increased fine-mode WSOC concentrations. The observed predominance of WSOC in the fine mode across marine, modified marine, and continental air masses highlights the importance of secondary formation and atmospheric aging processes, rather than direct primary emissions, in controlling WSOC concentrations at Cape Point. Overall, WSOC levels at this coastal site reflect an integration of natural and anthropogenic sources, transport history, and atmospheric processing. These results establish a regional baseline for WSOC aerosols in southern Africa and contribute to a broader understanding of organic aerosol formation in a data-sparse southern hemisphere coastal environment.



KEYWORDS: *water-soluble organic carbon (WSOC), size-segregated aerosols, natural aerosol sources, southern hemisphere, Global Atmosphere Watch (GAW)*

1. INTRODUCTION

Aerosols are derived from both natural and anthropogenic sources, and play a critical role in influencing atmospheric chemistry, biogeochemical cycling, radiative forcing and climate, as well as air quality and human health. Organic carbon aerosols make up 20−70% of atmospheric aerosols[1] and are emitted to the atmosphere from direct emissions of primary organic aerosols (POA), or via secondary organic aerosols (SOA) formed through gas-to-particle conversion and the oxidation of volatile organic compounds (VOCs).[2]

Organic carbon aerosols can be further characterized into water-soluble organic carbon (WSOC) and water-insoluble organic carbon (WIOC). The chemical composition of WSOC influences the hygroscopicity and CCN activity of aerosols, thereby controlling the atmospheric radiative budget through cloud formation.[3] Despite the critical role of organic aerosols in the atmosphere, long-term measurements of WSOC aerosols are scarce, particularly in the global south and the remote marine atmosphere; thus, the sources, formation pathways, seasonal variations, and chemical composition remain poorly defined.

Sites in the northern hemisphere generally have higher WSOC concentrations due to the higher contribution from continental sources, including both anthropogenic and natural sources.[4,5] Indeed, the impact of wildfire events over prolonged periods, has resulted in increased WSOC concentrations in the

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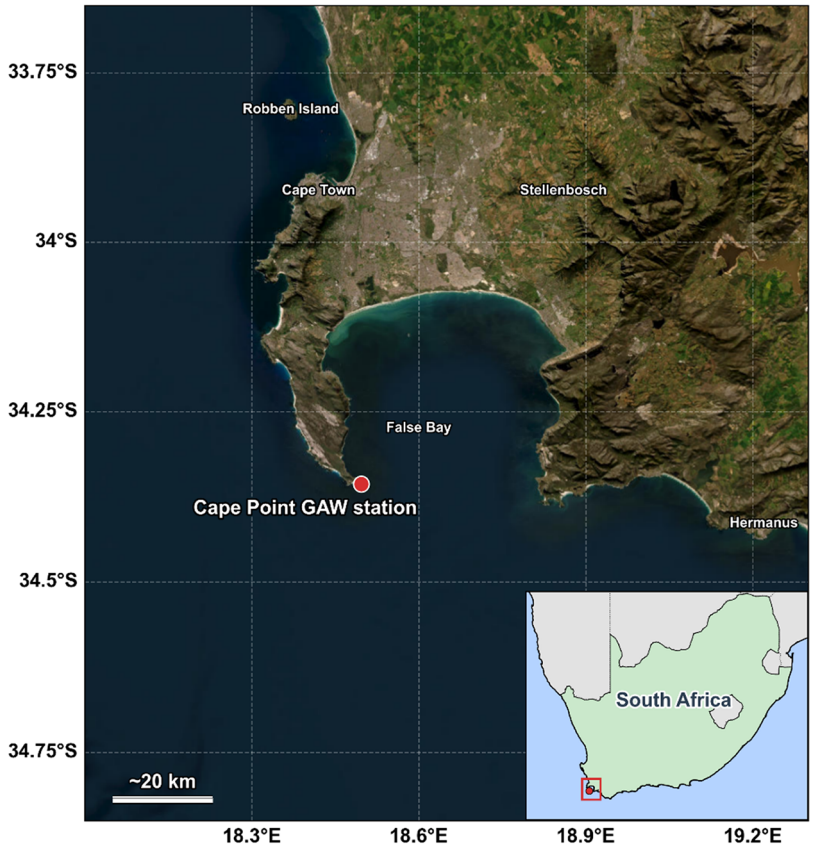

Figure 1. Map of the study site showing the Cape Point GAW station (red circle) situated at 34.3567°S, 18.4968°E. The main panel displays the satellite view of the surrounding localities and proximity to the city of Cape Town. The inset shows the broader regional context of the location within South Africa (highlighted in green).

atmosphere,[6,7] ultimately leading to the long-range transport of potentially toxic pollutants.[8]

The Cape Point Global Atmosphere Watch (GAW) station is one of 11 southern hemisphere-based GAW research stations (https://community.wmo.int/gaw-global-stations). The Cape Point GAW station is uniquely situated for the comparison of both continental and remote marine influence on organic aerosol composition and formation, as this coastal location receives air masses from the Southern Ocean and the African continent. Southern hemisphere sites generally have lower concentrations of WSOC aerosol compared to northern sites, such as Mace Head, due to a higher aerosol contribution from biogenic marine emissions.[9−11] WSOC concentrations observed at continental sites can be up to 10-fold higher than remote sites like Amsterdam Island for example, due to the contribution of urban pollution and biomass burning events.[4,5,12−14]

Here, we present findings from an eight-month-long aerosol sampling campaign at the Cape Point GAW station. This study aims to explore the sources of fine and coarse mode WSOC aerosols using air mass back trajectory analysis, radon-222, carbon monoxide (CO) concentrations, and satellite-derived wildfire and chlorophyll-*a* data.

2. METHODS

2.1. Study Site

The Cape Point GAW station is one of 11 southern hemisphere-based GAW stations. It is located at 34.3567°S, 18.4968°E at the southern tip of the Cape Peninsula, 230 m above sea level and 60 km south of Cape Town, South Africa.[15,16] The station receives air masses directly from the Southern Ocean and Antarctic continent,[15] as well as from the African continent. Therefore, it is uniquely situated for the comparison of continental and remote marine influence on aerosol composition and formation (Figure 1).

The Cape Point GAW station is considered representative of the southern hemispheric midlatitudes, with moderate temperatures, dry summers, and increased precipitation during winter.[15,17] The winter season is characterized by cold fronts moving from west to east over the continent, bringing heavy rainfall, and the potential for more pollution from the city of Cape Town.[15] CO is used as a tracer for biomass burning and various industrial combustion processes. CO concentrations have a well-established seasonal cycle at Cape Point with a summer minimum and a winter maximum evident in 40 years of continuous observations.[15,16] The peak in CO during winter is attributed to northwesterly winds bringing in more pollution from the city of Cape Town, combined with a decline in reactions with OH radicals.[15,16]

2.2. Sample Collection

Size-segregated aerosol samples were collected from 16 April 2018 to 10 November 2018 using a high-volume air sampler (TE-5170X; Tisch Environmental) fitted with a five-stage cascade impactor (TE-235; Tisch Environmental). Aerosol samples were collected on glass fiber filters precombusted at 450 °C for 4 h to remove impurities before collection. The aerodynamical diameter of the particles captured by each stage at a flow rate of ~0.82 m^3/min were: stage 1 (>7.2 μm), stage 2 (3−7.2 μm), stage 3 (1.5−3.0 μm), stage 4 (0.95−1.5 μm), stage 5 (0.49−0.95 μm) and back-up filter (<0.49 μm). Data from stages 1 to 4 were summed to make up the coarse mode fraction (supermicron), and stage 5 and the back-up filter were summed to make up the fine mode fraction (submicron). The conventional 1-μm boundary was used for comparison with other

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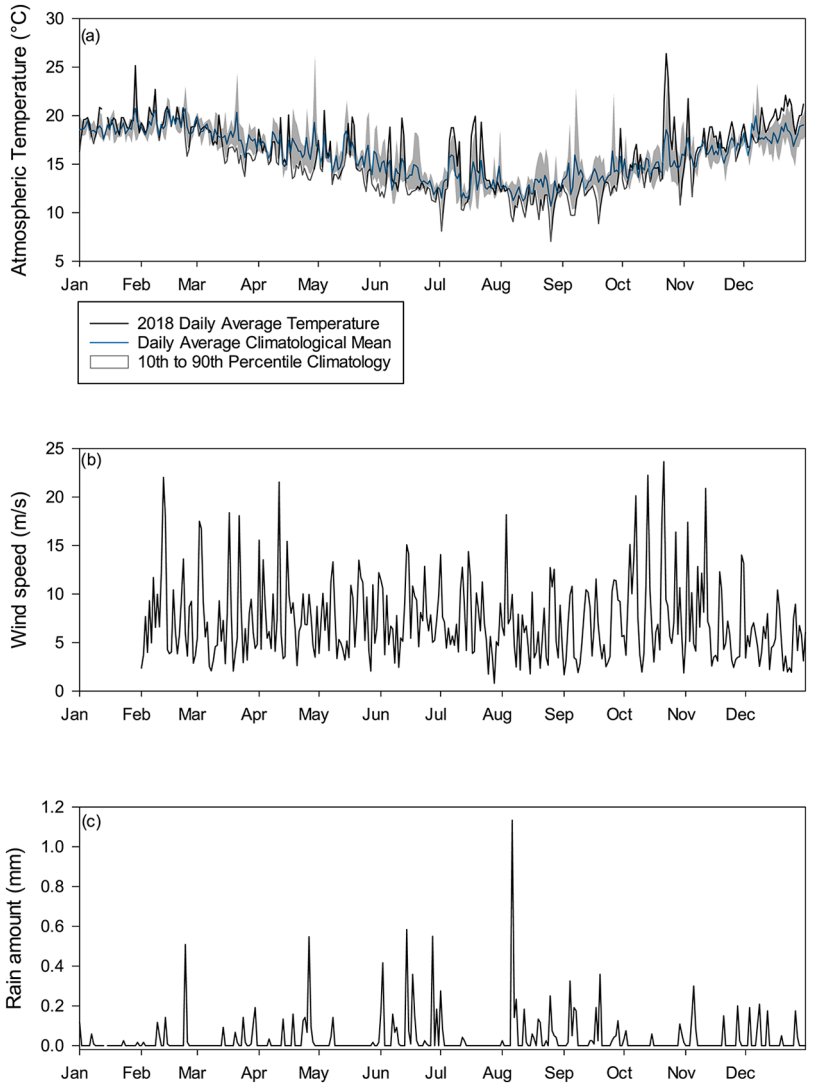

Figure 2. Daily average (a) atmospheric temperature (°C) for 2018 (black), a climatological mean (2017−2019; blue), and the 10th and 90th percentile of the climatology (gray shading), (b) wind speed (m/s), and (c) rain amount (mm) from January 1 to December 31, 2018 at the Cape Point GAW station.

values in the literature, however, due to the dominance of fine mode aerosol mass on the back-up filter (Table S1), whether stage 4 is considered fine mode or coarse mode does not impact the observed trends.

Filters were collected at least once per week (Table S2) from the cascade impactor and stored in individual zip-sealed plastic bags at −20 °C until analysis. Three field blanks were collected throughout the sampling campaign and were subject to the same analysis procedures as samples to assess any possible contamination during filter deployment or laboratory procedures.

A wind sector controller (Campbell Scientific Africa) was deployed during two intervals within the year from 5 July to 24 August 2018, and 30 August to 10 November 2018 (Table S2). The wind sector controller was programmed to switch on the air pumps when the wind was coming from within a specified angle range of >135° and <290° to restrict sampling to air masses originating from the marine sector. There were two periods of daily sampling from 13 to 17 May 2018, and 24 to 30 August 2018, during which the sector-controller was switched off. Filter samples were collected once a week during the sector controller's deployment and twice per week when the sector controller was not in use.

2.3. Sample Analysis

Each aerosol filter was subsampled and extracted by ultrasonication for 1 h with ultrapure water (18.2 MΩ·cm, Direct-Q, Millipore). Extracts were allowed to diffuse and settle for at least 12 h at 4 °C. Subsequently, the aqueous extracts were filtered with a 0.2 μm PTFE pore syringe filter to remove insoluble material. All samples were extracted and analyzed in duplicate.

Aerosol WSOC concentrations were determined for each aerosol sample extract using the nonpurgeable organic carbon method of the total organic carbon analyzer (TOC-L_{CHP}, Shimadzu). The instrument detection limit of the TOC-L_{CHP} is 0.438 mg C/L based on triplicate analysis of ultrapure water. Each aerosol extract was injected twice. If the two injections had a standard deviation greater than 0.02 mg/L, then a third injection was analyzed.

Field blank filter extractions had WSOC concentrations of 1.04 to 1.19 mg/L. Where the blank values were higher than the aerosol extracts, the WSOC concentration for that extract was set to zero. Of the 180 individual filter samples analyzed, eight were set to zero, seven of which were in the coarse mode and one in the fine mode. They were all 24-h samples, with the exception of one stage 1 filter sample that was a 192-h sample.

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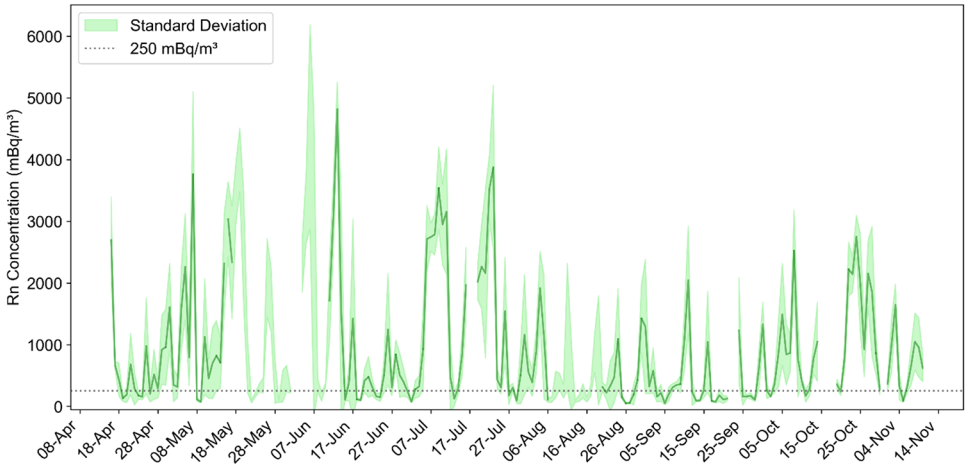

Figure 3. Daily average ^{222}Rn concentrations for the aerosol sampling period April to November 2018 with the standard deviation indicated by the green highlight. The threshold for marine air masses is represented by the dashed black line at 250 mBq/m^3.

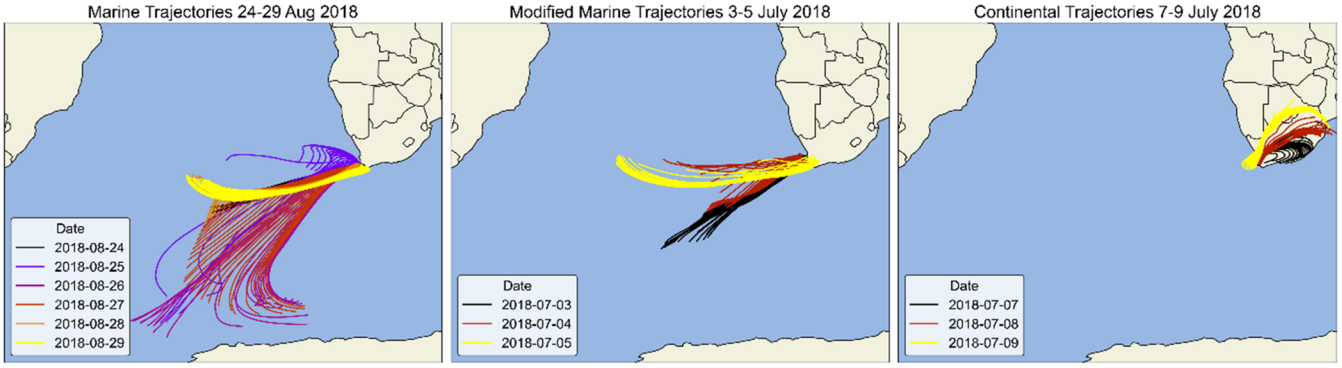

Figure 4. HYSPLIT air mass back trajectories showing cases of (M) marine air masses, (MM) modified marine air masses and (C) continental air masses. For reference, the complete set of HYSPLIT air mass back trajectories computed for each sampling day is shown in Figure S2.

2.4. Supporting Data

Air mass back trajectories (AMBTs) were generated using the NOAA HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT: http://www.ready.noaa.gov/) transport and dispersion model (Stein et al., 2015) using Global Data Assimilation System (GDAS, 1°) meteorological input and an altitude of 230 m above sea level. Each AMBT was computed for a backward analysis period of 72 h, with a new trajectory computed hourly for the entirety of the sample duration (Figure S1).

In addition to the HYSPLIT AMBTs, radon-222 (^{222}Rn) concentrations (which forms part of the GAW station's core measurement program) were used to assess the influence of continental air masses during the sampling period. ^{222}Rn is a stable isotope naturally emitted from rocks and soil, with a half-life of 3.8 days in the atmosphere, making it an ideal tracer for continental-influenced emissions. ^{222}Rn at Cape Point is measured continuously at an hourly interval, with a 1500 L dual flow loop two filter radon detector.[15,18]

With an atmospheric lifetime of approximately two months, CO is used as an indicator of polluted air masses (Labuschagne et al., 2018; Figure S2). Here, CO concentrations were used to assess the influence of fire during the sampling period. CO data, measured every 30 min, were obtained from the South African Weather Service, available through the World Data Center for Greenhouse Gases (WDCGG) data portal (https://gaw.kishou.go.jp). Satellite-derived fire information was obtained from the Advanced Fire Information System (AFIS) web portal (https://www.afis.co.za); which utilizes rapid response data from the Land, Atmosphere Near real-time Capability for EOS (LANCE) system funded by NASA.

This study used the Chlorophyll-*a* (Chl-a) product from the Global Ocean Color (Coppernicus-GlobColour), Bio-Geo-Chemical, Level-4 (daily interpolated) from Satellite Observations (1997-ongoing) obtained from the Copernicus Marine Data Store (10.48670/moi-00281); this gap-free Chl-a product, derived from multiple ocean color sensors and provided at a spatial resolution of 4km, was used to assess the influence of marine biogenic sources during the sampling period.

3. RESULTS

3.1. Atmospheric Conditions

The weather conditions (i.e., temperature, wind speed, and rainfall) experienced during the aerosol sampling time frame (16 April to 10 November 2018) were representative of the long-term climatology observed at Cape Point[15] (Figure 2). The summer and spring were characterized by warm and dry weather (Figure 2) accompanied by strong winds from the southeast, bringing in clean marine air from the South Atlantic and Southern Oceans. Wind direction had a distinct seasonality at Cape Point, as has been established in previous work,[15] with a dominant east/southeast wind most of the year and a shift to west/northwest winds during winter.

Although the sampling period was limited from April to November, it captured the lowest and highest daily average temperatures (6.9 and 26.5 °C) and wind speeds (0.8 and 23.6 m/s) of 2018. However, the bulk of the sampling period was during the wetter winter months. The notably dry period

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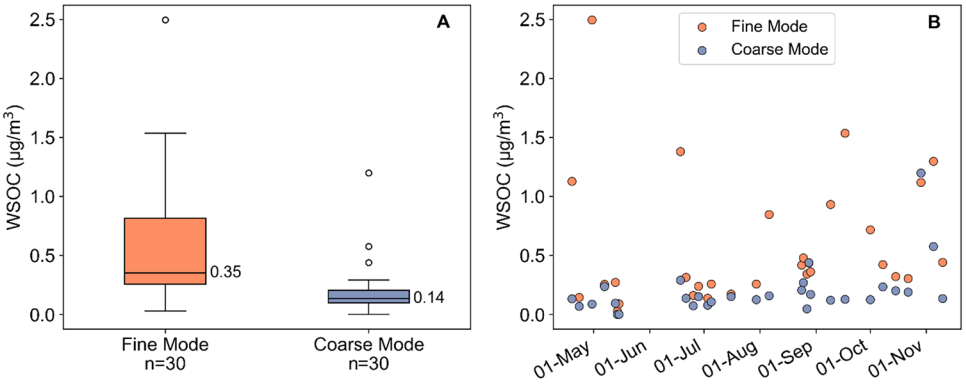

Figure 5. (a) box and whisker plot of WSOC concentrations ($\mu g/m^3$) for coarse (blue) and fine (orange) mode aerosols where the horizontal line indicates the median, the box indicates the first and third quartiles, the whiskers represent the minimum and maximum values within 1.5 × the interquartile range, and the circles represent the outliers of each data set, and (b) WSOC concentrations measured at Cape Point GAW station from 16 April to 11 November 2018. Measurements are differentiated by aerosol size fraction: coarse mode (blue) and fine mode (orange).

observed during July, corresponding to increased temperatures, did not significantly affect the observed WSOC concentrations.

3.2. Air Mass Characterization

A combination of ^{222}Rn concentrations (Figure 3) and HYSPLIT air mass back trajectory analyses (Figure 4) were used to characterize each aerosol sample as having predominantly continental, marine, or mixed sources. Marine (M) samples (n = 5) were classified as those with air masses approaching Cape Point from within the baseline wind direction (170−320°) and very low ^{222}Rn concentrations ranging from 0 to 250 mBq/m^3. The 250 mBq/m^3 threshold is typically used to indicate that air masses have originated from over the open ocean and have not encountered continental sources.[15] Samples with a ^{222}Rn concentration >250 mBq/m^3 were either classified as continental or modified marine. Samples were classified as modified marine (MM; n = 10) if the HYSPLIT air mass history indicated that air masses originated over the open ocean, followed by some interaction with the land mass. The remaining samples were classified as continental (C; n = 15) as they had both high ^{222}Rn and HYSPLIT AMBTs that originated over the continent.

Six of the continental samples were associated with fire events along the coastline and further classified as continental fire (CF). Wildfires occur in the Western Cape seasonally, during summer and autumn.[15] CO concentrations at Cape Point (Figure S1) are lower in background clean air masses and higher when continental air masses occur[16,19,20]. A threshold of 60 ppb was used here to screen samples for the potential influence of fires, as that is the well-established average during nonpollution periods.[16] These classifications using CO were corroborated with HYSPLIT and AFIS data, where AMBTs were in the proximity of locations with fires.

3.3. Size-Segregated Aerosol WSOC Concentrations

Fine mode aerosol WSOC concentrations ranged from 0.03 to 2.5 $\mu g/m^3$ while coarse mode concentrations ranged from below detection limit to 1.2 $\mu g/m^3$. The fine mode concentrations were significantly greater than the coarse mode concentrations (p < 0.05), with a median and standard deviation of 0.35 ± 0.55 $\mu g/m^3$ and 0.14 ± 0.22 $\mu g/m^3$, respectively (Figure 5a). Fine mode concentrations were dominated by the smallest size fraction (<0.49 μm) (Table S2). Furthermore, for a given sample day, the fine mode concentration was always greater than the coarse mode concentration, excluding one continental fire sample collected from 22 to 29 October 2018, discussed in Section 4.2 (Figure 5b).

3.3.1. Aerosol WSOC Concentration by Source Region. Continental fine mode WSOC aerosol concentrations ranged from 0.09 to 1.53 $\mu g/m^3$ and coarse mode ranged from 0.002 to 0.24 $\mu g/m^3$ (Figure 6). Continental aerosol samples had an average WSOC concentration of 0.50 ± 0.49 $\mu g/m^3$ in fine mode, and 0.15 ± 0.07 $\mu g/m^3$ in the coarse mode.

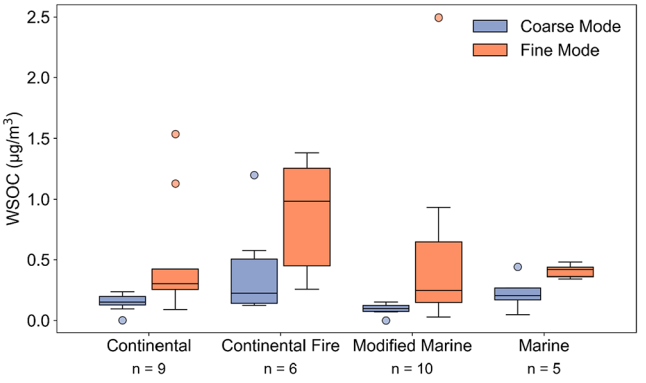

Figure 6. Fine (orange) and coarse (blue) mode WSOC concentrations ($\mu g/m^3$) for each air mass classification, continental fire (CF), continental (C), modified marine (MM), and marine (M). In the box and whisker plots, the horizontal line indicates the median, the box spans the interquartile range (IQR), the whiskers represent the minimum and maximum values within 1.5 × IQR, and the circles represent the outliers of each data set.

The continental fire WSOC concentrations ranged from 0.26 to 1.38 $\mu g/m^3$ in the fine mode, and 0.13 to 1.2 $\mu g/m^3$ in the coarse mode. Continental fire aerosols had an average WSOC concentration of 0.87 ± 0.49 $\mu g/m^3$ in the fine mode, and in 0.41 ± 0.42 $\mu g/m^3$ the coarse mode. Overall, the continental fire samples had significantly higher average WSOC concentrations than the continental aerosol samples (p < 0.01).

Marine aerosol WSOC concentrations ranged from 0.34 to 0.48 $\mu g/m^3$ in the fine mode, and 0.05 to 0.44 $\mu g/m^3$ in the coarse mode. The average marine WSOC concentration was 0.41 ± 0.06 $\mu g/m^3$ in the fine mode, and 0.23 ± 0.14 $\mu g/m^3$ in the coarse mode.

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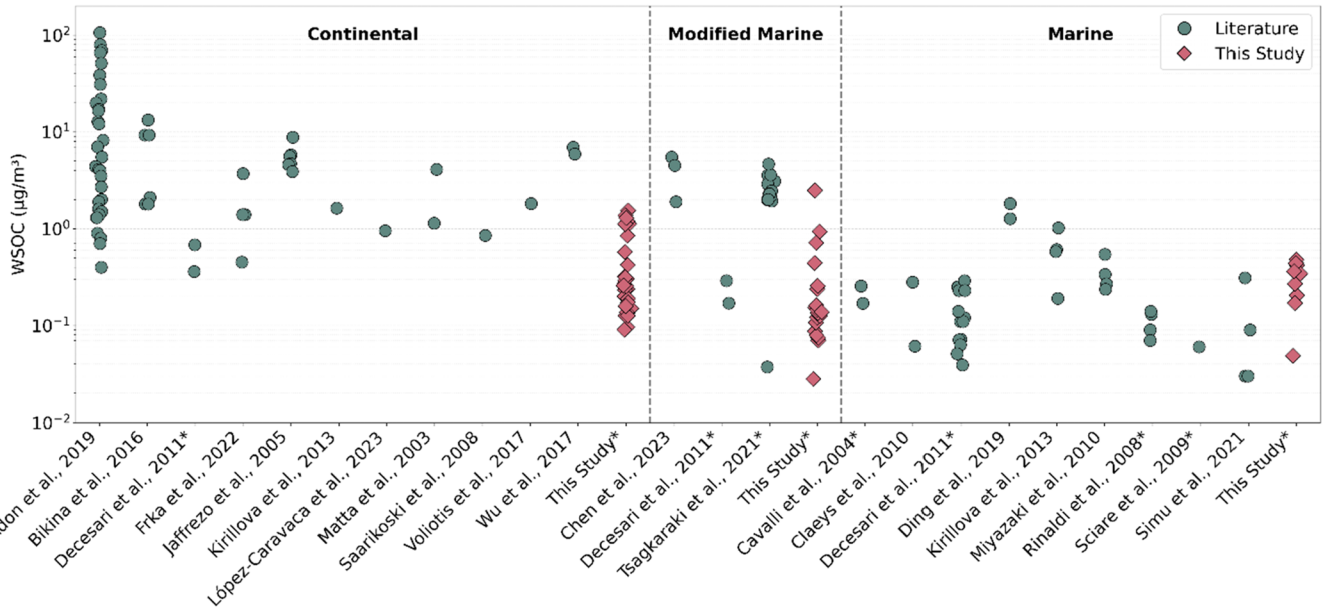

Figure 7. Aerosol WSOC concentrations on a logarithmic *y*-axis from previous literature (circles) compared to the aerosol WSOC concentrations reported here (diamonds) organized by aerosol source region including continental, marine, and modified marine. The studies that include data from a GAW station are denoted by an *.[4,5,10−12,14,21−34]

Aerosol samples classified as modified marine ranged from 0.03 to 2.49 $\mu g/m^3$ in the fine mode, and 0.001 to 0.15 $\mu g/m^3$ in the coarse mode. Modified marine aerosols had an average WSOC concentration of 0.56 ± 0.74 $\mu g/m^3$ and 0.095 ± 0.04 $\mu g/m^3$ in the fine and coarse mode, respectively. Across all classifications, the average fine mode WSOC concentration was significantly greater than the average coarse mode ($p < 0.01$).

4. DISCUSSION

4.1. Comparison of Cape Point GAW WSOC Concentrations to Literature Values

The WSOC concentrations observed here are compared to reported values from both northern and southern hemisphere sites, including other continental regions in Africa and major urban centers more broadly, coastal sites, other GAW stations (e.g., Mace Head, Amsterdam Island), and ship-based observations (Figure 7).

The highest observed continental WSOC concentration in this study was comparable to the lowest observed WSOC in other continental regions (Figure 7). Here, continental WSOC concentrations were relatively low compared to other coastal cities that are also impacted by pollution and wildfire (e.g., 1−14 $\mu g/m^3$ vs 0−2 $\mu g/m^3$).[12,21] Indeed, the continental WSOC concentrations observed here were only a factor of ∼2 higher than the marine WSOC samples. Although some sample days experienced continental air masses, almost all sample days were also influenced to some degree by marine air, potentially diluting the urban pollution with cleaner air. The strong winds associated with the region can clear urban pollution and prevent accumulation along the coast. Also, this region is characterized by descending air masses, which are less likely to have accumulated surface pollution as they are transported to Cape Point.[16]

The marine-influenced WSOC values observed here were comparable to other marine sites including coastal regions in the northern and southern hemisphere, and remote island sites (Figure 7). There are two marine sites that have higher WSOC values than this study: the Maldives Climate Observatory is at times influenced by continental outflow of pollution from the densely populated Indo-Gangetic Plain,[14] and the coastal stations within the heavily populated Bohai and Yellow Sea regions.[31] Indeed, it is probably more accurate to compare those two sites to what we characterize as modified marine, in which the data were of a similar magnitude. Another study, focused on coastal cities from densely populated urban regions in Eastern China,[21] had higher average WSOC concentrations than those characterized as modified marine in this study, due to the Chinese sites experiencing a mixture of marine sources with heavily polluted air masses. Mace Head, a GAW station that is well-characterized as being representative of marine and modified marine sources, has WSOC values comparable to the marine and slightly lower than the modified marine values observed at Cape Point.[23,29] Equivalent long-term coastal characterization of aerosols have been lacking for southern Africa. This study addresses that gap, providing the first WSOC data set of this kind for the region, and offering a valuable data point in an otherwise data sparse region.

4.2. Influence of Fire on WSOC Concentrations

The average WSOC concentration for continental fire samples was greater than continental samples, with continental fire samples having higher WSOC concentrations in both the coarse and fine mode fractions. The impact of fire events on aerosol WSOC concentrations is variable and dependent on the combustion conditions, intensity, fuel composition, duration, plume height and transport of the event.[6,35,36] Furthermore, the larger aerosol size-fraction can be impacted by partial combustion of organic material such as char and ash, or metal-containing particulates.[36−39]

A notable fire event was observed during the sampling week of 20 October to 3 November 2018. This sample period had the highest WSOC concentration in the coarse mode (1.20 $\mu g/m^3$), and the coarse mode WSOC concentration exceeded the fine mode concentration (Figure 5b). This time period also

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had the highest CO concentration (~80−125 ppb; Figure S2) observed, and a significant wildfire event along the southern coast of the Western Cape, as indicated by AFIS (Figure 8).

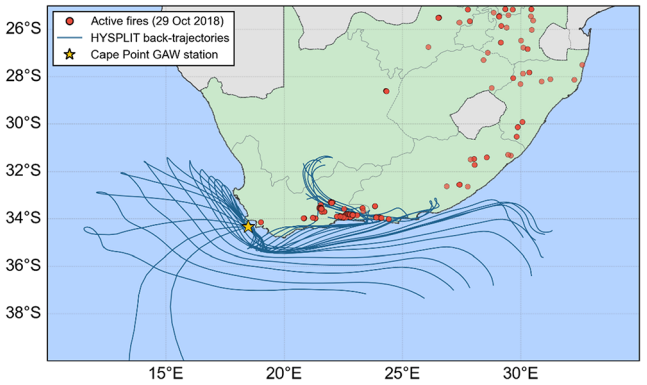

Figure 8. 72-h HYSPLIT air mass back trajectories for every hour on 29 October 2018 (blue lines) and fires identified using AFIS (red circles) from the Garden Route fires of 20 October to 3 November 2018.

The fire event started on 28 October and continued through the sampling period to 11 November 2018. It was a severe biomass burning event (category 3 to 5) at the Outeniqua Pass in the Garden Route district of the Western Cape, releasing large amounts of CO into the atmosphere for a sustained period of 13 days.[13] The burn area spanned between ~28,550 to 30,700 ha per day of forest and shrubs in a mountainous region.[13] It is likely that the increased coarse mode concentration observed at Cape Point was a result of aggregated aerosols, as well as atmospheric aging over this sustained burn period.

While Kganyago et al.,[13] predicted that the CO plume associated with the fire event would move to the east, the HYSPLIT AMBTs in this study (Figure 8) indicate that the fire event was accompanied by southeasterly winds, making it detectable as far west as the Cape Point GAW station. Further information detailing the conditions leading up to and investigating this wildfire have been comprehensively documented by Kganyago et al., including a comparison to other wildfire events in the area, vegetation burned, black carbon concentrations, aerosol optical depth data, and other satellite observations.

4.3. Influence of Marine Emissions on WSOC Concentrations

Satellite-derived chlorophyll-*a* (Chl-a) concentrations were used as a proxy for marine biological activity to determine the potential contribution of surface ocean biogenic emissions to the observed WSOC aerosol concentrations in the marine and modified marine samples. While Chl-a is not an ideal proxy for specific phytoplankton-derived organic precursors driving marine aerosol composition, it remains a practical and widely adopted metric for biological production.[40] For example, O'Dowd et al. employed a similar method looking at the contribution of biogenic organic emissions to marine aerosol at the Mace Head GAW station; and there has since been several studies which show the influence of marine biogenic emissions in aerosols using independent measurements of Chl-a.[32,40−44]

Here, satellite Chl-a concentrations were averaged over each aerosol sample's deployment time frame and over the oceanic region that HYSPLIT air mass back trajectories traversed (Figures 9 and S2). Chl-a typically varies seasonally in this

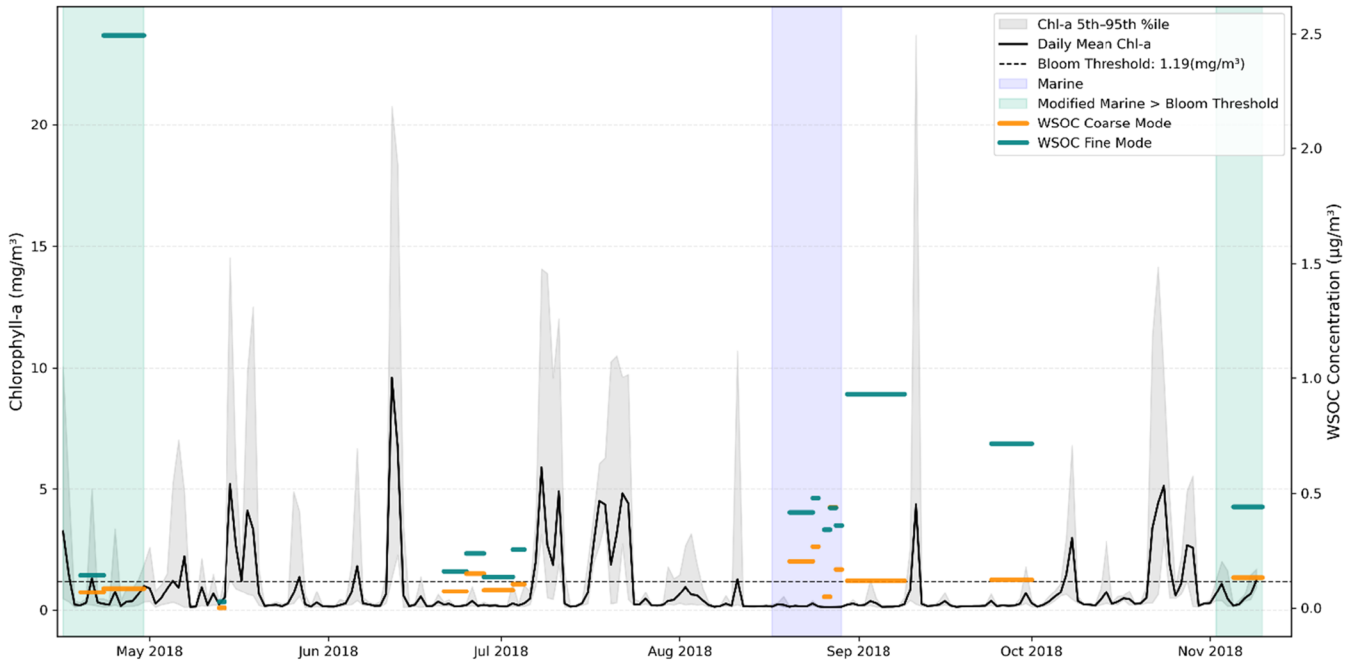

Figure 9. Time series of mean Chl-a (black line, left axis) averaged over the surface ocean area traversed by the HYSPLIT 72-h air mass back trajectories for the sampling period (April to November) with the 5th to 95th percentile indicated by the gray shading. Horizontal bars represent WSOC concentrations (right axis) in both the fine mode (teal) and coarse mode (orange). The horizontal extent of each bar denotes the filter sampling duration. Background shading corresponds to the time period and origin of air mass back trajectories for that sample (light blue for marine and green for modified marine). The dashed black line represents the bloom event threshold conditions at daily log mean +1 SD = 1.19 mg/m^3.

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region due to the upwelling of nutrient rich waters from September through March, driven by the dominant south-easterly winds, with weakened upwelling in the winter.[45,46] When averaged across each trajectory during the sampling period, we observed several episodic bloom periods, signifying high biological activity in the surface ocean. Here, bloom periods are statistically defined as when the Chl-a concentration is greater than the daily log mean plus one standard deviation, which was 1.19 mg/m^3 when averaged over April to October, 2018.[47]

Using this threshold, eight bloom periods were identified, three of which coincided with aerosol samples classified as modified marine (Figure 9). The daily log mean Chl-a concentration during these periods had a maximum of 3.26, 1.33 and 1.25 μg/m^3, respectively. The corresponding WSOC concentrations observed during these bloom periods ranged from 0.15 to 2.49 μg/m^3 in the fine mode, and 0.07 to 0.14 μg/m^3 in the coarse mode.

The remaining marine and modified marine sampling periods occurred during periods of lower biological activity, with a maximum daily log mean Chl-a of 0.15 to 0.71 μg/m^3. These samples also had low WSOC concentrations ranging from 0.16 to 0.93 μg/m^3 in the fine mode, and 0.05 to 0.44 μg/m^3 in the coarse mode. Although the number of events associated with high and low biological activity is small, it is suggestive that the total WSOC concentrations for the bloom periods is almost twice that of the periods with low biological activity. However, a higher-resolution sampling campaign with more time periods clearly associated with different levels of biological activity would be needed to statistically prove the influence of biological activity on WSOC concentrations.

To interpret the observed association between marine influence and elevated WSOC concentrations, it is important to consider the size-dependent processes governing marine aerosol formation. The fine mode WSOC concentrations across both the marine and modified marine air masses were significantly greater than the coarse mode fraction ($p > 0.01$), indicating a dominant role for secondary formation and atmospheric processing as opposed to primary sea-spray emission. Fine mode marine WSOC has been attributed to the oxidation of ocean-derived volatile organic compounds and dissolved organic precursors during atmospheric transport. During long-range transport, oxidative aging increases the WSOC fraction in the smaller particle range.[48−50] In contrast, the coarse mode aerosols, generated through the direct emission of sea spray, tend to be enriched with inorganic salts and WIOC, resulting in lower WSOC concentrations.[30,51−53] Thus, the fine mode WSOC reflects a cumulative effect of secondary organic aerosol production, as well as aerosol aging within the marine and modified marine air masses, rather than the direct emission of organic aerosols from the sea surface.

While it has been established that fine mode WSOC is associated with periods of high biological activity, four aerosol samples classified as modified marine air masses that had high fine mode WSOC concentrations did not coincide with elevated Chl-a concentrations. These samples were characterized by longer sampling durations (lasting between 6 and 10 days), and coincided with increased ^{222}Rn concentrations. This suggests that these samples had intermittent or partial continental influence during the collection period. Air mass back trajectory analysis (Figures S2 and S3) further confirmed that some air masses also passed over the city of Cape Town and the surrounding continental region before arriving at the Cape Point GAW station. Under these conditions, the fine mode WSOC is likely an accumulated signal derived from the aging of aerosols through long-range transport and anthropogenic influence. These samples underscore the mixed nature of modified marine air masses, and highlight the important use of complementary tracers for WSOC sources in a coastal environment.

Seasonal meteorology and atmospheric removal processes further modulate marine WSOC concentrations at Cape Point, influencing when marine and continental sources are detectable. Several aerosol samples classified as marine and modified marine were collected during the autumn-winter period and exhibited low WSOC concentrations, despite the expectation of increased continental influence due to biomass burning from domestic heating. However, these samples also coincided with periods of higher rainfall (Figure 2), which likely suppressed the accumulation of WSOC in the atmosphere. In addition, weakened upwelling during winter combined with reduced light availability and an increase in turbulent mixing, limits marine biological productivity in the surface ocean. Together, these seasonal processes explain the observed low WSOC concentrations, and emphasize a reflection of balance between source composition, atmospheric processing, and removal, rather than reflecting source alone.

5. CONCLUSIONS AND IMPLICATIONS

Situated at the intersection of Southern Ocean and African continental air masses, the Cape Point GAW station provides a unique natural laboratory for investigating organic aerosol sources and processes in a data-sparse region of the globe. This study presents the first size-segregated observations of WSOC aerosols from the Cape Point GAW station, providing new insight into the sources and processes contributing to the organic aerosol composition in a coastal Southern Hemisphere environment.

Across all air mass classfications, WSOC concentrations were consistently higher in the fine mode than in the coarse mode on average, and for all events, indicating a dominant contribution of submicron particles to the WSOC aerosol composition. In this study, a limited number of aerosol samples were classified as having pure marine sources, but a significant number of modified marine samples were collected, with evidence that they were also primarily influenced by marine emissions. Although it was not explicitly the focus of this study, there were also a large number of aerosol samples influenced by continental sources and regional biomass burning. Overall, the observed WSOC concentrations at Cape Point were higher than those reported for remote marine sites, but substantially lower than those reported at coastal locations strongly impacted by anthropogenic activity.

The predominance of WSOC in the fine mode across marine and modified marine air masses indicates that secondary formation and atmospheric aging processes drive the WSOC concentrations at Cape Point. The higher fine mode WSOC concentrations in marine air masses are consistent with the oxidation of ocean-derived organic precursors and aerosol processing during long-range transport, rather than the direct emission of sea spray. Modified marine air masses showed influence of both marine and continental sources, underscoring the mixed nature of coastal aerosol composition, and the importance of atmospheric aging in integrating signals from multiple source regions. These findings

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demonstrate that WSOC concentrations at Cape Point reflect not only the source, but transport history, chemical aging, and removal processes within the atmosphere.

This study highlights the value of combining size-segregated aerosol measurements with complementary tracers, including air mass back trajectories, radon-222 concentrations, carbon monoxide concentrations, and satellite-derived chlorophyll-*a*, to disentangle marine and continental contributions in complex coastal environments.

By establishing a regional baseline for WSOC concentrations and their driving mechanisms, these results contribute to a broader understanding of organic aerosol formation in the southern hemisphere, and provide a reference point for assessing future changes driven by climate variability, biomass burning activity, anthropogenic pollution, and ocean-atmosphere interactions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsearthspacechem.6c00101.

Tables detailing the study site sampling frequency, statistical summaries of WSOC concentrations at each sampling size, and coarse and fine mode WSOC concentrations separated by air mass classification. Figures illustrate the weekly average CO concentration in 2018, HYSPLIT air mass back trajectories for all sampling periods, and the corresponding average chlorophyll-*a* concentrations along each trajectory (PDF)

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Notes

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