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Effects of the VACES particle concentrator on secondary organic aerosol and ambient particle composition

L. M. Wingen^a , D. A. Herman^b, A. Keebaugh^b, G. Montoya^a, S. R. Renusch^b, B. J. Finlayson-Pitts^a , and M. T. Kleinman^b

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ABSTRACT

The effects of concentrating particles using the Versatile Aerosol Concentration Enrichment System (VACES) were investigated with a focus on the organic particle composition. The VACES uses water condensation to grow particles and allow enrichment in particle concentrations by virtual impaction, followed by diffusion drying to remove excess liquid water. Aerosol mass spectrometry was used to compare the submicron organic composition before and after the VACES for laboratory-generated secondary organic aerosol (SOA) from ozonolysis of α -pinene as well as ambient particles. Size distributions were retained after the VACES for both types of samples. SOA particles showed evidence of high molecular weight compounds forming after enrichment, suggesting that some oligomerization occurs during the water condensation and/or evaporation stages, but with only slight changes in the elemental composition. Oligomerization was also observed for ambient particles, especially those with higher O/C in the accumulation mode. Ambient ultrafine particles with low O/C were not as efficiently enriched. Such composition changes in the organic fraction may be relevant to other methodologies where particles are grown through water uptake and then dried, as well as to atmospheric processes involving water uptake and evaporation. In the context of particle mass, the extent of oligomerization is small. However, given the widespread use of particle concentrators in health effects and particle composition studies, whether this impacts interpretation of health effects and particle composition data when using particle concentrators needs further exploration.

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Introduction

Atmospheric particles have well documented negative effects on health (Dockery et al. 1993; Villeneuve et al. 2002; Pope et al. 2004, 2019; Nel 2005; Laden et al. 2006; Pope and Dockery 2006; Miller et al. 2007; Apte et al. 2018). Particles with diameters $\leq 2.5 \mu\text{m}$ ($\text{PM}_{2.5}$) are inhaled into the deep lung and the smaller diameters reach the alveoli (Hinds 1999; Nemmar et al. 2002; Oberdörster and Utell 2002; Oberdörster et al. 2004; Oberdörster, Oberdörster, and Oberdörster 2005; Simkhovich, Kleinman, and Kloner 2008; Lepistö et al. 2020). Exposure to $\text{PM}_{2.5}$ is associated with harmful effects on the respiratory, cardiovascular, and neurological systems as well as with total mortality (Bourdel et al. 2017; Apte et al. 2018; Kilian and Kitazawa 2018; U.S. EPA 2019). There are fewer health effects studies focusing on the subset of $\text{PM}_{2.5}$,

ultrafine particles (UFP), which are defined as those with diameters $\leq 0.1 \mu\text{m}$ ($\text{PM}_{0.1}$) or quasi-ultrafines with diameters $\leq 0.18 \mu\text{m}$ ($\text{PM}_{0.18}$). UFP are believed to contribute to higher toxicity because of their larger surface areas for a given mass, increased lung deposition efficiency, and predominantly organic composition, although the mechanism(s) remain unclear (Brown et al. 2001; Oberdörster 2001; Oberdörster and Utell 2002; Li et al. 2003; Oberdörster et al. 2004; Delfino, Sioutas, and Malik 2005; Oberdörster, Oberdörster, and Oberdörster 2005; Araujo et al. 2008; Stone et al. 2017; Thompson 2018). The mass concentration of $\text{PM}_{2.5}$ is dominated by larger particles, while UFP commonly dominate in number concentration.

Sources of $\text{PM}_{2.5}$ include both primary and secondary particles. Primary emissions in urban regions are

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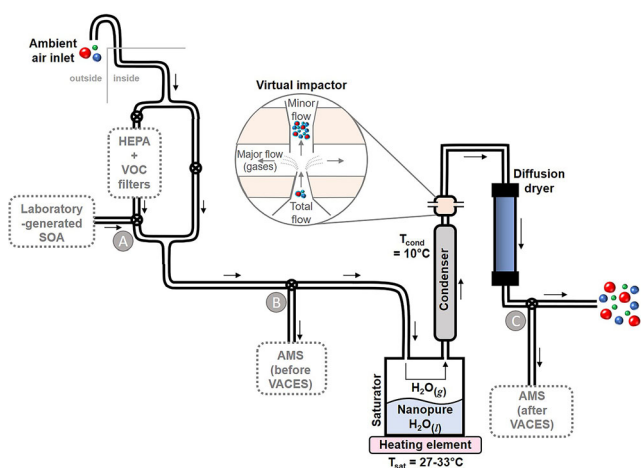


Figure 1. Schematic of the Versatile Aerosol Concentration Enrichment System (VACES).

typically dominated by automobile fuel combustion emissions and are a major contributor to UFP (Alfarra et al. 2004; Allan et al. 2004; Drewnick et al. 2004; Zhang et al. 2004, 2005a, 2005b, 2007; McFiggans et al. 2005; Docherty et al. 2008). Secondary particle sources include oxidation of volatile organic compounds (VOC) to produce secondary organic aerosol (SOA) particles as well as oxidation of gaseous SO_2 and NO_x to form particulate sulfate and nitrate (Finlayson-Pitts and Pitts 2000). SOA and secondary inorganics make up a large fraction of $\text{PM}_{2.5}$ mass, most often in the accumulation mode, which represents particles with diameters of approximately 0.2–2.5 μm (Zhang et al. 2007; Docherty et al. 2008; Jimenez et al. 2009; Shilling et al. 2013; Zhao et al. 2014).

Studies on the health effects of atmospheric particles often use particle concentrators to increase concentrations to levels typical of polluted conditions (Lippmann and Chen 2009). Many particle concentrators utilize a virtual impactor (Sioutas et al. 1997; Lawrence et al. 2004; Moffet et al. 2004; McWhinney et al. 2012; Gute et al. 2019), which divides the flow into major and minor portions, and allows particles with enough inertia to flow through a nozzle and into a second orifice at a lower flow rate, the “minor flow,” while the remaining “major flow” containing gases is removed. The adjustment of the ratio of total inlet flow to minor flow determines the theoretical enrichment factor of the initial particle concentration, assuming no particle losses. The addition of a particle growth stage upstream of the virtual impactor that uses water vapor condensation to increase the diameter and inertia of the incoming particles, extends enrichment down into the ultrafine particle diameter range (Sioutas, Kim, and Chang 1999; Kim et al. 2001b; Demokritou, Gupta, and Koutrakis

2002; Gupta, Demokritou, and Koutrakis 2004; Khlystov et al. 2005; Zhao et al. 2005; Su et al. 2006). Following virtual impactation, the minor flow passes through diffusion dryers to remove excess aerosol water, as in the case of the Versatile Aerosol Concentration Enrichment System (VACES) used here. Other concentrators, such as the Harvard Ultrafine Concentrated Ambient Particle System (HUCAPS), use mild thermal treatment and dilution to remove excess water (Demokritou, Gupta, and Koutrakis 2002; Gupta, Demokritou, and Koutrakis 2004; Su et al. 2006; McWhinney et al. 2012; Rastogi et al. 2012).

Particle concentrators with water condensation stages are used for in vivo animal and human studies (Li et al. 2003; Verma et al. 2011; Keebaugh et al. 2015; Kleinman et al. 2018; Taghvaei et al. 2019; Herman et al. 2020) and for in vitro health-related studies (Kim et al. 2001b; Cho et al. 2005; Ntziachristos et al. 2007; Steenhof et al. 2011; Krapf et al. 2017; Taghvaei et al. 2019), as well as to increase mass concentrations for analytical aerosol measurements (Geller et al. 2002; Sun et al. 2009; Salcedo et al. 2010; Saarikoski et al. 2014; Soleimani, Taghvaei, and Sioutas 2020; Shang et al. 2021a, 2021b). While many studies have been carried out on the effects of concentrators on particle size distributions and inorganic composition of ambient particles, less is known about the details of the organic fraction, which is under increasing scrutiny as a source of toxicity of inhaled particles (Baltensperger et al. 2008; Lippmann and Chen 2009; Gaschen et al. 2010; Keebaugh et al. 2015; Rohr and McDonald 2016; Mesquita et al. 2017; Ridley et al. 2018; Hwang et al. 2021). The presence of liquid water in and/or on organic particles and the rapid drying stage that follows can allow chemical reactions such as hydrolysis and oligomerization to be accelerated at the surface or throughout the particles, depending on their solubility in water, thus changing their original composition. In this study, the effects of particle concentration enrichment using the VACES on organic composition and size distributions were investigated for laboratory-generated α -pinene ozonolysis SOA particles and compared to the results from enrichment of ambient particles.

Experimental methods

Operation of VACES

A schematic of the VACES is provided in Figure 1, based on the design of Kim et al. (2001a, 2001b). Ambient outdoor air was drawn in from above the

roofline of a single-floor laboratory at a flow rate of 100 L min^{-1} . Air flow containing ambient particles was used or, alternatively, this air was filtered through a bypass line with HEPA and VOC filters to add laboratory-generated particles to the VACES. For either case, particle-laden air flow passed through the headspace of a saturator one-third filled with doubly deionized water and temperature-controlled to $T_{\text{sat}} = 27\text{--}33^\circ\text{C}$. The water-saturated particle flow then passed through a condenser maintained at $T_{\text{cond}} = 10^\circ\text{C}$ so that the particles grew from water uptake under the super-saturated conditions. The saturation ratio, calculated from the ratio of the water vapor pressure at T_{sat} to that at T_{cond} , is 2.9–4.1 (see Figure S1, online supplemental information). The higher mass droplets subsequently flowed through an inertial virtual impactor (expanded view in Figure 1) as the minor flow, while the remaining flow of gases was pumped away as the major flow. After the virtual impactor, the minor flow passed through a diffusion dryer filled with silica gel desiccant to remove excess water.

The ratio of the total flow (typically 100 L min^{-1}) to the minor flow (typically 5 L min^{-1}) defines the theoretical concentration enrichment factor (typically $\text{EF}_{\text{theor}} = 20$), assuming no particle losses. Between the two different ambient particle sampling periods in this study, the VACES was reconfigured, with an adjusted inlet flow into the saturator of 300 L min^{-1} ; this was then split into three identical legs each at 100 L min^{-1} total flow through three condensers, and 10 L min^{-1} minor flow through three virtual impactors, $\text{EF}_{\text{theor}} = 10$. There was no significant difference in the results using the two EF_{theor} configurations. Total particle number concentrations were measured every 15 min with a condensation particle counter (CPC, TSI model 3025A) upstream (ambient) and downstream of the VACES and minor adjustments made to the flows ($< \pm 10\%$) every 15 min to maintain EF_{theor} .

Secondary organic aerosol particle measurements

SOA particles were generated by ozonolysis of α -pinene to form a polydisperse particle distribution in a Teflon chamber run in batch mode. The chamber was filled with 400 L of clean air (Scott-Marrin, $\text{NO}_x < 0.001 \text{ ppm}$, $\text{SO}_2 < 0.001 \text{ ppm}$). Ozone was generated (Polymetrics, Model T-816) at a concentration of 2% in O_2 (Oxygen Services, Ultra High Purity, 99.993%) in a 30 mL glass cell and was flushed into the chamber with additional clean air to a total

volume of 450 L and a concentration of 1.2 ppm O_3 before reaction. Liquid α -pinene ((1R)-(+)- α -pinene; Sigma Aldrich, >99%) was injected to give a final gas phase concentration after evaporation of 0.7 ppm. After reacting for ~ 20 min, particle size distributions were measured by SMPS to confirm that particle growth had stabilized.

With the VACES operating under the same conditions as above, SOA particles were introduced at point A with a mild venturi effect drawing $\sim 100 \text{ mL/min}$ of the chamber sample into the total flow. During addition of SOA, the inlet ambient flow was filtered with a HEPA filter and a Purafil®/charcoal filter to remove particles and VOCs, respectively. High particle concentrations were generated in the Teflon chamber to ensure their detection after dilution into the total flow.

Measurements before and after the VACES were taken at points B and C, respectively (Figure 1). AMS mass concentration detection limits using the VACES were defined as three standard deviations of average 10-min sampling times for sampling of filtered air. These filtered VACES mass concentrations were $\leq 0.05 \mu\text{g m}^{-3}$ for all AMS species ($\leq 0.03 \mu\text{g m}^{-3}$ for organics) within 10-min sampling times.

Ambient particle measurements

The VACES was operated at the Air Pollution Health Effects Laboratory (APHEL) at the University of California, Irvine, located approximately 5 miles inland from the Pacific Ocean, <1 mile from a wetland nature reserve, and is surrounded by several heavily trafficked roads and freeways.

Ambient particles were concentrated with the VACES over two time periods: Period 1, spring/summer (April 27–August 23, 2012) and Period 2, summer/fall (August 20–October 21, 2016). Measurements of ambient particles, typically between 8 am and noon PST, were taken before and after the VACES at points B and C, respectively. Sampling times were in the range of 10–45 min. For one to four time periods each day, size distributions, fragment intensities, and elemental composition were averaged for upstream periods and compared to the corresponding downstream periods (collected immediately afterward).

Aerosol mass spectrometry

Submicron particle measurements were made with a high-resolution time-of-flight aerosol mass spectrometer (AMS, Aerodyne, Inc.) (DeCarlo et al. 2006).

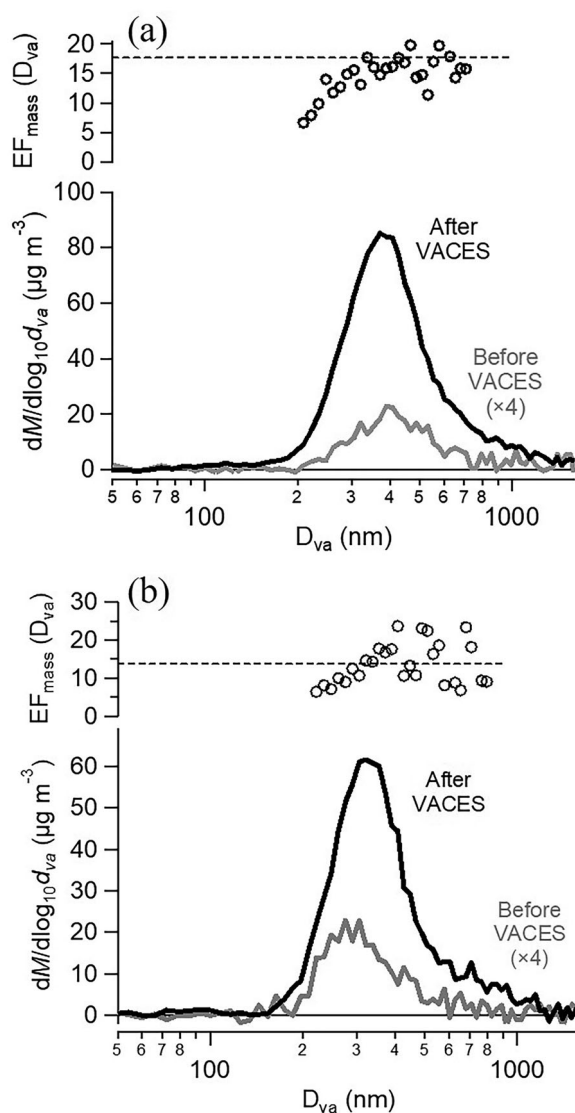


Figure 2. AMS size distributions of SOA particles generated from α -pinene ozonolysis introduced before (grey lines) and measured after the VACES (black lines) and size-dependent EF_{mass} (circles). The dashed line shows the average EF_{mass} for (a) Expt. 1, 17.7 ($EF_{theor} = 20$) and (b) Expt. 2, 13.8 ($EF_{theor} = 15$).

Briefly, aerosol particles are sampled at $\sim 0.08 \text{ L min}^{-1}$ through a $100 \mu\text{m}$ orifice into an aerodynamic lens, which focuses particles in the range of 50–1000 nm vacuum aerodynamic diameter. Particles travel through a time-of-flight vacuum chamber for particle size distribution measurement, are flash vaporized at 600°C , and ionized by electron impact ionization (70 eV). All results are from V-mode mass spectra.

The AMS was calibrated using a scanning mobility particle sizer (SMPS; TSI Inc., model 3080 classifier with long DMA, model 3776 CPC). The SMPS was used to calibrate the AMS with respect to mass concentrations and vacuum aerodynamic diameters, D_{va} . AMS calibration of D_{va} was carried out with

carboxylate modified polystyrene latex spheres (CMLs, Life Technologies, Grand Island, NY) (Kidd, Perraud, and Finlayson-Pitts 2014) and size-selected NH_4NO_3 (Fisher, $\geq 98\%$) particles atomized from aqueous ($18.2 \text{ M}\Omega \text{ cm}$) solutions. Calibrations from 50 nm to 800 nm electrical mobility diameter were in good agreement for the two particle types. The AMS standard vaporizer temperature was increased to 850°C for CML calibrations. Ionization efficiency and mass concentration calibrations were carried out using size-selected 250, 300, and 350 nm NH_4NO_3 particles. Note that changes in size and composition of particle diameters below $\sim 50 \text{ nm}$ and $> 1 \mu\text{m}$ are not measurable with AMS.

Analysis was performed using software packages SQUIRREL v1.62F and PIKA v1.22F with Igor Pro (WaveMetrics, v. 6.37) with default values for relative ionization efficiencies. AMS collection efficiency (CE) has been shown to be ~ 0.5 for most ambient particles as well as for laboratory-generated SOA primarily due to bounce of particles at the vaporizer (Matthew, Middlebrook, and Onasch 2008; Sun et al. 2010; Middlebrook et al. 2012; Docherty et al. 2013) and was taken to be the same before and after the VACES. Any increases in CE, for example for liquid particles, would lead to consistent increases in enrichment efficiency after VACES, which were not observed.

Results and discussion

SOA particles

Mass-weighted size distributions collected before and after the VACES for two different experiments show that the mode diameters did not shift consistently in one direction or the other, as shown in Figure 2 and summarized in Table 1. The average mode diameters shifted by less than $\pm 5\%$ and the width, indicated by the geometric standard deviation, changed by less than 3%. Thus, particle size distributions are well preserved, suggesting that all particles grew to sufficient sizes to be transferred efficiently through the virtual impactor, and that the particles dried back to their original sizes, in agreement with both organic and inorganic particles in previous studies (Sioutas, Kim, and Chang 1999; Kim et al. 2001b; Geller et al. 2002; Freney et al. 2006; Saarikoski et al. 2014). Table 1 also summarizes the enrichment factors, size distributions and elemental composition of SOA. The mass enrichment factors are within experimental error of the theoretical values. Size-dependent EF_{mass} values, calculated using the mass concentrations in each diameter bin (Figure 2), show a slight trend toward

Table 1. Size distribution, enrichment, and elemental composition data for SOA particles from AMS.

SOA	Mass concentration ($\mu\text{g m}^{-3}$)		Enrichment factor (EF)		D_{va} (nm) mode diameter and GSD ^a		Elemental composition O:C, H:C		
	Before VACES	After VACES	Measured EF_{mass} (2 s) ^b	EF_{theor}	Before VACES (GSD)	After VACES (GSD)	Before VACES (± 2 s)	After VACES (± 2 s)	Change in O:C, H:C (%)
Initial concentrations (ppm)									
Expt. 1 [α -Pinene] ₀ = 0.7 [O ₃] ₀ = 1.2	2.83	50.0	17.7 \pm 7.7	20	390 (1.48)	372 (1.44)	0.39 (\pm 0.01), 1.60 (\pm 0.01)	0.35 (\pm 0.01), 1.63 (\pm 0.01)	-10%, +1.7%
Expt. 2 [α -Pinene] ₀ = 0.7 [O ₃] ₀ = 1.2	2.45	33.7	13.8 \pm 3.4	15	306 (1.42)	321 (1.41)	0.39 (\pm 0.02), 1.60 (\pm 0.02)	0.36 (\pm 0.01), 1.63 (\pm 0.01)	-7.7%, +1.9%

^aGeometric Standard Deviation (GSD) is obtained from lognormal fits to each size distribution.

^b2 s represents two standard deviations.

lower enrichments at smaller diameters. Similar trends have been reported in previous studies (Hering and Stolzenburg 2005; Maciejczyk et al. 2005; Su et al. 2006; McWhinney et al. 2012; Rastogi et al. 2012; Gute et al. 2019).

While the mass spectrum does not change dramatically (Figures S2a and b), there are small shifts in relative contributions of three dominant fragment families ($C_xH_y^+$, $C_xH_yO_1^+$, and $C_xH_yO_{>1}^+$) after enrichment. Oxidized fragments, particularly those with more than one oxygen, decrease (Figures S2c and d) and the overall O/C ratio decreases by 8–10% (Table 1). A similar loss of the oxygenated fragment, CO_2^+ , was observed in a previous study for ambient particles (Saarikoski et al. 2014). The changes are also seen in the Van Krevelen diagram (Figure S3), where the slope lends insight into the possible reactions taking place (Canagaratna et al. 2015; Chen et al. 2015). A slope of -1 indicates a change in both carbonyl and alcohol groups or a change in carboxylic acid groups. A slope of -0.5 can indicate either a change in both carboxylic acid and alcohol groups without molecular fragmentation or a change in carboxylic acid groups with fragmentation. For SOA samples, the average slope is -0.66 and the direction of the samples is toward lower O/C and higher H/C. This indicates a small loss of oxygenated functional groups and points to a net loss of carboxylic acids and alcohols when SOA passes through the VACES.

There are a number of possible oligomerization reactions that can occur in an aqueous environment or upon subsequent drying of SOA. For example, glyoxal and methylglyoxal, produced from ozonolysis of α -pinene and other monoterpenes (Yu, Flagan, and Seinfeld 1998; Fick et al. 2003; Fick, Nilsson, and Andersson 2004; Nunes et al. 2005), are highly water soluble and have been shown to oligomerize with enhanced rates during drying (Loeffler et al. 2006; De Haan et al. 2009; Yasmeen et al. 2010; Petters et al.

2020) and in the presence of carboxylic acids (Corrigan, Hanley, and De Haan 2008; Qin et al. 2020). Organic hydroperoxides in terpene SOA can decompose in water to generate free radicals such as RO and OH (Tong et al. 2016, 2018; Wei et al. 2020a) which may then initiate further chemistry and contribute to oligomerization through radical-radical combination or radical-neutral chain reactions. Such reactions would lead to decreases in O/C and increases in H/C (Barsanti and Pankow 2004, 2005, 2006; Kroll and Seinfeld 2008; De Haan et al. 2009; Yasmeen et al. 2010; Petters et al. 2020). Acceleration of aqueous phase reactions in microdroplets has also been reported due to increased concentrations and acidity during drying (Yan, Bain, and Cooks 2016; Banerjee et al. 2017; Petters et al. 2020; Wei et al. 2020b). In short, some oligomerization in the VACES is perhaps not surprising.

The lifetime of oligomer formation was estimated using an aldol condensation rate constant of $\sim 10^4 \text{ M}^{-1} \text{ s}^{-1}$ (Krizner et al. 2009). When a 3–5 μm droplet is formed, a dissolved 400 nm SOA particle will give an organic concentration of 10^{-3} – 10^{-2} M. Assuming 1% of this is available to undergo oligomer-forming reactions, the reaction lifetime is given by $\tau = \ln 2/(k [\text{Org}]) = 0.5$ – 2 s. This estimate does not take into account possible changes in rates that increase with acidity during drying or droplet interface reactions, but shows that reaction rates can be sufficiently fast for such chemistry to occur within the ~ 2 s residence time of the VACES.

Mass spectra were also examined for changes in the amount of high molecular weight (HMW) compounds by calculating the fraction of peaks above m/z 150 relative to the sum of all peaks, f_{HMW} , before and after the VACES. Figures 3a and b show difference mass spectra for the two SOA experiments, where there is an increase of 22–32% in f_{HMW} after the VACES (Figure 4). The mass spectra are also expressed as

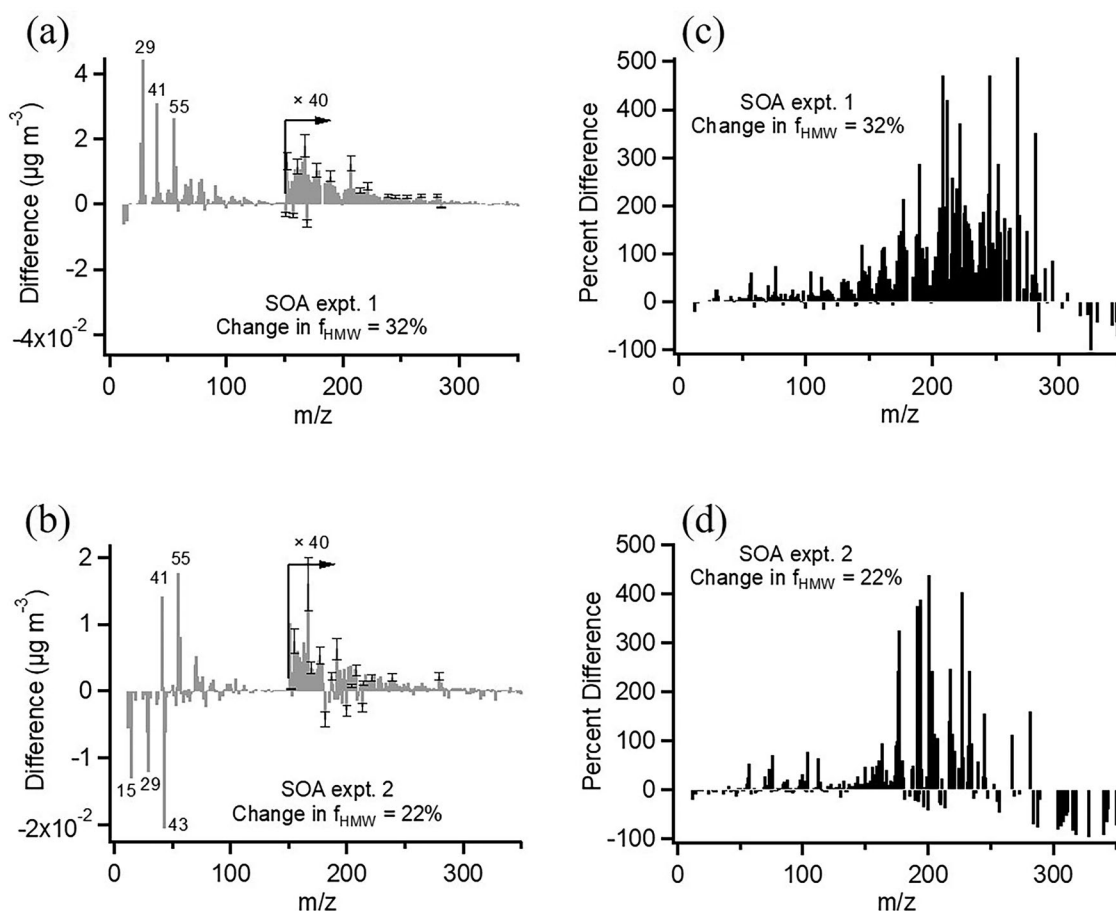


Figure 3. (a, b) Difference mass spectra of SOA before and after the VACES. Each spectrum is the difference between after the VACES divided by its EF_{mass} and before the VACES. Positive peaks at $m/z > 150$ show gain in HMW compounds after the VACES; (c, d) Difference mass spectra expressed as a percentage relative to the initial mass spectrum. The HMW increases after the VACES are statistically significant from those before the VACES ($p < 0.05$).

percent difference observed after the VACES relative to the initial spectrum (Figures 3c and d) where the increases above $m/z > 150$ are clearly seen. HMW compounds such as highly oxidized molecules (HOMs) as well as oligomers are known to form during α -pinene ozonolysis, especially at the relatively high reactant concentrations used for this study (Gao et al. 2004; Tolocka et al. 2004; Hall and Johnston 2012; Kristensen et al. 2014, 2016; Kourtchev et al. 2016; Molteni et al. 2019). Electron impact ionization generally results in significant fragmentation so that the majority of peaks appear at $m/z < 150$, but some peaks at larger masses indicative of oligomeric molecules do survive. Size distributions of several peaks with $m/z > 150$ are shown in Figure S4 to indicate their diameters and relative intensities. Because sampling of the original particle stream and enriched particles occurred over approximately two hours, it is possible that there was an increase in the oligomers during this aging time in the chamber (Qi et al. 2010). To test for this, the SOA was sampled again before the

VACES after two hours of aging in the reaction chamber. Neither the f_{HMW} (which increased by only 1.9%) nor the O/C (0.37 ± 0.03) and H/C (1.61 ± 0.01) changed significantly (Figure 4) compared to the unaged SOA, ruling this out as a source of oligomerization and suggesting HMW compounds formed during enrichment. Similar observations of high molecular weight increases have been reported for ambient air and $(\text{NH}_4)_2\text{SO}_4$ particles using the Harvard particle concentrator which uses heat to remove the excess water (McWhinney et al. 2012).

Changes in gas-particle partitioning are also possible within the VACES. α -Pinene SOA is a mixture of particles and semivolatile products and the latter may partition into the particles as the sample passes through the condenser if its concentration is greater than its saturation vapor pressure (Khlystov et al. 2005). Such compounds may only partially desorb in the virtual impactor and dryers when they return to room temperature. However, if this occurred to a significant extent, measured enrichment factors would be

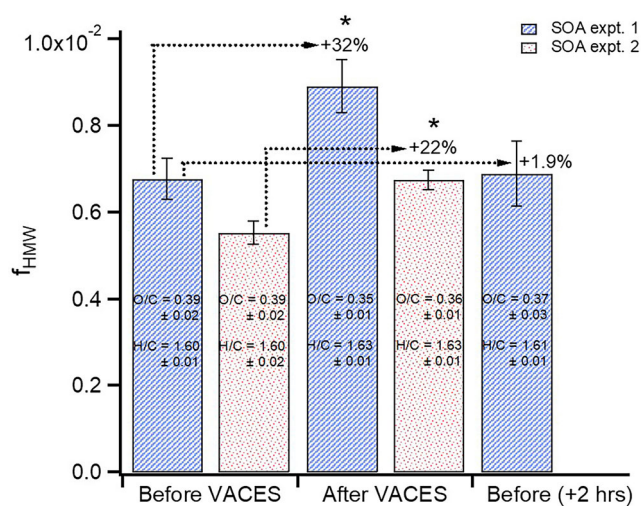


Figure 4. Fraction of high molecular weight fragments, f_{HMW} , before and after the VACES for the two α -pinene SOA experiments with a 22–32% increase after the VACES. Error bars represent 2 σ uncertainty of each measurement over 20–40 min. No significant change occurred after 2 hrs. of aging. Asterisks indicate values are statistically different ($p < 0.05$) from the corresponding value before the VACES.

expected to be larger than EF_{theor} along with diameter increases after the VACES, which were not observed in the present studies, although this has been observed in previous studies of inorganic salts and ambient air particles (Su et al. 2006; McWhinney et al. 2012; Saarikoski et al. 2014; Soleimani, Taghvae, and Sioutas 2020). Thus, partitioning from the gas phase induced by the VACES is likely to be minor here. Additionally, partitioning of HMW compounds from the vapor phase into the particles was considered to explain increases in f_{HMW} , but their small expected vapor pressures make this process unlikely to contribute.

Ambient particles

Size distributions of ambient particles before and after the VACES are shown in Figure 5. An accumulation mode at ~ 300 – 700 nm is common to all samples and contains both organics and inorganics. Bimodal distributions with a UFP mode near ~ 100 nm containing primarily organics were observed on many days (Figures 5b and c). These distributions are similar to other reported urban profiles with both primary and secondary particles (Finlayson-Pitts and Pitts 2000; Alfarra et al. 2004; Drewnick et al. 2004; McFiggans et al. 2005; Zhang et al. 2005b, 2007; Docherty et al. 2008). The data in Figure 5 show that again the overall shapes of the size distributions before the VACES and the distributions of the various inorganic and

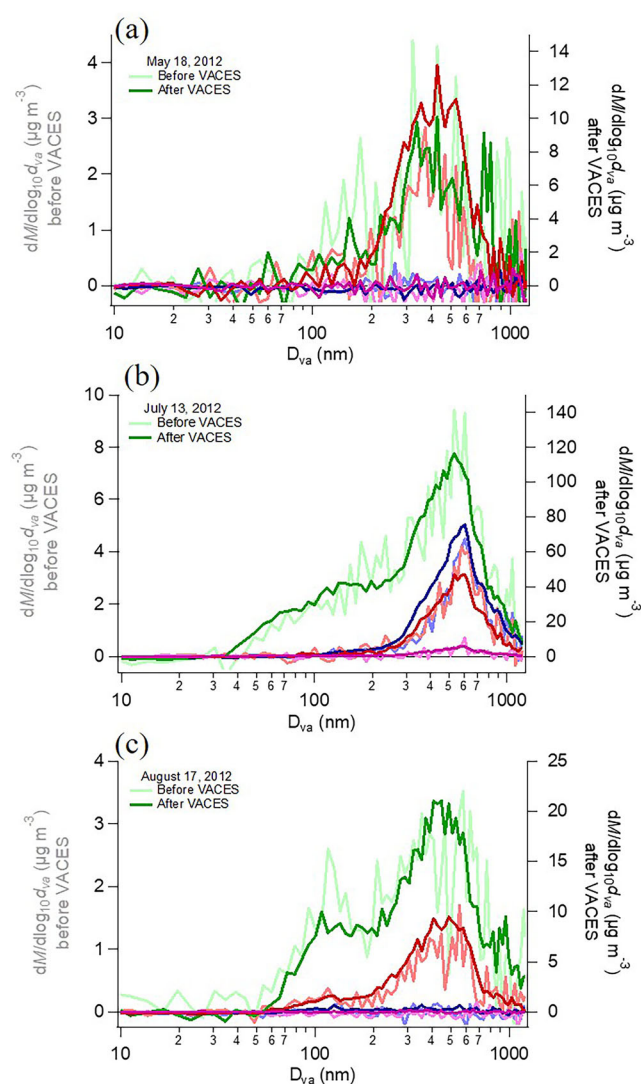


Figure 5. (a–c) Size distributions of ambient particles for three typical sampling periods before (light colors) and after the VACES (dark colors). (Green = organics, red = sulfate, blue = nitrate, pink = chloride).

organic components are retained, in agreement with several previous studies of particle concentrators (Kim et al. 2001b; Misra et al. 2004; Khlystov et al. 2005; Maciejczyk et al. 2005; Zhao et al. 2005; Freney et al. 2006; Taghvae et al. 2019; Soleimani, Taghvae, and Sioutas 2020; Shang et al. 2021a, 2021b). A previous study of the VACES using AMS reported gas phase condensation forming small nitrate particles under high ambient mass concentration conditions, which was not observed here, but in that case the mass increase of nitrate was $<10\%$ of the total mass after the VACES (Khlystov et al. 2005). Our results suggest little to no mixing of different particle sizes within VACES.

A convenient way to examine the enrichment efficiency of organics is through the ratio of the mass

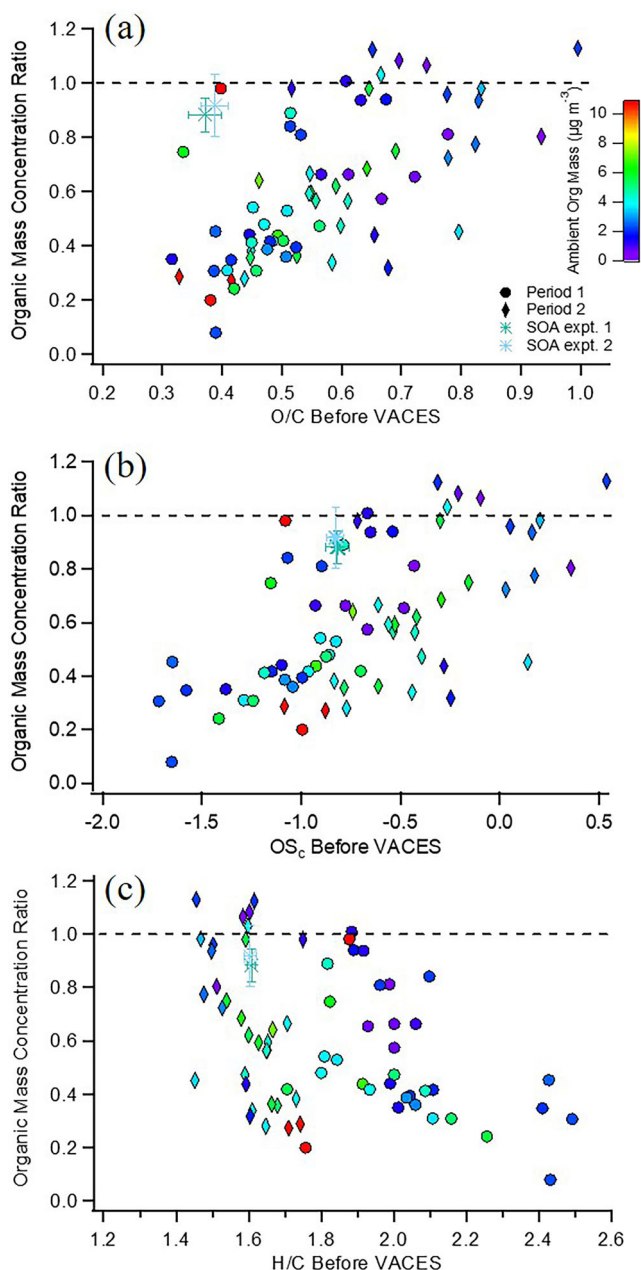


Figure 6. Organic mass concentration ratios (Equation (1)) after VACES enrichment versus (a) O/C of ambient particles (b) OS_c of ambient particles and (c) H/C of ambient particles for Period 1 (Spring/Summer, circles, $EF_{\text{theor}} = 15$) and Period 2 (Summer/Fall, diamonds, $EF_{\text{theor}} = 10$). SOA data are included (asterisks). Data points are colored by their measured ambient organic mass concentrations.

concentration measured after the VACES to that before the VACES where M_{after} is scaled down by its expected EF_{theor} :

$$M_{\text{ratio}} = \frac{\left(M_{\text{after}} \cdot \frac{1}{EF_{\text{theor}}}\right)}{M_{\text{before}}} \quad (1)$$

A mass concentration ratio of one indicates that the measured mass concentrations were enriched by

the intended enrichment factor, while $M_{\text{ratio}} > 1$ indicates over-enrichment and < 1 indicates under-enrichment. M_{ratio} was calculated for each time period (one to four each day) in both seasons. Similar expressions have been used in previous studies of particle concentrators (Khlystov et al. 2005; McWhinney et al. 2012). Equation (1) allows for comparisons over months of operation even if absolute values of EF_{theor} change.

Figure 6a shows M_{ratio} as a function of the initial (unconcentrated) O/C of ambient particles for studies during two different time periods, one in the spring/summer and one in the summer/fall. Those with lower O/C are significantly under-enriched relative to the expected EF_{theor} , and there is no significant trend with mass concentrations. The mass concentration ratio shows a similar trend with the average oxidation state of carbon, OS_c (Figure 6b), another indicator of oxidation level which is defined as $2O/C - H/C$ (Kroll et al. 2011). Figure 6c shows the corresponding plot of M_{ratio} plotted as a function of H/C of ambient particles. There is a trend toward under-enrichment of particles with higher H/C in both seasons. In short, the VACES tends to under-enrich ambient particles with lower initial O/C and higher H/C, i.e., the least oxidized particles. Ambient UFP typically have low O/C and OS_c , and high H/C relative to accumulation mode organic particles, which has often been shown using mass spectral markers (Alfarra et al. 2004; Allan et al. 2004; Drewnick et al. 2004; Zhang et al. 2004, 2005a, 2005b, 2007; McFiggans et al. 2005; Docherty et al. 2008). This trend in composition with particle diameter also emerges in this study. Figure S5 shows size distributions of several mass spectral markers over a range of time periods. In general, the marker m/z 44 (predominantly CO_2^+), which is intense in oxygenated organics, lies in the accumulation mode and m/z 57 (predominantly $C_4H_9^+$), which is commonly observed for traffic-related emissions, is significant for the UFP mode. The additional peaks, m/z 43 and 55, have both oxidized and unoxidized sources and appear in both modes in this study. The UFP mode of these ambient particles is composed primarily of unoxidized compounds. Thus, the under-enrichment of low O/C particles by the VACES falls disproportionately on UFP.

Figure 6 also compares M_{ratio} for both SOA samples to ambient particles. SOA particles (asterisks) appear to be much more efficiently enriched than ambient particles with the same initial O/C ratio (Figure 6a). However, this difference is not as significant when their OS_c is examined. The average carbon oxidation state of SOA ($OS_c = -0.82$) falls at the upper end of wide-ranging enrichments exhibited by

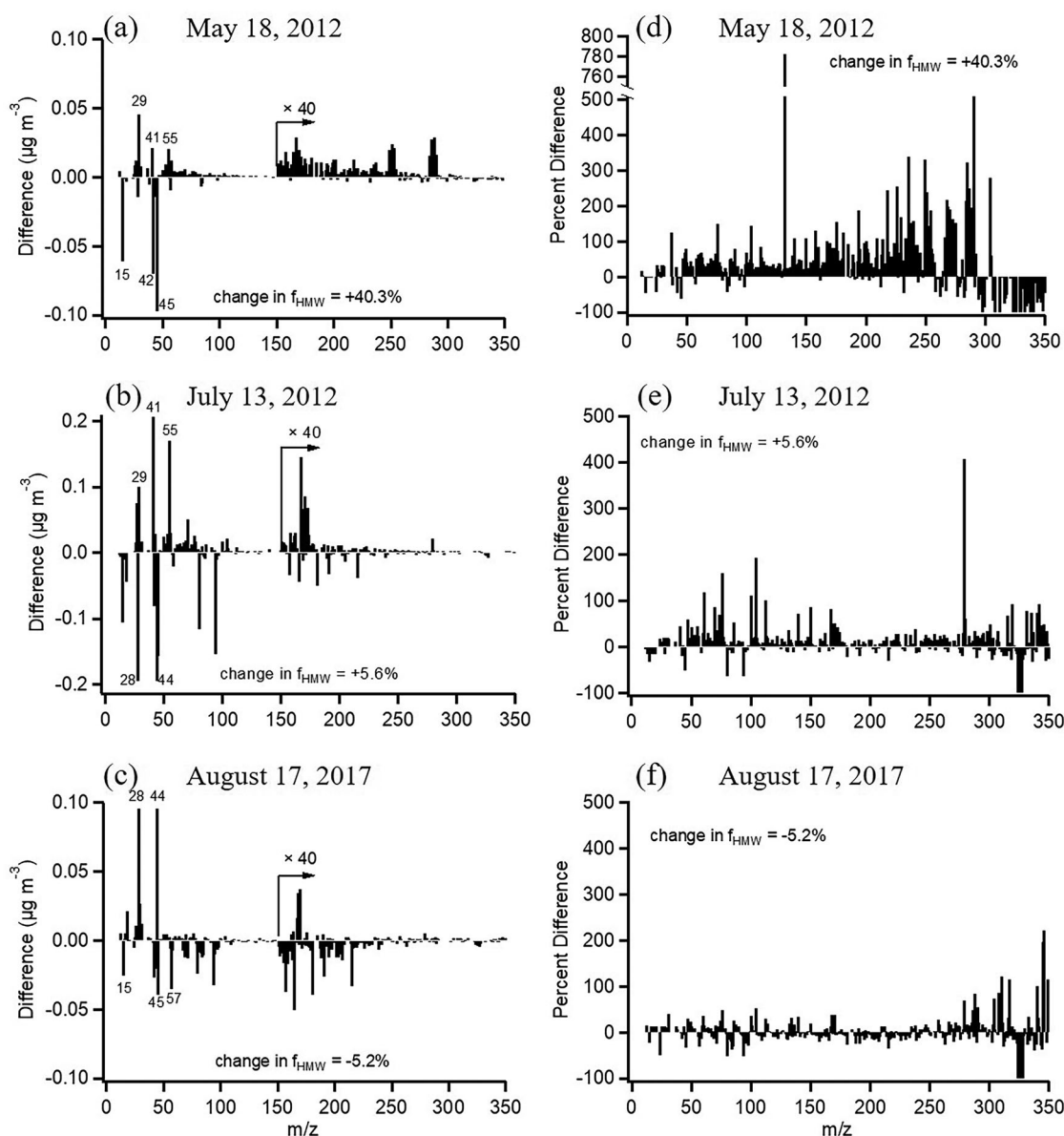


Figure 7. (a–c) Difference mass spectra for ambient particles for three typical sampling periods. Each spectrum is the difference between after the VACES divided by its $E_{\text{F}_{\text{mass}}}$ and before the VACES. Positive peaks at $m/z > 150$ show gain in HMW compounds after the VACES and negative peaks show loss after the VACES. (d–f) The difference mass spectra expressed as a percentage relative to the initial mass spectrum.

ambient particles of the same OS_c . The least oxidized particles with $\text{OS}_c < -1.1$, typical of hydrocarbon-like organic aerosol (Kroll et al. 2011), are less enriched than SOA. OS_c may be more representative of composition here because it is less sensitive to changes from loss of water during measurement that can occur in the AMS (Kroll et al. 2011; Canagaratna et al. 2015). With respect to H/C, SOA also lies within the wide range of similar H/C ambient particles. This comparison suggests bulk oxidation measurements (O/C, OS_c , or H/C) of ambient organic particles are not complete indicators of their ability to be enriched in the VACES, i.e., ambient particle samples with

O/C = 0.4 are not efficiently enriched, while the larger SOA particles are. It is likely that diameter and bimodality of ambient particles contribute to this and that the low O/C of ultrafines is not represented in the average due to their smaller mass concentrations.

A search for an enhancement in high molecular weight fragments ($m/z > 150$) was also made for the ambient particle data. Large increases ($>100\%$) were seen on some days, with decreases of $\sim 50\%$ on others, reflecting the variability typical of ambient particles. Difference mass spectra of ambient particles for several sampling periods, with the HMW region enlarged, are shown in Figures 7a–c. A gain in HMW

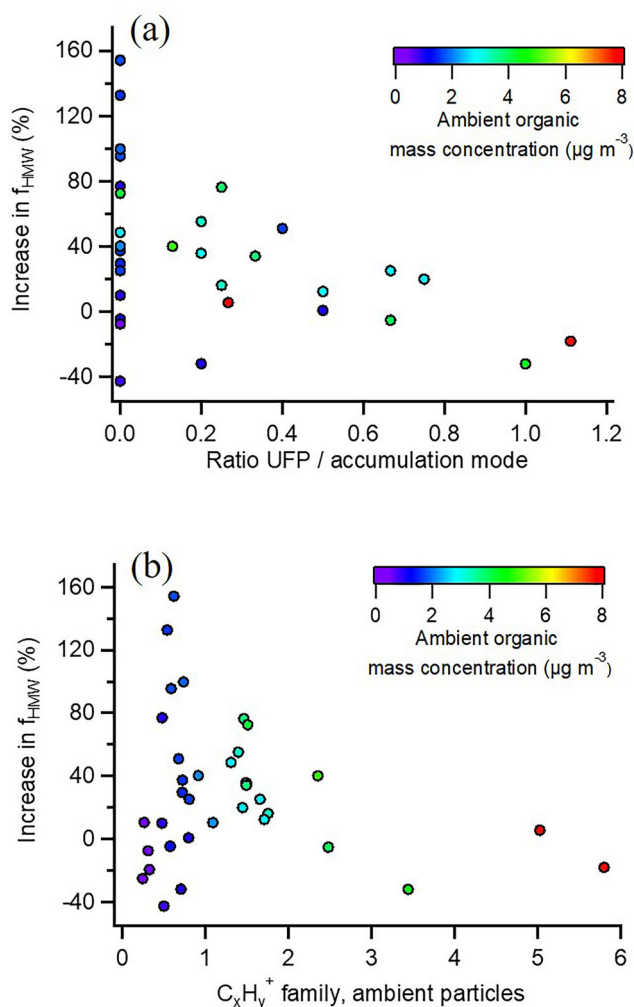


Figure 8. Change in f_{HMW} after VACES for ambient particles (a) as a function of ratio of UFP to accumulation mode mass (b) as a function of C_xH_y^+ composition of ambient particles. Data points are colored by the mass concentration of organics of ambient (unconcentrated) particles before the VACES.

compounds is seen for the May 18 time period, but is negligible for the other two periods. This is also evident when the mass spectra are expressed as a percent difference relative to the initial spectrum (Figures 7d–f). From Figure 5, only accumulation mode diameter particles were present on May 18 and no UFP mode was detected, thus the individual mass concentrations of UFP and accumulation mode particles were examined for all periods.

Figure 8a shows the change in HMW compounds plotted against the ratio of the UFP to accumulation mode mass concentration measured before the VACES. Periods with the smallest contributions of UFP and larger accumulation modes, exhibited the largest increases in f_{HMW} values. Periods that did not follow the trend were those with low ambient mass concentrations (purple) which had low signal-to-noise in size distributions and at higher m/z , increasing the

uncertainty in f_{HMW} and individual mode masses. A similar trend is shown in Figure 8b in which the change in HMW compounds is plotted against the C_xH_y^+ family of ions measured before the VACES, an indicator of UFP composition. Larger increases in HMW compounds were observed for particles with less C_xH_y^+ ions, i.e., more oxidized organic particles. It is possible that the components of UFP may also yield fragments with $m/z > 150$ after the VACES but may be masked by the under-enrichment of UFP in the VACES.

The mass spectra of ambient particles collected before and after the VACES show significant fragments containing C_xH_y^+ , $\text{C}_x\text{H}_y\text{O}_1^+$, and $\text{C}_x\text{H}_y\text{O}_{>1}^+$ (Figure S6). Fragments containing $\text{C}_x\text{H}_y\text{N}^+$ also appear in most ambient spectra at m/z 30, corresponding to CH_4N^+ , and m/z 42–45, corresponding to $\text{C}_2\text{H}_y\text{N}^+$ ($y=4-7$) and tend to be under-enriched after the VACES. Analysis of the signal intensities as a function of carbon number (Figure S7) shows that most $\text{C}_x\text{H}_y\text{N}^+$ fragments contain one or two carbon atoms after the VACES as well as before, suggesting they do not contribute significantly to oligomerization. Comparison with the NIST database suggests that these $\text{C}_x\text{H}_y\text{N}^+$ fragments correspond to low molecular weight primary or secondary aliphatic amines, diamines, amides, or amino acids (NIST 2021). Such compounds have a number of potential sources in this study including marine biological activity at the ocean or a nearby wetland reserve, automobile exhaust, port activity, biomass burning or cooking, and agricultural activity (Ge, Wexler, and Clegg 2011; Gaston et al. 2013; Sintermann and Neftel 2015; Poudel et al. 2017). Changes in amines and ammonia have been observed previously in particle concentrators (Su et al. 2006; Jung et al. 2010; Saarikoski et al. 2014). For example, in one study using the VACES, amines were observed to be over-enriched, which was attributed to uptake during neutralization of acids in the particles (Saarikoski et al. 2014). Similarly, an increase in amines in the 100–300 nm range with the VACES system has been reported, while in the same study, there was a loss of amines from volatilization using the Harvard concentrator system, which thermally dries the particles (Su et al. 2006). The under-enrichment observed here using diffusion dryers may similarly be due to volatilization during drying. Small enrichments in gaseous ammonia have been reported in the VACES for ambient and laboratory-generated particles (Jung et al. 2010), but are likely to be minor in the current study since the observed nitrogen-containing fragments are higher before the VACES than after.

The supersaturation of water vapor, which is determined by T_{sat} , is a major factor in determining the ability of a particle to grow to the size range that allows it to pass through the virtual impactor, and hence in determining enrichment factors (Gupta, Demokritou, and Koutrakis 2004; Petäjä et al. 2006). Studies characterizing water-based condensation particle counters have shown that activation of smaller particles is more efficient when the temperature difference between the saturator and condenser is larger (Petäjä et al. 2006; Wlasits et al. 2020). As part of the current studies, T_{sat} was increased in separate experiments during ambient particle enrichment while holding T_{cond} constant at 10 °C. Figure S8 shows size distributions collected at T_{sat} of 30 °C and 33 °C (saturation ratios of 3.5 and 4.1, respectively, Figure S1), demonstrating that increased enrichment of organic UFP can occur at higher T_{sat} . This increase in saturation ratio resulted in a decrease in O/C from 0.57 at $T_{\text{sat}} = 30$ °C to 0.33 at $T_{\text{sat}} = 33$ °C and an increase in H/C from 1.77 to 1.90. Since UFP generally have lower O/C ratios, a larger contribution from the UFP mode can change the O/C significantly. Consistent with this, fragments at m/z 55 and 57, characteristic of hydrocarbons, increase with T_{sat} and m/z 43 (from both $\text{C}_2\text{H}_3\text{O}^+$ and C_3H_7^+) also increases with T_{sat} . However, saturation ratios > 3.5 can induce homogeneous water nucleation (Hinds 1999), which accelerates liquid water accumulation in the virtual impactor and decreases enrichment factors. Thus, T_{sat} is generally kept at or below 31 °C to avoid this.

A number of studies of uptake of water or butanol on organic particles have been carried out with respect to understanding particle growth in condensation particle counters. Uptake of water and butanol to detect the smallest particles (~ 1 – 2 nm) was shown to depend on the particle composition, for example solubility in the condensing fluid (i.e., H_2O in the VACES) (Hering and Stolzenburg 2005; Petäjä et al. 2006; McGraw, Wang, and Kuang 2012; Hering, Spielman, and Lewis 2014; Hering et al. 2017; Kangasluoma and Attoui 2019; Wlasits et al. 2020). Under-enrichment of less oxidized ambient particles is likely a combination of size and composition. The SOA particles have mode diameters in the ~ 300 – 400 nm range, whereas a large fraction of low O/C ambient particles had diameters < 200 nm. Obtaining reliable and stable VACES data requires a sufficiently long sampling time that smaller SOA particles had already grown to larger sizes so that data on SOA UFP could not be accessed experimentally. As seen in Figure 2, there is a trend to smaller

enrichment factors at smaller diameters, consistent with the results of a number of other studies (Hering and Stolzenburg 2005; Maciejczyk et al. 2005; Su et al. 2006; McWhinney et al. 2012; Rastogi et al. 2012; Gute et al. 2019). Thus, ambient particles with a significant contribution from the smaller UFP mode are expected to be less efficiently enriched. In addition, UFP have lower OS_c and O/C than accumulation mode particles (Alfarra et al. 2004; Allan et al. 2004; Drewnick et al. 2004; Zhang et al. 2004; McFiggans et al. 2005; Zhang et al. 2005a, 2005b, 2007; Docherty et al. 2008), suggesting they are less polar and hence less soluble. For example, when UFP were isolated from a whole air sample with a 180-nm cut-point slit impactor (Kim et al. 2001b; Misra et al. 2002) the O/C after the VACES was 0.22 ± 0.03 ($\text{OS}_c = -1.38 \pm 0.2$), which was much lower than the 0.45 ± 0.04 ($\text{OS}_c = -0.75 \pm 0.07$) for the combined UFP and accumulation modes after the VACES. The lower O/C (OS_c) of isolated UFP are not well represented in the O/C measurements of whole/bimodal particle samples and thus their less polar composition may contribute more to under-enrichment when there is a larger UFP mode.

Summary and conclusions

As particle concentrators and other similar water condensation methods are used to increase particle concentrations for both health effects and particle composition studies, it is important to understand what changes, if any, are induced by the uptake of water followed by drying. The Versatile Aerosol Concentration Enrichment System (VACES) was characterized with a focus on the submicron organic composition of particles using aerosol mass spectrometry applied both to SOA particles from the reaction of ozone with α -pinene and to ambient air particles. Size distributions for SOA particles were conserved within instrumental uncertainty. SOA particles after the VACES showed evidence for oligomerization, even though there were only slight changes in the overall elemental composition. Oligomerization was also observed for ambient particles, specifically for higher O/C particles contained in the accumulation mode. Ambient ultrafine particles with low O/C were under-enriched so that oligomerization, if it was occurring, may not have been detectable. Whether this is significant for health effects studies and composition measurements using particle concentrators remains to be explored.

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Data availability statement

The data that support the findings of this study are archived and openly available at <http://doi.org/10.7280/D1VH7W>.

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