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Environmental Significance Statement

Water-soluble organic compounds ($WSOC_p$) make up a significant contribution towards the total organic mass in the atmosphere. These compounds are likely to have impacts on human health and climate. Thus, the characterization of the pathways responsible for the formation of these compounds is essential in understanding such impacts. In this work, we provide evidence for the formation of water-soluble species through absorptive partitioning and aqueous processing. We highlight that water mediates $WSOC_p$ formation through aqueous processing under specific temperature conditions. We demonstrate that particle drying does not induce any primary nor secondary $WSOC_p$ evaporation in the winter. Analyses show that aqueous $WSOC_p$ in the winter is controlled by the presence of sufficient amounts of, the temperature-dependent, aerosol water and biomass burning precursors.

Aqueous processing of water-soluble organic compounds in the eastern United States during winter

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Abstract

Aqueous multi-phase processes are significant contributors to organic aerosol (OA) mass in the atmosphere. This study characterizes the formation of water-soluble organic matter during the winter in the eastern United States through simultaneous measurements of water-soluble organic carbon in the gas and particle phases ($WSOC_g$ and $WSOC_p$, respectively). The formation of secondary $WSOC_p$ occurred primarily through two pathways: (1) absorptive partitioning of oxygenated organics to the bulk OA and (2) aqueous phase processes. $WSOC_p$ formation through the former pathway was evident through the relationship between the fraction of total WSOC in the particle phase (F_p) and the total OA concentration. Conversely, evidence for nighttime aqueous $WSOC_p$ formation was based upon the strong enhancement in F_p with increasing relative humidity, indicating the uptake of $WSOC_g$ to aerosol liquid water (ALW). The F_p -RH relationship was only observed for temperatures between 0 – 10 °C, suggesting conditions for aqueous multi-phase processes were enhanced during these times. Temperature exhibited an inverse relationship with ALW and a proportional relationship with aerosol potassium. ALW and biomass burning precursors were both abundant in the 0 – 10 °C temperature range, facilitating aqueous $WSOC_p$ formation. To assess the impact of particle drying on the $WSOC_p$ concentrations, the particle measurements alternated between ambient and dried channels. No change was observed in the concentration of particles before and after drying, indicating that the $WSOC_p$ formed through the uptake of $WSOC_g$ into OA and ALW remained in the condensed phase upon particle drying at all temperature ranges. This work contributes to our understanding of sources, pathways, and factors affecting aqueous aerosol formation in the winter.

1 Introduction

Water-soluble organic carbon ($WSOC_p$) represents an important component of fine organic aerosol (OA) in the atmosphere[1-4]. $WSOC_p$, collectively made up of thousands of individual compounds, has direct impacts on particle hygroscopicity[5-6], light absorption[7] and thereby on the climate system. Further, these species may have profound impacts on human health[8]. $WSOC_p$ has two predominant sources in the atmosphere: it is emitted directly from biomass burning[9-13], and it is formed through secondary processes from many VOC precursors[2,14-16].

A prominent pathway for secondary $WSOC_p$ formation is the uptake and reaction of water-soluble VOCs in atmospheric aerosol liquid water (ALW)[17-18]. Because $WSOC_p$ often represents a large fraction of total OA mass (typically 30 – 80%), such aqueous processes also contribute significantly to secondary OA (SOA), as well. While the abundance of water-soluble gaseous precursors is key in the aqueous processing of atmospheric particles, ALW is also a critical

parameter in this process[1]. The initial uptake of water-soluble gases into ALW is an equilibrium process[19], suggesting that any evaporation of ALW will shift this equilibrium and might consequently lead to a loss in condensed-phase organics back to the gas phase[18]. Particle drying is a natural phenomenon that occurs in the atmosphere due to changes in relative humidity (RH) throughout the day and through changes in RH that accompany vertical atmospheric transport. In previous work conducted by our group, we reported a seasonal dependence of OA evaporation induced by particle drying. During the summer, we observed significant $WSOC_p$ evaporation due to particle drying, which was attributed to reversible aqSOA formation U.S.[18]. This was not observed in other seasons, except for the late spring[20].

During winter, biomass burning – especially that produced from residential heating – represents an important OA source in many locations[21-22]. Studies show that water-soluble organics in the particle phase make up almost 40% of wood-burning emissions (e.g.,[23]) and that more than 50% of biomass-burning OA is water soluble (e.g.,[12]). Biomass burning emissions include an array of water-soluble gases that may contribute to $WSOC_p$ such as phenols[24]. In the eastern U.S., biomass burning is a significant contributor to $WSOC_p$ concentrations in the winter[25]. Biomass burning emits various VOCs, hence, secondary OA formation may be substantial[26-27]. Further, significant amounts of primary OA are also emitted, many of which are semi-volatile and could ultimately lead to further processing of OA[28]. Laboratory studies provide evidence for dynamic transformations of numerous compounds emitted from biomass combustion and significant potential to form aqueous $WSOC_p$[24,29-35]. Field and modeling studies demonstrate secondary OA formation in the aqueous phase from biomass burning in diverse locations that include Fresno, U.S.[36], Paris, France[37], Douai, northern France[38], Los Angeles, U.S.[39], the Po Valley, Italy[40], and China[41-44].

SOA formation has been studied more intensely during summer than winter because the summertime corresponds to a peak in biogenic VOC emissions and enhanced photochemical activity in many locations. For example, SOA chamber studies utilize lower tropospheric summertime temperatures far more frequently than winter temperatures[45]. Further, large-scale intensive field campaigns investigating SOA formation in the U.S. have historically been more frequent in the summer than in the winter[46]. Similarly, studies of $WSOC_p$ formation have also been less frequent during winter ~~(e.g.,~~ [2,15,18,47-52]~~)~~, especially those investigating secondary aqueous pathways[18]. Studies of this type have been frequently conducted in China, due to the severe winter haze episodes that affect air quality in many cities[42-44]. Significant differences exist in the fuels used for residential heating between the U.S. and China. In the U.S., residential heating relies mainly on wood burning whereas in China, coal burning is used extensively for heating purposes[53]. This suggests there may also be key differences in the $WSOC_p$ mass and its formation pathways in the U.S. during winter.

The purpose of this work is to characterize $WSOC_p$ formation and its potential sources in Baltimore, Maryland during the winter. We also characterize the effect of particle drying on primary and secondary $WSOC_p$, including that formed through aqueous processes. Baltimore is located in the highly populated and heavily trafficked Mid-Atlantic region of the U.S. It is strongly influenced by emissions from industrial activities and major interstate routes[52]. Biomass burning contributes approximately 17% to wintertime $PM_{2.5}$ mass concentrations in the region, as well[54]. Isoprene emissions dominate the VOC budget in the region during summertime but are very low during winter[55]. Thus, this study contrasts prior results by investigating the formation of aqueous organic aerosol through secondary and irreversible processes from biomass burning for residential heating.

2 Materials and Methods

2.1 Measurement location

Ambient measurements were conducted at a suburban location (39.2546° N, -76.7094° W) on the campus of the University of Maryland, Baltimore County (UMBC). A suite of instrumentation was placed on the rooftop of the UMBC Engineering Building, approximately 20 – 25 m above ground level. UMBC is almost 10 km from downtown Baltimore, about 10 km from Baltimore – Washington International Airport (BWI) and approximately 60 km from Washington, D.C. Wintertime measurements were carried out from 4 to 21 February and from 6 to 23 March, 2015. This sampling period included a wide range of meteorological conditions (Table 1) and source influences.

2.2 Water-soluble organic carbon measurements

The measurements presented in this work have been described in detail elsewhere[18,20,55]. Briefly, a Mist Chamber (MC)[56] and a Particle-Into-Liquid-Sampler (PILS)[57-58], were used to sample $WSOC_g$ and $WSOC_p$, respectively, and were both connected to a Total Organic Carbon Analyzer (TOC; model 900 Turbo, GE Analytical). The air sample passed through a 47 mm quartz fiber filter before it enters the MC to remove any particles in the sample. The air sample to the PILS was first passed through a parallel plate carbon denuder to remove interference from semi-volatile organic compounds. Dynamic blanks were measured every other day for the PILS and MC systems in the same way the sampling took place except that the vacuum pumps were turned off. Blanks were used to quantify the method limit of detection (LOD, which is calculated as three times the standard deviation of the blanks) for $WSOC_p$ (0.33 μg-C m^{-3}) and $WSOC_g$ (0.43 μg-C m^{-3}).

The characterization of the effect of particle drying on $WSOC_p$ concentrations was conducted by directing the $WSOC_p$ air sample through a silica gel diffusion dryer ($WSOC_{p,dry}$) and comparing its concentration to the $WSOC_p$ measured in a parallel, unperturbed channel[18,20,55]. Total drying time in the silica drier was ~7 s. This amount of time far exceeds the required time for aerosol water evaporation, which is on the order of 10^{-3} s for fine particles[59]. This drying time may not allow for complete evaporation of condensed organics but is sufficient to provide evidence of evaporation if it occurs. More detailed discussion about this point is provided in El-Sayed et al.[55]. Particle losses though the diffusion dryer were measured and were found to be minimal[55]. The dry channel was maintained at a relative humidity (RH) of ~20% while the ambient channel was maintained at ambient RH[20]. A $WSOC_{p,dry}$ /$WSOC_p$ ratio of unity implies that the $WSOC_p$ did not evaporate with drying[55] whereas a ratio less than unity occurs if particle drying results in some $WSOC_p$ evaporation[18]. A single cycle of $WSOC_p$ – $WSOC_{p,dry}$ – $WSOC_g$ measurements was completed every 14 minutes, which allowed for the characterization of dynamic changes in the factors influencing SOA formation during the winter. A total of 2440 $WSOC_p$ – $WSOC_{p,dry}$ – $WSOC_g$ measurement cycles were carried out for this study[60].

2.3 Aerosol Liquid Water (ALW)

A climatology of wintertime ALW concentrations was derived based upon five years of aerosol composition measurements in Baltimore. Organic and inorganic concentrations of fine particulate matter ($PM_{2.5}$) were provided by the Maryland Department of the Environment (MDE) at their HU-Beltsville site (AQS ID 240330030, approximately 25 km from UMBC

(latitude of 39.2557° N and longitude of 76.7110° W). Inorganic and OA concentrations on 24-h filters were measured by MDE once every three days during the winter months (defined here as November to March). Data were accessed through the U.S. Environmental Protection Agency Air Quality Database[61]. Averaged ALW associated with inorganic components (W_{inorg}) was calculated using the ISORROPIAv2.1 aerosol thermodynamic equilibrium model (http://isorropia. eas.gatech.edu, 2018)[62]. Concentrations of aerosol inorganic composition (Na^+, NH_4^+, K^+, SO_4^{2-}, Mg^{2+}, Ca^{2+}, NO_3^- and Cl^-), temperature, and RH were used as model inputs. The liquid water associated with OA (W_{org}) was calculated according to Petters and Kreidenweis (2007)[63] using OA concentrations as inputs with an assumed kappa value of 0.126[64]. The total ALW concentration was calculated as the sum of the inorganic water (W_{inorg}) and organic water (W_{org}) content based upon the five years (2011 to 2015) of observations, corresponding to 174 aerosol samples available for these years. The spatial distribution of aerosols in the Baltimore area is regional in nature, characterized by similar concentrations over scales of tens of kilometers[65-66]. This is further supported by strong correlations between OA concentrations measured at Essex and HU-Beltsville, two sites approximately equal distances from the UMBC site, over a two-year period ($R^2 = 0.60$, Fig. S1). Therefore, the ALW derived from the measurements at HU-Beltsville are likely representative of those at the UMBC site where the WSOC measurements were conducted.

2.4 CO measurements

Carbon monoxide (CO) concentrations were measured using a CO analyzer (Thermo Scientific Model 48C), with 10-min averaging during the study period. Calibration of the CO analyzer was performed prior to the sampling season. Blank measurements were obtained throughout the study and were used to determine the LOD for the CO data, which was calculated as 18 ppb_v. The normalized $WSOC_p$ concentrations against CO were previously used to provide insight into the production of $WSOC_p$ mass, given that CO is considered a conservative compound relative to $WSOC_p$ and can help characterize similar processes for different airmass origins and boundary layer conditions[51,67]. This is a common method used to quantify SOA mass in aircraft studies, as well[2,4,68-69]. In our case, the background levels for $WSOC_p$ and CO were estimated as the 10th percentile for both measurements and calculated as 0.05 μg m^{-3} and 0.15 ppm, respectively.

2.5 OCEC measurements

Aerosol organic carbon (OC) and elemental carbon (EC) measurements were carried out using a Sunset Labs OCEC Field Analyzer. The OCEC Analyzer was placed downstream of a $PM_{2.5}$ cyclone (BGI Instruments) and a parallel plate carbon denuder. The OCEC Analyzer sampled at 8 L min^{-1} in semi-continuous mode, with 30 min sample collection followed by 15 min of off-line sample analysis according to NIOSH method 5040. The OCEC runs an external methane standard with each sample. Blank measurements were obtained once every day at midnight and were used to determine the LOD for OC and EC, which were 0.5 and 0.05 μg-C m^{-3}, respectively[70]. The uncertainty of the OC and EC concentrations were ± 0.2 and 0.1 μg-C m^{-3}, respectively. The OCEC analyzer produced a measurement every 45 minutes, compared to 14 min for WSOC. Therefore, the WSOC data were averaged to the OCEC times when comparisons between the two instruments were made. In addition, the OCEC analyzer was offline during 6 to 10 March 2015 for instrument maintenance.

3 Results and Discussion

3.1 Study Overview

Table 1 presents an overview of measured chemical and meteorological parameters during the study. Generally, $WSOC_g$ concentrations were higher than in other seasons in Baltimore[18,20], with a median value of 10.6 μg-C m^{-3} (Table 1). Table 1 shows that the $WSOC_p$/OC fraction was quite high (average of ~0.85), likely due to the abundance of secondary species and an overall decreasing contribution of primary OA emissions from motor vehicles[71]. As for the meteorological data, RH and temperature concentrations spanned a wide range capturing dry to very moist and below to above freezing conditions, respectively. Water-soluble organic carbon in the gas ($WSOC_g$) and particle ($WSOC_p$) phases are considered good surrogates for secondary organic gases and particles, respectively[2,14,47,72]. Further analyses were carried out by segregating the data into daytime (08:00 to 18:00, local time) and nighttime (20:00 to 07:00, local time) periods and based on temperature (< 0 °C, 0 – 10 °C and > 10 °C). These results are discussed below.

Table 1. Summary statistics of wintertime ambient measurements in Baltimore. All concentrations are reported in μg-C m^{-3} unless otherwise noted.

Winter measurements	median	mean	standard deviation	range
$WSOC_g$	10.6	12.5	6.8	1.6 – 42.6
$WSOC_p$	1.8	1.9	1.0	0.1 – 6.6
$WSOC_{p,dry}$	1.8	1.9	1.0	0.1 – 6.7
CO*	0.32	0.35	0.12	0.13 – 0.87
OC	1.9	2.2	0.4	0.4 – 7.5
EC	0.3	0.4	0.3	0.1 – 1.9
Relative Humidity (%)	48.0	51.9	18.1	21.0 – 91.0
Temperature (°C)	1.1	2.8	6.5	-15.9 – 20.1

*Concentration of CO in ppm_v

3.2 Primary and Secondary sources of $WSOC_p$

In this study, we use the $WSOC_p$ measurement to provide insight into the formation of OA. Previous studies have provided evidence that $WSOC_p$ is a good surrogate for SOA in many environments[2,9,14], with typically minor contributions from primary sources[73-74]. However, under significant biomass burning influence, this assumption does not necessarily hold[49], since $WSOC_p$ is also emitted directly from biomass combustion[75-77].

We evaluated the assumption of $WSOC_p$ as a surrogate for SOA during the wintertime. First, we applied the EC-tracer method to estimate the abundances of primary and secondary organic aerosol mass during the wintertime in Baltimore[78]. The results of this analysis (Fig. S2) show that, on average, the concentration of SOA was approximately a factor of two higher than primary organic aerosol during the sampling period (67.9% ±19.1 and 32.3% ±17.7%, respectively) suggesting that $WSOC_p$ was predominantly secondary in nature.

Correlations between $WSOC_p$ and two commonly used primary emission markers, CO and EC, also suggest that $WSOC_p$ was a reasonable surrogate for SOA throughout much of the study. Under the three defined temperature intervals, $WSOC_p$ was correlated with EC and CO only when temperatures were < 0 °C (R^2 = 0.44 and 0.59, respectively, Figs S3a and S4a). For the temperature range 0 – 10 °C, very weak correlations were observed between $WSOC_p$ and either EC or CO (R^2 values of 0.11 and 0.09, respectively; Figs. S3b and S4b). There was no correlation for temperatures > 10 °C (Figs. S3c and S4c). This suggests an important primary component of $WSOC_p$ only under the coldest conditions. This is supported by the diurnal profiles of $WSOC_g$ and $WSOC_p$ (Fig. S5), which were inconsistent with the diurnal profiles of CO and EC (Fig. S6). Note that EC and CO were highly correlated in all three temperature intervals (Fig. S7), suggesting motor vehicles as their major source[79].

While these analyses do not preclude the contribution of primary $WSOC_p$ during our study, these results collectively suggest that the majority of measured $WSOC_p$ was secondary in nature. This finding is supported by observations in other parts of the eastern U.S., where more than half (~60%) of the OA mass was found to be secondary during the winter[25].

3.3 $WSOC_p$ formation through absorptive partitioning to OA

The formation of $WSOC_p$ is first investigated through the relationship between the partitioning coefficient (F_p) and OC concentrations (Fig. 1). The partitioning coefficient is the fraction of WSOC in the particle phase ($F_p = WSOC_p / (WSOC_g + WSOC_p)$). An increase in F_p with OC suggests that WSOC partitioning was dependent on the amount of pre-existing OA and is inferred as secondary organic mass formed through gas-phase processes and absorptive uptake to the bulk OA[15,50,80]. Across our entire study, mean and median F_p levels increased with increasing OC concentrations, a relationship that was statistically significant at the 95% confidence level. A similar F_p dependence on OC was previously observed in Los Angeles[15,51], where photochemical oxidation and absorptive partitioning contributes prominently to OA formation[52,81]. We note that the F_p-OC relationship was observed during the daytime and nighttime in Baltimore (Fig. S8). Note that the remaining 3 hours were considered transitional between daytime and nighttime conditions and were thus excluded from these analyses. Daytime and nighttime meteorological data are provided in the supplemental information (Table S1).

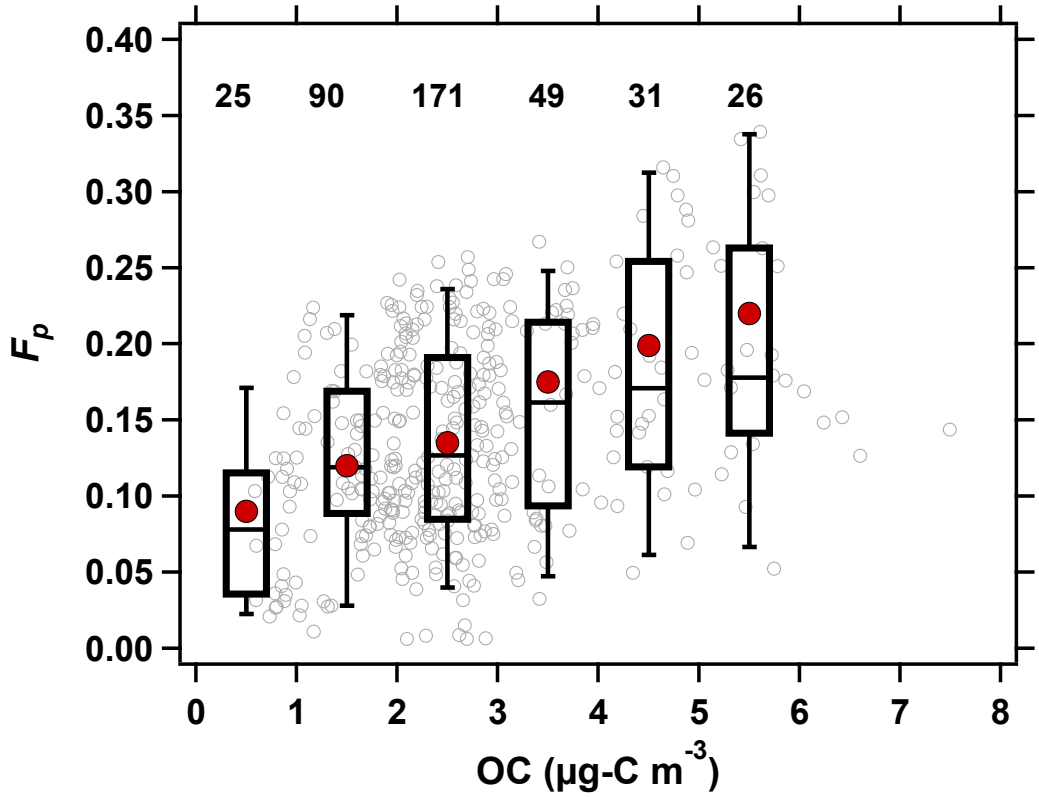

Figure 1. Scatter and box plots of the hourly particulate WSOC fraction, F_p, as a function of OC. Data were binned based on OC concentrations. For each bin, mean (red circles), median values (horizontal line), quartiles, as well as 5th and 95th percentiles (vertical lines) are shown. Numbers at the top represent the number of observations within each bin.

3.4 WSOC$_p$ formation through aqueous processes

ALW is essential for facilitating the formation of secondary WSOC$_p$ in deliquesced particles. During winter, the climatology of ALW in Baltimore shows a clear temperature dependence (Fig. 2). Typical wintertime ALW concentrations in Baltimore, including those in 2015 data, are consistently low when the temperature is below 0 °C (average ALW = 0.4 µg m^{-3}). The level of ALW increases (> 1 µg m^{-3}) at temperatures above 0 °C, until it reaches a maximum value (> 8 µg m^{-3}) at temperatures above 15 °C. On freezing days (defined with average daily temperatures < 0 °C), the atmosphere was cleaner with an average $PM_{2.5}$ mass concentration of 10.9 ± 2.9 µg m^{-3} compared to 15.3 ± 3.5 µg m^{-3} on days with average daily temperatures > 0 °C. In addition, on days with average daily temperatures < 0 °C, the atmosphere was drier, with average RH levels < 40% compared to average RH levels > 65% on days where temperatures > 0 °C. This observation was likely due to the association of the lowest temperatures with air masses from Canada and/or the arctic (Fig. S9). Temperature dependance of the daily $PM_{2.5}$ concentrations corresponding to the same months between 2011 – 2015 are shown in Fig. S10.

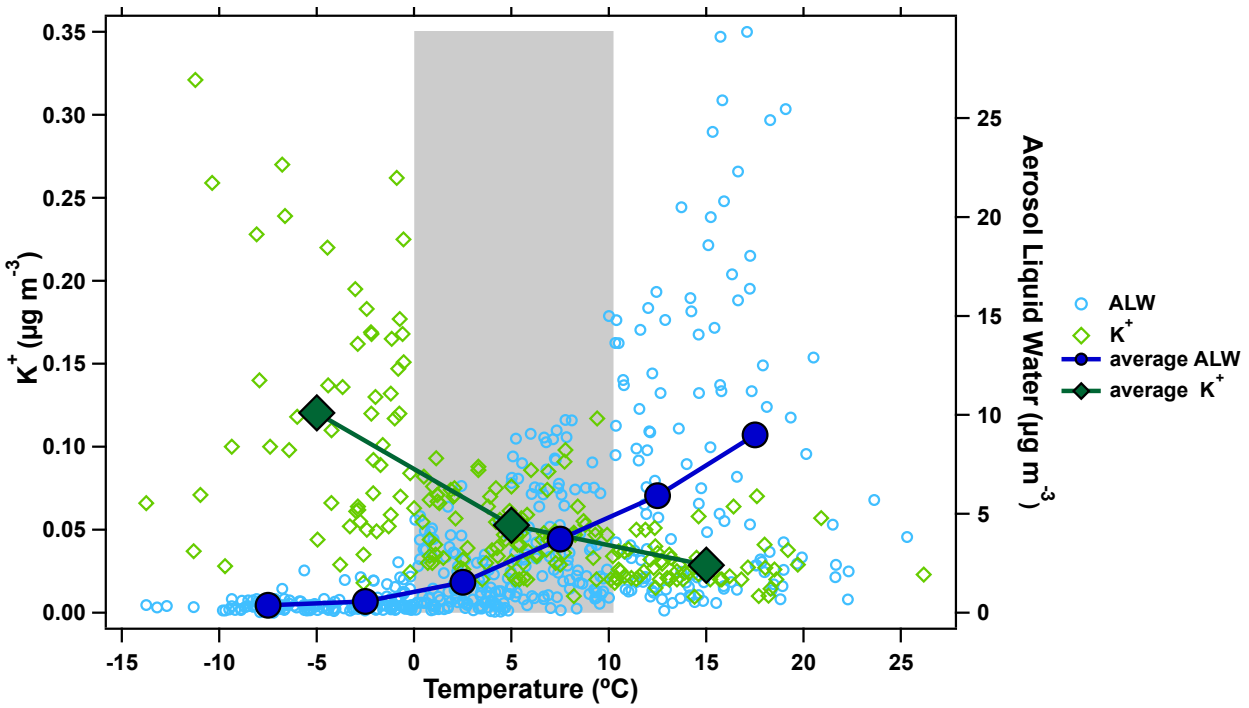

Figure 2. Scatterplot of aerosol potassium concentrations (K^+, green diamonds) and ALW (blue circles) as a function of temperature during the months of November through March in Baltimore over 2011 – 2015. The gray shaded area is representative of the temperature range where aqueous processing of $WSOC_p$ was observed.

The impact of aqueous processes on secondary OA formation has previously been inferred based on an enhancement in F_p with increasing RH[17-18,51,55]; and is due to the uptake of $WSOC_g$ to ALW[17,82]. When the wintertime data were segregated into daytime and nighttime periods, the formation of $WSOC_p$ through aqueous processes was initially not observed since there was no enhancement in F_p as a function of RH in either period (Fig. S11). However, because the wintertime ALW content showed a strong relationship with temperature (Fig. 2), the nighttime $WSOC_p$ data were further segregated based on temperature (< 0 °C, 0 – 10 °C and > 10 °C) as shown in Fig. 3. At night, an enhancement in F_p was observed with increasing RH for temperatures between 0 and 10 °C (Fig. 3b), suggesting the formation of $WSOC_p$ in the aqueous phase in this temperature range. For temperatures < 0 °C and > 10 °C, there was no relationship between F_p and the RH (Figs. 3a and 3c, respectively), suggesting that aqueous $WSOC_p$ was not substantially formed under such conditions. Approximately 60% of our nighttime observations were within the 0 – 10 °C temperature range: thus, the enhancement in F_p shows an important role of multi-phase chemistry in the formation of $WSOC_p$ during winter. Note that such dependance on temperature was not observed for the daytime data (Fig. S12).

Aqueous processing likely contributed to secondary $WSOC_p$ during the night rather than the daytime due to higher nighttime RH (median daytime and nighttime RH were 45% and 60%, respectively, Table S1) and hence, higher ALW at night. Average nighttime ALW concentrations across the entire study were more than three times higher (2.0 µg m^{-3}) than during the day (0.6 µg m^{-3}), consistent with ALW patterns in summer and with those determined in prior studies[83]. Figure S13 shows two case studies demonstrating the increase in F_p as a function of RH only at temperatures between 0 – 10 °C. The nighttime relationship between F_p and RH

observed was previously observed in the summer[18,20] and fall[55] in Baltimore~~, as well~~. These results show that aqueous processes can affect aerosol concentrations in the eastern U.S. throughout all seasons.

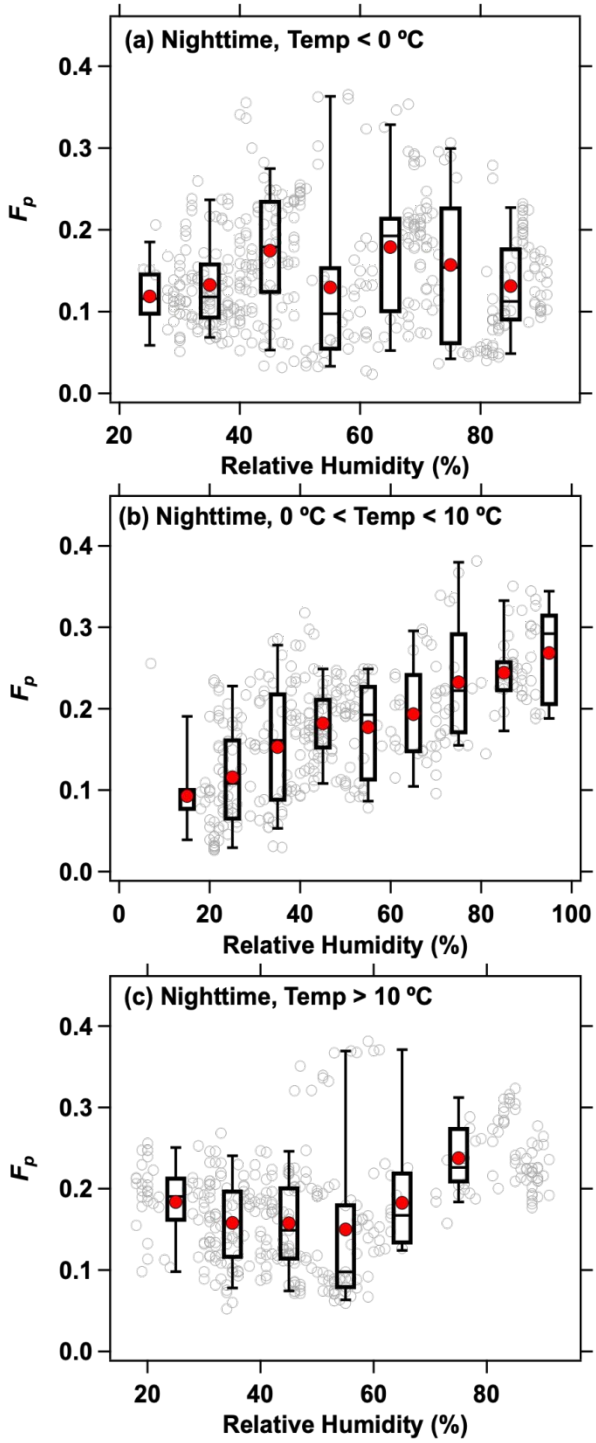

Figure 3. Scatter and box plots of the particulate WSOC fraction, F_p, as a function of RH at night (20:00 to 07:00, local time) for different temperature ranges: (a) < 0 °C (b) 0 – 10 °C, and (c) >10 °C. For each bin, mean (red circles, median (horizontal line), quartiles (lower and upper box values), as well as 5th and 95th percentiles (vertical lines) are shown.

The apparent conditional formation of aqueous $WSOC_p$ in the 0 – 10 °C temperature interval is further analyzed through the $\Delta WSOC_p/\Delta CO$ ratio (Fig. 4). This ratio was used to quantify the production of $WSOC_p$ mass against the conservative atmospheric compound, CO with background levels of 0.05 μg m^{-3} and 0.15 ppm, respectively. The $\Delta WSOC_p/\Delta CO$ analysis shows a strong $WSOC_p$ enhancement when temperatures were between 0 – 10 °C compared to conditions when temperatures were < 0 °C or > 10 °C. Together, the results shown in Figs. 3 and 4 suggest that aqueous processes made a major contribution to the enhanced $\Delta WSOC_p/\Delta CO$ in the 0 – 10 °C temperature interval. This is also evident by the lack of a consistent pattern in the diurnal profiles of $\Delta WSOC_p/\Delta CO$ at temperatures < 0 °C and > 10 °C (Fig. S14). In the 0 – 10 °C temperature interval, a pronounced $\Delta WSOC_p/\Delta CO$ enhancement was observed in the middle of the day (between 11:00 AM and 3:00 PM, local time) and at night (between 8:00 PM and 1:00 am, local time). The $\Delta WSOC_p/\Delta CO$ enhancement during the day, when no relationship was observed between F_p and RH, suggests influence of photochemical processes and absorptive partitioning to OA, as shown in Fig. 1. On the other hand, the enhancement of $\Delta WSOC_p/\Delta CO$ at night suggests the uptake of $WSOC_g$ to ALW, supported by Fig. 3b.

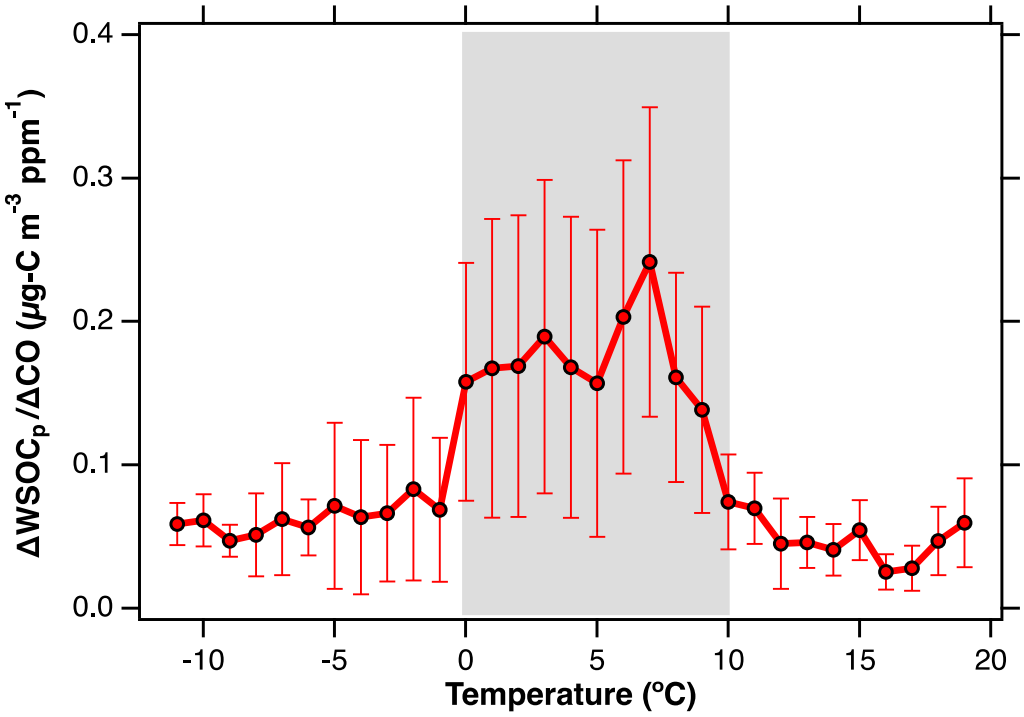

Figure 4. Mean$\Delta WSOC_p/\Delta CO$ as a function of temperature. Error bars represent +/– one standard deviation. The gray shaded area shows the temperature range where aqueous processing of $WSOC_p$ was observed.

Collectively, our results suggest that secondary $WSOC_p$ formation from gas-phase oxidation and absorptive partitioning occurred consistently throughout the winter, but that aqueous $WSOC_p$ formation took place only during the night.

3.5 Effect of drying on $WSOC_p$

We have previously shown that there was no statistically-significant difference in the concentrations of $WSOC_p$ and $WSOC_{p,dry}$ for the entire wintertime data set (see Figs. 1 and S1 in El-Sayed et al.[20]). A detailed comparison of the $WSOC_p$ and $WSOC_{p,dry}$ concentrations for daytime and nighttime periods throughout the winter is shown in Fig. S15, ~~as well~~. A $WSOC_{p,dry}$ /$WSOC_p$ ratio of unity implies that the $WSOC_p$ did not evaporate with drying, including any $WSOC_p$ that formed through partitioning to the OA ~~as well~~[20]. These results indicate that ALW evaporation did not impart any effect on $WSOC_p$ throughout the winter. This is supported by Fig. S16, which shows no change in the $WSOC_{p,dry}$ /$WSOC_p$ ratio as a function of RH.

However, due to the above temperature analysis that shows aqueous $WSOC_p$ formation in the 0 – 10 °C temperature range (at night), we also applied the $WSOC_{p,dry}$/$WSOC_p$ ratio analysis to the same temperature and temporal conditions. Figure 5 shows a comparison of the $WSOC_p$ and $WSOC_{p,dry}$ concentrations for nighttime periods in the winter for the three defined temperature intervals. Under all three conditions, the slopes were close to unity and the intercepts were close to zero, indicating the strong similarity in the $WSOC_p$ and $WSOC_{p,dry}$ concentrations at all temperatures. This indicates that the $WSOC_g$ compounds that were taken up in aerosol water, causing the enhancement in F_p (Fig. 3), remained in the condensed phase upon drying. It should also be noted that our measurements indicate no effect of drying on any of the OA components we measured during the winter season. This includes no effects of particle drying on the primary component of $WSOC_p$ that is emitted directly into the atmosphere, or the secondary portion formed through absorptive and/or aqueous partitioning in the atmosphere.

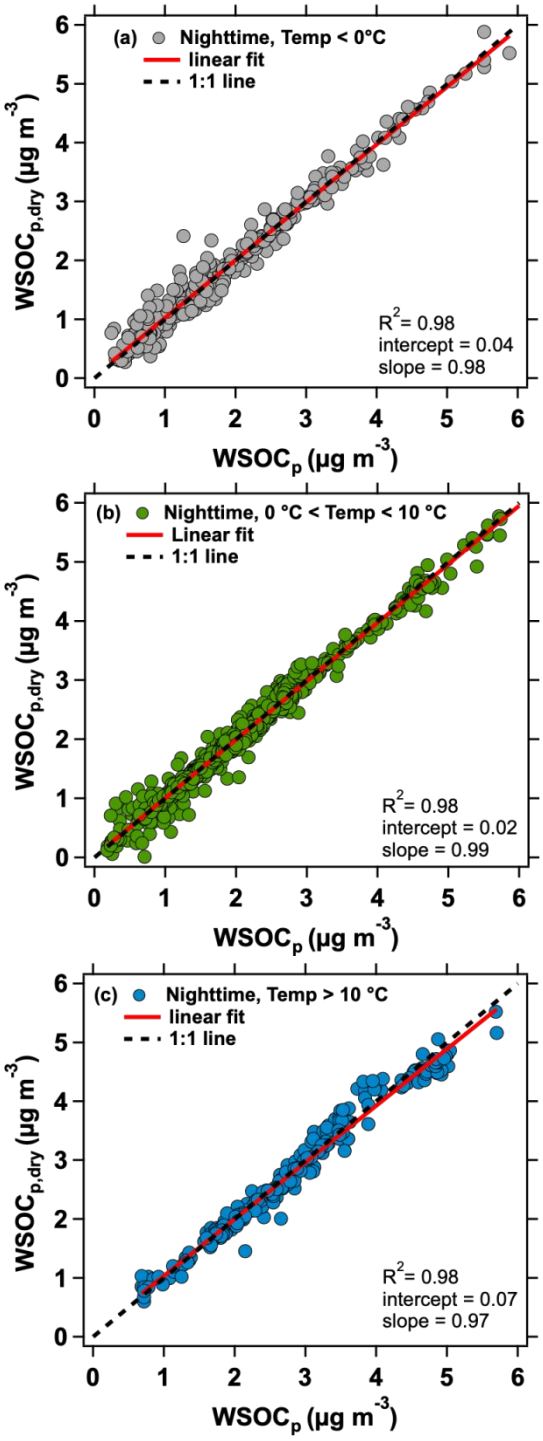

Figure 5. Scatter plots of $WSOC_{p,dry}$ versus $WSOC_p$ for nighttime periods under different temperature conditions: (a) < 0 °C (b) 0 – 10 °C, and (c) >10 °C. The solid red lines represent the linear fits to the data using least squares regression analysis; the fit parameters are given in each panel. The 1:1 line (black dashed line) is given for visual reference.

3.6 $WSOC_g$ and anthropogenic emissions

Biomass burning is a significant contributor to primary and secondary $WSOC_p$ concentrations in the winter in the eastern U.S.[25]. Aerosol potassium (K^+) is frequently used as an indicator of biomass burning[84-87]. However, several studies have reported that residential biomass burning from a fireplace produces much higher potassium emissions during flaming combustion compared to emissions from wildfires or prescribed burning in which smoldering processes are more dominant[88-91]. Potassium emission factors are also variable depending on the fuel type[92]. Therefore, using potassium as a biomass burning marker may underestimate smoldering combustion emissions and emissions from certain biomass fuels. The background concentration of K^+ (0.015 μg m^{-3}) in Baltimore was defined as the 10th percentile K^+ concentration during winter for 2011 – 2015. Average daily concentrations of $WSOC_g$ and K^+ were correlated (R^2 = 0.61, Fig. S17b) during our study, suggesting that local emissions from residential wood combustion contributed to $WSOC_g$ levels. On the other hand, daily $WSOC_p$ and K^+ concentrations showed no correlation (R^2 = 0.007, Fig. S17a). For the 0 – 10 °C temperature range, the average K^+ concentration (~0.06 μg m^{-3}) was a factor of four higher than the background wintertime concentration (Fig. 3), suggesting that biomass burning was still occurring in the same temperature range where aqueous secondary aerosol formation was identified. This is emphasized since no correlations were observed between $WSOC_g$ and the vehicular tracers CO (R^2 = 0.06) and EC (R^2 = 0.10) (Figs. S18b and S19b, respectively) in this temperature range.

Scatter and boxplots of $WSOC_g$ and $WSOC_p$ concentrations as a function of wind speed (Figs. S20a and S20b, respectively) support local formation and/or direct emissions of these compounds during the winter. $WSOC_g$ and $WSOC_p$ concentrations decrease dramatically at higher wind speeds. The highest concentrations of $WSOC_g$ and $WSOC_p$ were associated with wind speeds below 2 m s^{-1}, suggesting that the direct emission and formation of these water-soluble organic compounds were primarily taking place locally rather than being transported from elsewhere. This result is consistent with recent work conducted in the northeastern U.S. – including Maryland – suggesting a significant contribution of biomass burning emissions from residential heating towards secondary OA levels in the winter[25]. These observations suggest that biomass burning emissions associated with residential heating contributed significantly to the gaseous precursors which were subsequently taken up into either OA or ALW to form secondary $WSOC_p$.

3.7 Factors affecting aqueous $WSOC_p$

Enhancements in F_p with increasing RH were observed in the 0 – 10 °C temperature range (Fig. 3b), the same temperature range where both ALW concentrations (~5.0 μg m^{-3}) and the biomass burning marker K^+ were also elevated (Fig. 2). At temperatures less than 0 °C, despite the abundance in biomass burning emissions, there was insufficient ALW (< 1 μg m^{-3}) to facilitate aqueous $WSOC_p$ formation. On the other hand, at temperatures greater than 10 °C, there was an abundance of ALW (~12.0 μg m^{-3}), but the low K^+ concentrations (~0.02 μg m^{-3}) indicate minor contributions from residential biomass burning. Conditions for aqueous $WSOC_p$ formation occurred when ALW and sufficient biomass burning emissions were both present. In Baltimore, such conditions occur at night when the temperature is ~0 – 10 °C. Figures 6a and 6b depict the

24-hr averages of F_p as a function of K^+ colored by ALW and temperature, respectively. Figure 6 shows that the 24-hr averages of F_p and K^+ are correlated ($R^2 = 0.77$), suggesting a strong relationship between the partitioning of gases into the particle phase and biomass burning emissions. This includes both gas- and aqueous-phase partitioning. The dependence of this relationship on ALW content and temperature is evident and shows that WSOC partitioning towards the particle phase enhances with K^+ concentrations as ALW concentrations and temperatures decrease.

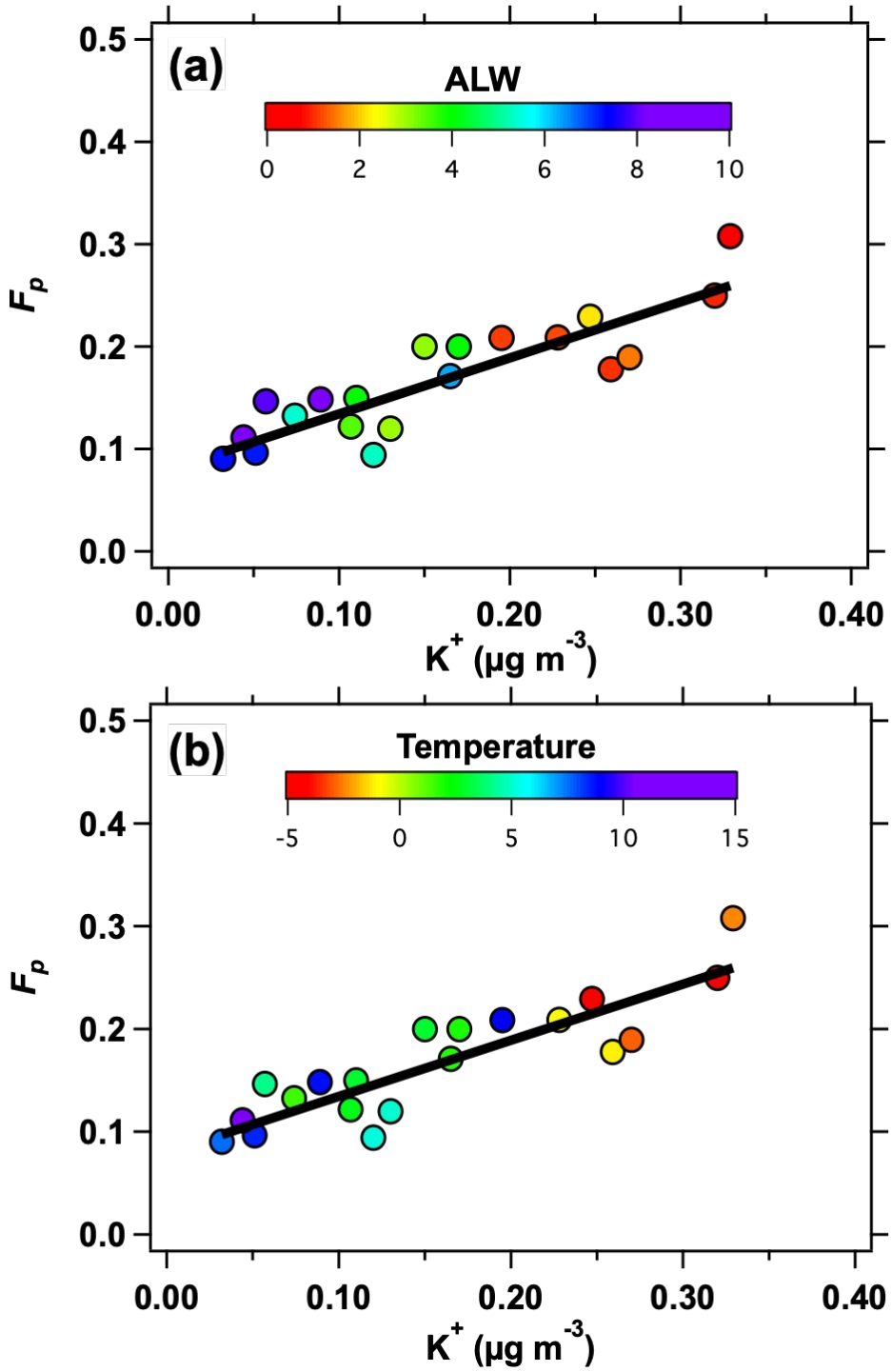

Figure 6. Daily averages of the partitioning coefficient F_p as a function of potassium concentrations color-coded based on (a) ALW concentrations and (b) temperature. Gray area represents the range of K^+ concentrations between 0 – 10 °C where aqueous $WSOC_p$ formation is observed.

The winter results underscore the combined importance of water-soluble precursors as well as ALW for the formation of aqueous $WSOC_p$ during cold seasons. Our results highlight the importance of biomass burning emissions as precursors for aqueous $WSOC_p$ mass. In the winter and in the temperature range ($0 < T < 10$ °C), aqueous $WSOC_p$ formation in the Mid-Atlantic U.S. is associated with biomass burning precursors as well as ALW.

Numerous studies carried out in other locations support our current findings, as well. Evidence of aqueous secondary OA formation from wood burning was reported in Italy in both rural and urban areas[41]. In Fresno, CA, evidence for aqueous secondary OA formation during the winter has previously been observed[93]. In Los Angeles, CA, nighttime aqueous secondary OA formation was suggested based on an increase in secondary OA at higher RH levels, possibly due to the dissolution of water-soluble primary emissions from biomass burning[39]. In Beijing, aqueous secondary OA formation from primary emissions – including biomass burning – contributes to episodes of high aerosol concentrations during winter[41]. In Paris, a modeling study showed that there was an underestimation of oxygenated organic aerosol (OOA) in winter, likely due to secondary OA formation through aqueous processing of biomass burning emissions[37]. In northern France, higher concentrations of the biomass burning mass spectrometry factor were associated with low wind speeds and were correlated with RH, which was attributed to aqueous processing of primary emissions to form secondary OA[38]. In India, aqueous processing of secondary OA was interpreted in fogs due to correlations between particulate mass and aerosol water and was suggested to be from biomass burning based on relationships between the biomass burning mass spectrometry factor and OOA[94].

The ambient observations at diverse locations are supported by laboratory studies that show biomass burning is a likely source of aqueous secondary OA, as well. Phenolic compounds are emitted in high abundances from biomass burning[95]. Laboratory studies suggest that phenols represent a key class of aqueous secondary OA precursors, as they are highly soluble and can form lower-volatility products through an array of aqueous reactions[31,35]. Laboratory experiments sampling "whole" biomass burning emissions also report significant potential for aqueous secondary OA formation in cloud conditions[24].

4 Conclusions

In the eastern U.S., aqueous $WSOC_p$ was observed during the winter under conditions when biomass burning emissions and sufficient ALW were both present. Our results underscore the important role of aerosol water in the formation of OA, even in the winter. These results suggest that the emissions from residential wood combustion contribute to aqueous $WSOC_p$ formation. Our results in the eastern U.S. add to the growing body of work indicating the importance of aqueous processing in the formation of organic mass from biomass burning emissions. This process is expected to contribute to OA levels in areas with high biomass burning and relatively high ALW concentrations, regardless of season. Although wood combustion for residential heating was the major form of biomass burning during this study, the results presented herein likely have implications beyond residential wood burning. Most other types of biomass burning,

such prescribed burns, burning agricultural crop residue and wildfires, emit $WSOC_g$ that can form secondary species in the aqueous phase[24,96-97]. Therefore, aqueous-phase processing of biomass burning emissions in clouds and deliquescent particles is likely a widespread phenomenon that has importance for local and regional air quality as well as global climate. However, the magnitude of OA formed from this process remains highly uncertain given that unspeciated compounds represent such a high fraction of gaseous emissions from biomass burning[98-99]. Future studies are warranted to characterize the gaseous compounds emitted from different types of biomass burning in order to evaluate their impact on OA formation.

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