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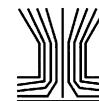
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Impact of the Versatile Aerosol Concentration Enrichment System (VACES) on Gas Phase Species

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The performance of the Versatile Aerosol Concentration Enrichment System (VACES) was assessed in terms of the enrichment factor (EF) for highly soluble vapors. Gases ranged in their behavior from a slight enrichment for ammonia ($EF(\text{NH}_3) = 1.9 \pm 0.8$) to strong depletion of nitric acid ($EF(\text{HNO}_3) = 0.12 \pm 0.06$). H_2O_2 fell in between, with $EF(\text{H}_2\text{O}_2)$ averaging $0.37 (\pm 0.25)$ and ranging from 0.07 and 0.91 depending on conditions. Detailed results for H_2O_2 indicate that there are two competing processes at play: soluble gases are lost to condensed water in the VACES, particularly in the saturator water bath but also other locations, depleting outlet gas-phase concentrations and resulting in EFs well below 1. Working in the opposite direction, H_2O_2 (and other soluble gases) can also be concentrated together with particles. Presumably, the gases are absorbed into the particles as they take up water, pass through the concentration step, and are released once particles are re-dried. Depending on conditions and the gas solubility, depletion and concentration play larger or smaller roles. The relative importance of these competing processes appear to follow in order of Henry's law solubilities, with modest particle-mediated concentration (resulting in EFs >1) dominating for ammonia, the least soluble gas, and loss in the water bath and other condensed water in the VACES dominating for H_2O_2 and HNO_3 , which are more soluble (i.e., have higher Henry's law coefficients).

INTRODUCTION

Numerous epidemiological studies have demonstrated that elevations in PM₁₀ and PM_{2.5} are correlated to increases in acute morbidity and mortality (Pope et al. 1995; Thurston et al. 1994). Yet, the vast majority of the human population and

typical animal models do not elicit measurable physiological changes to normal levels of air pollutants on short time scales. One approach to understanding these health effects is to expose animal models to particle concentrations greatly in excess of ambient. To address this issue, several researchers have developed devices to concentrate ambient particles (Barr et al. 1983; Gordon et al. 1999). Many ambient aerosol concentrators employ virtual impactors that require high pressure drops to concentrate the fine and ultrafine particles that are thought to have significant health effects, but animals cannot survive at low pressures without special care, and these low pressures are expensive to establish and maintain. Research groups at Harvard University and the University of Southern California (USC) have developed devices that concentrate ambient particles with a modest pressure drop in the virtual impactor by first growing the particles by water condensation (Kim et al. 2001b). These large droplets need only a small pressure drop to be concentrated in a virtual impactor by ten fold or more. Subsequently, the particles are dried back to their original size and composition, and exposed to the animal models. The Versatile Aerosol Concentration Enrichment System (VACES) designed by the USC group (Kim et al. 2001b) is portable and relatively inexpensive so is very popular with those investigating the health effects of ambient PM.

Because the purpose of particle concentrators is to provide ambient air in which a large fraction of the gas phase has been removed but the particles are otherwise physically and chemically unaltered, several studies have investigated potential artifacts introduced into the particles by concentrators. Previous studies by the USC group (Kim et al. 2000; Kim et al. 2001a, b) showed that the VACES causes no significant artifacts to particles. Kim et al. (2000) confirmed that there is no loss of particulate nitrate during particle concentration. Kim et al. (2001a; 2001b) concluded that PM mass, number and chemical composition (including nitrate, sulfate, EC and some trace metals) are preserved during particle concentration enrichment in the laboratory and field conditions. Zhao et al. (2005) evaluated the VACES using a Rapid Single-Particle Mass Spectrometer (RSMS). They

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found small differences in chemical composition between samples with and without the VACES. However, due to changes in the composition of ambient air and statistical variation in RMS measurements, there was no evidence showing that the VACES altered particle composition substantially. Arellanes et al. (2006) performed a pilot study to investigate the impact of the VACES on particulate concentrations of hydrogen peroxide. They found that differences were within uncertainties of the measurements, but noted that because the urban particles they studied generate H_2O_2 in quantities that far exceed (by a factor of about 700) the quantity that could reasonably be expected to be contained in the aerosol liquid water (governed by Henry's law), the impact of the VACES on particulate peroxides is not expected to be substantial. We note that unless otherwise indicated, " H_2O_2 " used here refers to the species in the gas phase or dissolved in water. H_2O_2 generated by ambient particles (Arellanes et al. 2006; Wang et al. 2010) is indicated as $\text{H}_2\text{O}_2(\text{p})$. Ammonium sulfate particles, used for much of the work here, do not generate H_2O_2 as ambient particles do, but take up H_2O_2 from the gas phase according to Henry's law for gas-liquid partitioning.

This study aims to experimentally assess possible artifacts generated by the VACES, focusing on several chemical variables that have not been investigated previously. A set of artifacts involves the possible concentration enhancement, or depletion, of highly soluble vapors, such as hydrogen peroxide, nitric acid and ammonia in the gas phase of the VACES effluent. An understanding of potential perturbations to gas phase concentrations is necessary for accurate interpretation of VACES results. Generally it is assumed that gas phase pollutants are unchanged by the VACES, thus changes in target parameters (such as physiological changes in animals exposed to the VACES effluent) between unconcentrated samples and samples concentrated by the VACES may be attributed to the particles. If indeed gas phase pollutants are also enriched or depleted by the VACES, the cause of differences in outcomes for concentrated and unconcentrated samples is more difficult to establish.

Consider a water soluble gas, such as H_2O_2 . While it is highly soluble, because the liquid water content of aerosols is so small, in the absence of clouds or fog, more than 99% of H_2O_2 is in the gas phase (Arellanes et al. 2006). Many organoperoxides and other organic and inorganic compounds also fit this description. As air containing H_2O_2 and other gaseous and particulate pollutants enters the VACES (Figure 1), the air first encounters the water bath that warms and humidifies the air. While water evaporates from the bath into the air, H_2O_2 may condense into the bath water, creating a negative artifact for gaseous H_2O_2 levels. Next the air is rapidly cooled, supersaturating water in the air and causing the particles to grow rapidly into aqueous drops. H_2O_2 originally present in the gas phase will partition rapidly into the additional liquid water present in the new aqueous phase associated with the droplets. The particles, containing substantial liquid water, are now concentrated by passing through the virtual impactors, and the H_2O_2 orig-

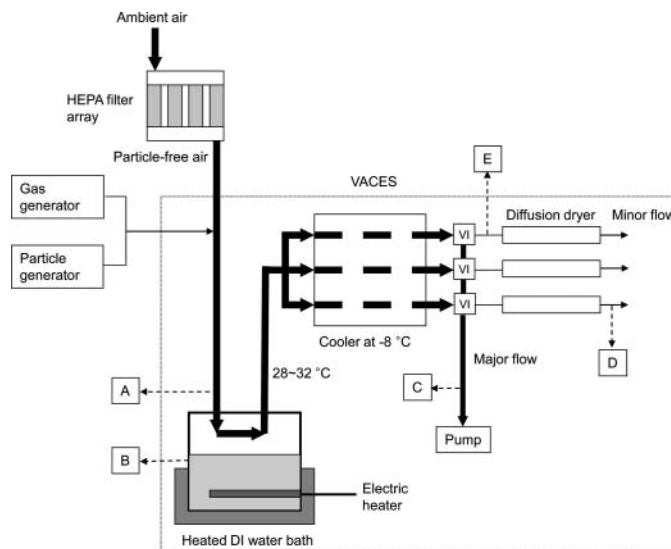


FIG. 1. Schematic diagram of the VACES and an experimental setup. (Location A: sampling location at the inlet of the VACES, location B: sampling location at the water bath, location C: location for major flow measurement, location D: sampling location at the outlet of the VACES after the diffusion dryer, location E: sampling location at the outlet of the VACES before the diffusion dryer) Note: The gas generator is a permeation source for HNO_3 experiments and a bubbler with H_2O_2 solution for hydrogen peroxide experiments to generate H_2O_2 gas.

inally present in the gas phase, is carried through the virtual impactor in the droplets and concentrated as well. The particles are subsequently dried, releasing any dissolved H_2O_2 back to the gas phase creating a positive artifact. The dryers, however, create another potential negative artifact as they likely also take up H_2O_2 together with water. The magnitude of the negative artifact, a reduction in the concentration of high solubility compounds because of dissolution into the water bath and/or loss to other surfaces in the VACES, is difficult to predict. The magnitude of the positive artifact, a potential increase in concentration of soluble gases occurring during concentration of the particles, is also unknown; however it may approach the EF of the particles (i.e., a factor of 10–30) depending on how VACES is operated.

The objective of this work is to characterize aspects of VACES that may need improvement, if necessary, by exploring potential artifacts in gas phase concentrations of high solubility gases.

EXPERIMENTAL SETUP AND PROCEDURES

Two sets of experiments were conducted in this study: H_2O_2 measurement and NH_3 and HNO_3 measurement. In brief, EF of PM and soluble gas species were measured by comparing their concentration at the inlet and outlet of VACES. EF (PM) was measured by comparing number distributions and mass on Teflon filters. HNO_3 was measured using denuder filter packs and H_2O_2 was measured using stripping coils. For H_2O_2 experiments, H_2O_2 uptake in the water bath of the VACES was also

measured. Details of each experiment will be provided in the following sections.

The VACES Principles of Operation

The VACES has been described in detail in previous work (Kim et al. 2001a, b; Sioutas et al. 1999; Zhao et al. 2005) and is only briefly summarized here. As shown in Figure 1, ambient air is drawn at 105 Lpm per channel into a saturator, consisting of a warm water tank (volume ranging from 4 to 6 liter) that warms and humidifies the air flow above it. Next, the warm, humid air passes through cylindrical, cooled pipes. As the air cools in these pipes, it supersaturates, causing water vapor to condense on the aerosol particles, and resulting in rapid growth. Next, the droplet-laden air passes through virtual impactors (VI) that concentrate the drops in the minor flow air. Finally the air passes through diffusion dryers, returning the particles to their original sizes.

The dimensions of the water bath are 8" (D) \times 11" (W) \times 10" (H), which provides an 8" \times 11" water surface to humidify the inlet air. Total volume of water in the bath varies during the experiments because of the water consumption. At the beginning of each experiment, the water surface is set about 1" below the exit of the inlet tube when waving watermarks on the water surface are seen. The distance between water surface and the inlet tube is adjusted periodically by either adding water or lowering the inlet tube exit as the water level goes down.

Instrumental Setup and Particle Measurements

Ambient air was sampled from outside the UC Davis laboratory through an inlet duct. A HEPA filter array consisting of six HEPA filters in parallel (TSI Inc., PN#1602300) was installed before the VACES to remove ambient particles with 99.9% efficiency (>40 nm). Laboratory generated particles (ammonium sulfate and magnesium sulfate) and soluble gases (H_2O_2 , NH_3 , and HNO_3) were injected upstream through a 1 1/4" ID, 180 cm long corrugated Teflon tube to be mixed with ambient air (either particle free or not) before entering the VACES. Particles were generated with either an atomizer or nebulizer. The nebulizer (BGI Inc.) contained a 0.5% (w/v) ammonium sulfate solution and produced particles with a geometric mean diameter at 50 ± 6 nm over the period of whole experiment. The atomizer (TSI, Model 3076) was used to generate ammonium sulfate aerosols from a 200 mM ammonium sulfate solution with a size distribution centered at 40 nm, and was used only on 3/27. Upstream and downstream particle samples were collected from locations A and D in Figure 1 by SMPS (Scanning Mobility Particle Sizer, TSI Inc., Model 3936L25) and/or on filters. SMPS and/or filter mass was used to determine VACES EF(PM) values and filter samples were used for composition analysis. An automated valve switched samples between upstream and downstream about every 10 min for SMPS measurements. The size distributions of lab generated particles were very stable which varied less than 5% in terms of concentration during the

experiment, while the ambient particle concentrations varied about 10% during the experiment. The VACES EF(PM) was experimentally determined as the ratio of downstream total particle counts (or mass) to the upstream value. Inlet temperature (T_{in}) and humidity (RH_{in}) were measured at location A in Figure 1, water temperature inside the saturator were measured at location B in Figure 1 and the air temperature was measured slightly above the location B within the water bath, and the major flow rate was measured at location C in Figure 1, while minor flow rate, outlet temperature T_{out} , and RH_{out} were monitored at location D in Figure 1.

Hydrogen Peroxide Measurements

Gas sampling was achieved by attaching two independent stripping coils, connected via black conducting tubing, to the VACES inlet (location A in Figure 1) and outlet (location D in Figure 1). Briefly, the stripping coil (described in detail by Hasson et al. 2001; Hartkamp and Bachausen 1987) is a 1 m \times 2 mm ID coiled glass tube through which gas samples were collected. Sampling was performed at the VACES inlet approximately 15 cm above the water saturator region and outlet, which was located just before or following one of the two diffusion dryers. Particles present in the flow were also sampled into the stripping coils, although it is noted that except possibly for the case of concentrated, undried effluent of the virtual impactors in the VACES (not measured in this study), particles contain too little liquid water to absorb more than 1% of the gas phase H_2O_2 , so particle-borne peroxides are of little consequence to the present study. Stripping coils drew flow from the VACES through a tee at 4.5 Lpm, for 20 minutes per sample, with a measured collection efficiency of $90 \pm 3\%$ (Arellanes et al. 2006). In between runs, the stripping coils were flushed for 10 min with stripping solution (18 $\text{M}\Omega\text{cm}^{-1}$ Milli-Q water filtered through 0.22 μm pore polyethersulfone filters, 0.1 mM Na_2EDTA adjusted to pH 3.5 with 0.1 N H_2SO_4) to prevent sample cross contamination. H_2O_2 in the stripping solution was monitored daily. Peroxide signal from the stripping solution was low and fairly consistent throughout the measurements, averaging $(2.3 \pm 1) \times 10^{-8}$ M. H_2O_2 in the stripping solution and other aqueous samples was quantified using high performance liquid chromatography with fluorescence detection. Sample collection techniques and H_2O_2 quantification have been described in detail elsewhere (Arellanes et al. 2006; Hasson and Paulson 2003).

H_2O_2 in extraction solutions was measured by high performance liquid chromatography (HPLC)-fluorescence, as described in detail elsewhere (Hasson et al. 2001; Arellanes et al. 2006). Normally, peroxides are separated on a C-18 reversed-phase HPLC column based on their polarity, however because earlier measurements established that organic peroxides were very low or absent from ambient aerosols (Hasson and Paulson 2003) and we used only H_2O_2 for this study, only a short guard column (Alltech) was used for this study, and H_2O_2 eluted at

0.5 min. The eluent is mixed with fluorescent reagent containing horseradish peroxidase enzyme and para-hydroxyphenyl acetic acid (PHOPAA). The enzyme catalyzes a stoichiometric reaction between hydroperoxides and PHOPAA, resulting in quantitative conversion of H_2O_2 to PHOPAA dimer. The PHOPAA dimer is then detected via fluorimetry. Calibrations were performed 3 times a week with titrated H_2O_2 standard solutions. The response was linear in the concentration range 10^{-8} to 10^{-6} M.

Aqueous-phase H_2O_2 was monitored in the saturator water by withdrawing small aliquots before and after each day's sampling from location B in Figure 1. VACES EF(number) was determined by SMPS which alternately sampled the inlet and outlet flows at the start of each 20 minute run. The SMPS measures 8–300 nm particles. For nebulized aerosol, the particle count above 300 nm is negligible. Relative humidity was continuously measured at both inlet and outlet for all runs. Particle masses were measured by weighing tared (Teflon) filters after a sampling event (ThermoElectronics, CAHN 28 Microbalance).

Gas-phase H_2O_2 was generated by passing zero generated air through a bubbler containing approximately 200 mL of 1.0 M H_2O_2 at a flow of 1 Lpm. This flow was mixed with the VACES inlet flow, which was unfiltered ambient air at 315 Lpm.

Measurements (Table 1) were made in one of three regimes: (1) With ambient aerosol and the outlet sampling position (location D in Figure 1) situated at the exit of one silica gel diffusion dryers (3/16 and 3/17 and 3/22-3/27); (2) With ambient aerosol and the outlet position just upstream of the dryer (location E in Figure 1), so that the gas did not come into contact with the silica gel (3/18); and (3) With generated ammonium sulfate aerosol, and the outlet position (location D in Figure 1) following the diffusion dryer (3/29 and later).

Ammonia and Nitric Acid Measurements

The effect of the VACES on gaseous $\text{NH}_3/\text{NH}_4^+$ and $\text{HNO}_3/\text{NO}_3^-$ concentrations were determined using denuder-filter packs (DFPs). Each DFP contained two denuders in series: one coated with a 50:50 (v/v) solution of methanol and aqueous 1% K_2CO_3 to collect HNO_3 , and the next coated with a 1.5% solution of citric acid (w/v) in methanol to collect NH_3 . To coat each, 10 mL of solution was pipetted into the denuder, which was then capped, gently agitated for 1 minute, drained and dried using zero air. In order to minimize contamination, denuders were prepared within 24 h of use and sealed with Parafilm until transport. Behind each pair of denuders was a 47-mm diameter Teflon filter pack to collect particles. The filter pack contained a 47-mm Teflon filter (Zefluor, 2 μm pore, Pall Co.) followed by a Nylon filter (Nylasorb, 1 μm pore, Pall Co.). 2 μm pore size Teflon filters very efficiently collect submicron particles (e.g., 99.9% for 0.3 μm DOP particles according to the manufacturer, with only a small drop-off in efficiency at smaller sizes (Liu and Lee 1976)). Filters were cleaned prior to use by placing each filter in a clean HDPE bottle and shaking for six

hours with purified water (Milli-Q), rinsing with Milli-Q, then drying and storing in a vacuum oven just above room temperature. Just prior to each experiment, the components of the DFP were assembled and transported to the sampling site.

For each experiment DFPs were set upstream (location A in Figure 1) and downstream (location D in Figure 1) of the VACES. The VACES was run with a major flow rate of 105 Lpm and minor flow rates of 5 Lpm per channel. The upstream DFP was connected 15 cm upstream of the VACES water bath and pulled 15 Lpm for sampling. Two of the downstream channels, each with a flow of 5 Lpm, were used for each experiment. One downstream channel was used for particle number measurements by the SMPS, and another was used for the downstream DFP. Both DFP flows were controlled with critical orifices and flow rates were measured before and after every experiment. DFP sampling times ranged from 1 to 3 h depending on the aerosol and gas concentrations at the inlet and outlet of the VACES. The silica gel in the VACES diffusion dryer was replaced at the beginning of each experimental day and was used at most for two experiments. Before sampling, the VACES was run for 1 to 2 h to reach steady-state operation condition (determined by monitoring the outlet temperature and relative humidity). Ambient air was used as the default input air stream into the VACES, in some cases with the upstream HEPA particle filter array. In some experiments magnesium sulfate or ammonium sulfate particles generated by a nebulizer were added after dilution. In a few experiments gaseous nitric acid was added upstream of the VACES by using a temperature-controlled permeation source (trace source disposable permeation tube, KIN-TEK).

After each experimental day the DFPs were removed and denuders were extracted within 1 h by adding 6.0 mL of Milli-Q, gently agitating for 1 minute, and pouring the extract solution into a Nalgene bottle that was refrigerated until analysis. Filters were extracted by placing them separately into 50 mL HDPE bottles, wetting with 100 μL of ethanol, adding 8.0 mL of Milli-Q, shaking for 3 h, and pouring the extract into a Nalgene bottle that was refrigerated until analysis. Concentrations of cations and anions in the denuder and the filter extracts were determined using a Dionex DX-120 Ion Chromatograph with the eluents, columns, and suppressors described previously (Newberg et al. 2005). Limits of detection (LODs; determined as 3.3 times the standard deviation of multiple injections of a standard near zero) for IC measurements of NO_2^- , NO_3^- , SO_4^{2-} , NH_4^+ , and Mg^{2+} were in the range of 0.1 ~ 0.2 μM , which is equivalent to 0.6 to 1.6 nmol in 6.0 or 8.0 ml of extraction volume. Relative percent differences for replicate sample analyses were nearly always within 5%. Simultaneously with the sample DFP, a separate blank DFP was prepared, extracted, and analyzed using the same methods described above for the sample DFP. Blank levels for the ions were generally greater than LODs and were subtracted from the associated sample values. Sample values that are less than three times of the blank level for a given experiment are not reported.

TABLE 1

Summary of peroxide measurements. [H₂O₂] inlet and outlet were measured at locations A and D, respectively, (Figure 1), except on March 18, when the outlet concentration was measured at location E (Figure 1)

Date	Run	[H ₂ O ₂] Inlet (ppb)	[H ₂ O ₂] Outlet (ppb)	Gas phase H ₂ O ₂ EF	Particle EF by number	Particle EF by mass	Aerosol
16 Mar	1	4.5	1.2	0.27	10		ambient
	2	93	35	0.38	5		ambient
	3	50	33	0.66	2		ambient
	4	51	28	0.55	1		ambient
17 Mar	1	130	56	0.43	7		ambient
	2	135	31	0.23	2		ambient
	3	45	22	0.49	2		ambient
	4	74	25	0.34	2		ambient
16–17 Mar			Avg.	0.42			
			St. Dev.	0.15			
18 Mar	1	77.4	48.4	0.63	6		ambient
	2	98	50	0.51	6		ambient
	3	124	66	0.53	6		ambient
	4	164	70	0.43	3		ambient
	5	134	68	0.51	6		ambient
	6	137	78	0.57	4		ambient
	7	166	58	0.35	3		ambient
18 Mar			Avg.	0.5			
			St. Dev.	0.09			
22 Mar	1	160	5	0.03	8		ambient
26 Mar	1	27	2	0.07	10		ambient
26 Mar	2	17	4	0.24	3		ambient
27 Mar	1	17	12	0.71	1		(NH ₄) ₂ SO ₄
29 Mar	1	14	2	0.14	4		(NH ₄) ₂ SO ₄
29 Mar	2	12	1.9	0.16	5	2	(NH ₄) ₂ SO ₄
29 Mar	3	5	1.7	0.34	5		(NH ₄) ₂ SO ₄
30 Mar	1	26	4	0.15	6		(NH ₄) ₂ SO ₄
30 Mar	2	25	1.8	0.07	6	2	(NH ₄) ₂ SO ₄
2 Apr	1	44	40	0.91		16	(NH ₄) ₂ SO ₄
3 Apr	2	83	71	0.86		28	(NH ₄) ₂ SO ₄
4 Apr	1	48	37	0.77		19	(NH ₄) ₂ SO ₄
4 Apr	2	35	16	0.46		15	(NH ₄) ₂ SO ₄
5 Apr	1	200	69	0.35		14	(NH ₄) ₂ SO ₄
5 Apr	2	160	55	0.34		12	(NH ₄) ₂ SO ₄
6 Apr	1	120	23	0.19		9	(NH ₄) ₂ SO ₄
6 Apr	2	140	28	0.2		13	(NH ₄) ₂ SO ₄
16–17 Mar and 22 Mar to 6 Apr			Avg.	0.37		12	
			St. Dev.	0.25			

After Apr 2nd, the particle number concentrations were not recorded due to a problem with the SMPS.

RESULTS AND DISCUSSION

Effects of VACES on H₂O₂

H₂O₂ Enrichment and Depletion

The gas phase measurements of H₂O₂ at the inlet and outlet of the VACES are shown in Table 1, for the VACES operating over a wide variety of particle enrichment factors. The average ($\pm \sigma$)

H₂O₂ enrichment factor (EF(H₂O₂)) is 0.37 ± 0.25 , indicating that H₂O₂ tended to be depleted rather than enhanced by the VACES. The large standard deviation does not appear to be due primarily to noise, however. Rather two competing processes are acting in the VACES to varying degrees. The first is depletion of H₂O₂ from the gas phase due to dissolution of H₂O₂ into condensed water at several locations throughout the VACES,

TABLE 2
H₂O₂ Uptake in the Saturator water

Date	Avg. gas [H ₂ O ₂] inlet (ppb)	Ave. gas [H ₂ O ₂] outlet (ppb)	End of day saturator [H ₂ O ₂] (μM)	Moles of H ₂ O ₂ passing saturator ¹	Moles of H ₂ O ₂ in saturator ²	Moles of H ₂ O ₂ lost in VACES ³
Estimated Uncertainty	10%	10%	5%	15%	25%	20%
17 Mar	110	38	46	3.5·10 ⁻⁴	1.2·10 ⁻⁴	2.3·10 ⁻⁴
18 Mar ^{1,2}	145	71	120	8.2·10 ⁻⁴	4.7·10 ⁻⁴	4.2·10 ⁻⁴
22 Mar	160	4.3	29	3.9·10 ⁻⁴	1.5·10 ⁻⁴	3.8·10 ⁻⁴
26 Mar	22	3	39	1.4·10 ⁻⁴	7.8·10 ⁻⁵	1.2·10 ⁻⁴
27 Mar	17	12	27	8.0·10 ⁻⁵	5.4·10 ⁻⁵	2.4·10 ⁻⁵
29 Mar	12	2.1	34	7.6·10 ⁻⁵	6.8·10 ⁻⁵	6.2·10 ⁻⁵
30 Mar	29	3.3	25	1.3·10 ⁻⁴	5.0·10 ⁻⁵	1.2·10 ⁻⁴
31 Mar	20	0.1	11	1.2·10 ⁻⁴	2.2·10 ⁻⁵	1.2·10 ⁻⁴
4 Apr	47	31	110	2.9·10 ⁻⁴	2.2·10 ⁻⁴	1.0·10 ⁻⁴
5 Apr	210	71	440	1.4·10 ⁻³	8.8·10 ⁻⁴	8.9·10 ⁻⁴
6 Apr	145	29	320	9.5·10 ⁻⁴	6.4·10 ⁻⁴	7.6·10 ⁻⁴
average				4.3·10⁻⁴	2.5·10⁻⁴	2.9·10⁻⁴
Peroxide taken up by the saturator/total, amount lost in VACES					58 ± 15%⁴	85 ± 20%⁵

Shading indicates ambient aerosols, no shading is ammonium sulfate aerosols.

¹Calculated from column 2 and the total time of experiments for the whole day (not shown, usually 7.7–8.1 hours).

²Calculated from column 3 and an estimate of the volume of the water in the saturator at the end of the day (not shown, usually 2L, but higher in some cases). That the volume was not measured repeatedly each day contributes a potentially systematic uncertainty, as indicated.

³Calculated from the difference between column 1 and column 2, and the total time of experiments for the whole day.

⁴The ratio of the averages of the moles of H₂O₂ in the saturator to the moles of H₂O₂ passing over the saturator.

⁵The ratio of the averages of the moles of H₂O₂ in the saturator to the moles of H₂O₂ lost in the VACES.

and the second is concentration of H₂O₂ mediated by particles that carry H₂O₂ with them as they pass through the concentration step as large aqueous particles.

Uptake of H₂O₂ into Condensed Water in the VACES

Table 2 shows all data for which there were reliable inlet and outlet H₂O₂ concentrations, as well as saturator water H₂O₂ concentrations. The peroxide concentration in the saturator water bath was monitored at least twice each day: after filling the reservoir with deionized water at the beginning of the day (peroxide levels were undetectable or very low at this point) and again at the end of the day after all measurements were completed. Also shown in Table 2 is the average inlet H₂O₂ concentration for the relevant period (usually the whole day), and the moles of H₂O₂ that passed over the water bath during the course of the day. The latter was calculated by summing the sampling times for each day and adding warm-up and change-over time, using a flow rate of 315 Lpm, and multiplying the resulting value by the average inlet concentration of H₂O₂. The column indicating “moles of H₂O₂ in the saturator” contains substantial uncertainty as the volume of water in the saturator was not measured, but rather estimated.

A nearly perfect relationship ($R^2 = 0.96$) between the quantity of H₂O₂ that passed over the saturator and the quantity of H₂O₂ in the saturator bath is shown in Figure 2. The average

uptake of H₂O₂ from the gas into the saturator is about 58 ± 15% (Table 2). The confidence interval was derived by propagating all sources of random and systematic errors (Table 2). A comparison of the H₂O₂ in the saturator to average number of moles H₂O₂ lost in the VACES indicates that 85 ± 31% of the “missing” peroxide is in the saturator water bath ($R^2 = 0.87$,

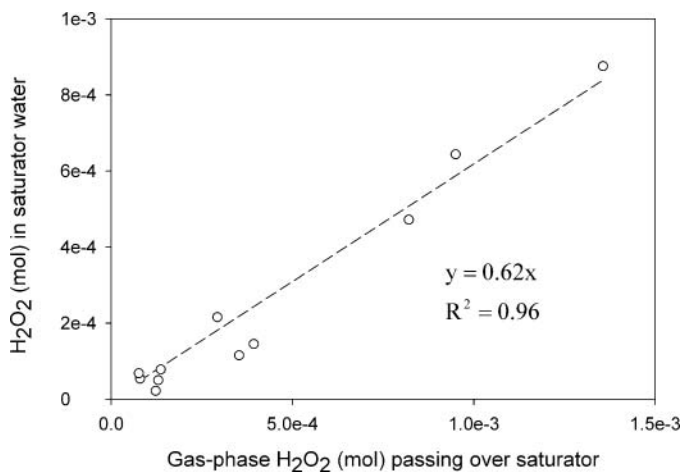


FIG. 2. The relationship between peroxide flowing over the saturator over the course of the day and the peroxide measured in the saturator at the end of the day.

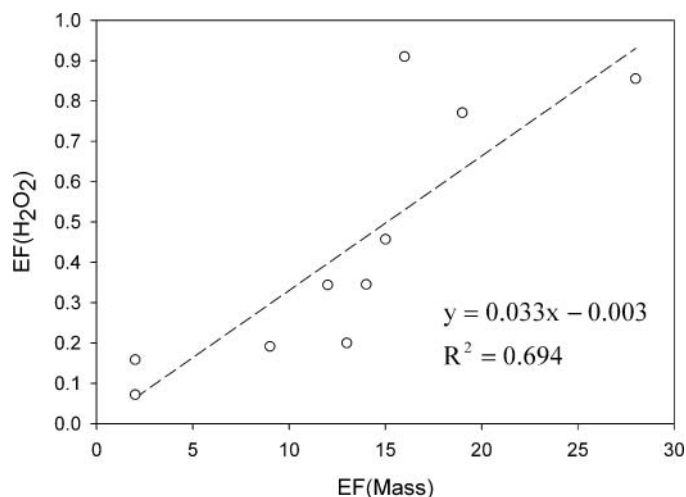


FIG. 3. The relationship between the gas-phase inlet and outlet H_2O_2 and the VACES EF calculated from inlet and outlet aerosol masses. Ammonium sulfate aerosol was used as the test aerosol.

not shown). The equilibrium concentration of H_2O_2 in water in contact with gas phase H_2O_2 concentrations used here (governed by Henry's Law) ranges from 2–20 mM, greatly exceeding the measured water bath concentrations ($<450 \mu\text{M}$), thus the water bath is far from being saturated with H_2O_2 . Clearly a large fraction of the gas-phase H_2O_2 lost in the VACES is in the saturator, and the excellent correlation between the inlet gas- and saturator water- H_2O_2 concentrations indicates a simple uptake mechanism. Elevated H_2O_2 was found in samples of ice and water that had accumulated in other parts of the VACES, such as the virtual impactors and condensing tubes. The quantity of this uptake might be expected to vary with the precise geometry of each instrument, and flow rates of individual runs.

Enrichment of H_2O_2 as a By-Product of the Particle Concentration Step

From 3/26 through the end of the study on 4/6, generated ammonium sulfate particles ($6\text{--}13 \mu\text{g}/\text{m}^3$) were directed through the VACES. The wide range of enrichment factors studied provides data to examine the impact of the quantity of aqueous particles passing through the VACES (i.e., the $\text{EF}(\text{mass})$) on the outlet H_2O_2 concentration. Figure 3 shows the relationship between $\text{EF}(\text{H}_2\text{O}_2)$ and $\text{EF}(\text{mass})$, and shows a strong correlation ($R^2 = 0.69$). There were also correlations between the outlet H_2O_2 and the $\text{EF}(\text{mass})$ ($R^2 = 0.58$), outlet H_2O_2 and outlet particle mass ($R^2 = 0.65$) and $\text{EF}(\text{H}_2\text{O}_2)$ and outlet particle mass ($R^2 = 0.76$). There is no correlation (as expected) between inlet H_2O_2 and $\text{EF}(\text{mass})$, nor between $\text{EF}(\text{number})$ and any of the other parameters. The relationship between outlet H_2O_2 concentration and $\text{EF}(\text{mass})$ indicates that the particles are successfully carrying, and as a result, concentrating H_2O_2 through the VACES (the “positive artifact”), counterbalancing depletion caused by H_2O_2 uptake in the water bath. At the high-

est PM mass enrichment factors, the $\text{EF}(\text{H}_2\text{O}_2)$ approaches unity (Table 1).

In the face of competing processes, it is interesting to consider which situation takes place under common VACES operating conditions. It appears that H_2O_2 is depleted from the gas phase in constant proportion to the gas-phase concentration (Figure 2), while the enrichment of H_2O_2 via the particles, in the case of constant particle chemical composition, depends on the particle $\text{EF}(\text{mass})$. Presumably the critical factor is not the particle mass but rather the quantity of liquid water they take up as they pass through the condenser and carry through the virtual impactors in the concentration step.

It is noted that Arellanes et al. (2006) found good agreement within experimental error between $\text{H}_2\text{O}_2(\text{p})$ associated with ambient particles sampled directly and after passing through the VACES. Because urban particles generate far more $\text{H}_2\text{O}_2(\text{p})$ when they are extracted in aqueous solutions than they carry due to equilibrium with the gas phase, any perturbation by the VACES of H_2O_2 dissolved in the particle liquid water is unlikely to be detected in such a comparison of H_2O_2 associated with particles. The contribution of dissolved H_2O_2 in ambient particles is small compared to H_2O_2 generation by ambient particles because they contain little liquid water (both before concentration and after redrying post concentration in the VACES). However, the total amount of H_2O_2 associated with ambient particles (including both dissolved and generated) is essentially always less than 1% of the gas phase concentration (provided the gas phase concentration is above around 100 ppt), and can be ignored when considering the gas phase. The topic of the current study, gas phase H_2O_2 , in contrast, is quite sensitive to gas-liquid partitioning into the “cloud” droplets created as part of the VACES aerosol concentration method.

The Effects of the VACES on Gaseous Ammonia and Nitric Acid

In the absence of particles, our results show that VACES does not affect the concentrations of gaseous ammonia (experiments #5 and 6 in Table 3): when particle-free filtered air was used, the EF value for NH_3 ($\text{EF}(\text{NH}_3)$) was nearly unity. This indicates that, in contrast to the H_2O_2 results, the saturator water bath was not an important sink for $\text{NH}_3(\text{g})$ in our experiments. This is probably because the water bath had reached equilibrium with gaseous ammonia in the air stream, which is possible because of two factors: (1) Unlike in the H_2O_2 experiments, during the NH_3/HNO_3 experiments the water in the bath was not replaced, but rather was topped off with fresh water as needed to maintain the correct level, and (2) the ambient air had relatively high ammonia mixing ratios (an average value of nearly 7 ppbv; Table 3) and low levels of acidity. Based on the average $\text{NH}_3(\text{g})$ mixing ratio in our experiments, and taking into account CO_2 dissolution, we estimate that the saturator bath had a pH of 7 at equilibrium, which is in the range of values measured for Davis fog drops (Anastasio and McGregor 2001). Under these conditions, and assuming efficient dissolution of $\text{NH}_3(\text{g})$ into the water bath, it would have taken approximately 80 h of

TABLE 3
Test matrix and results for ammonium and nitric acid experiments

Expt #	Date	HEPA particle filter	Aerosol	HNO ₃ source	RH _{out} (%)	EF (Number)	EF (NH ₃)	EF (HNO ₃)	N _{inlet}
1	28 Mar	N	ambient	N	29.4	–	1.1	–	–
2	15 Mar	N	ambient	N	47.8	10	2.2	–	–
3	13 Feb	N	ambient	N	21.3	6.6	1	0.075	–
4	13 Feb	N	ambient	N	15.6	–	1.7	0.19	–
5	28 Mar	Y	N	N	26.5	–	1	–	–
6	15 Mar	Y	N	N	33.4	–	0.9	–	–
7	21 Mar	Y	MgSO ₄	N	–	7	3	–	1.7·10 ⁴
8	21 Mar	Y	MgSO ₄	N	–	4.7	2.3	–	1.3·10 ⁴
9	7 Mar	Y	MgSO ₄	N	33.5	11	1.4	–	8.8·10 ²
10	7 Mar	Y	MgSO ₄	N	28.8	8.6	–	–	9.1·10 ²
11	28 Feb	Y	(NH ₄) ₂ SO ₄	N	44.5	4.9	1.7	–	7.3·10 ⁴
12	28 Feb	Y	(NH ₄) ₂ SO ₄	N	34	4.2	0.95	–	2.5·10 ³
13	24 Jan	Y	(NH ₄) ₂ SO ₄	Y (70°C)	47.4	4.9	–	0.1	–
14	12 Jan	N	(NH ₄) ₂ SO ₄	Y (60°C)	–	7.2	3.3	–	–

Temperature in HNO₃ source column is the permeation tube temperature. Cells with no values are either invalid (e.g., sample values that were not at least 3 times greater than the corresponding blank values) or not applicable. EF(N) was determined by the ratio of total particle number concentration measured by SMPS at the inlet and outlet of the VACES. Ambient concentrations during test were as follows: NH₃ = 284 ± 109 nmol/m³ (n = 11), HNO₃ = 29.2 ± 4.2 nmol/m³ (n = 3).

running the VACES for the water bath to reach equilibrium with ambient NH₃(g). Thus equilibrium with ammonia was likely reached during the few weeks of VACES testing prior to our ammonia experiments. However, it is important to note that our result of EF(NH₃) ≈ 1 in the absence of particles is probably strongly dependent upon both of the factors described above: under conditions where the water bath is changed frequently, or where ammonia does not dominate over gas-phase acids, we expect that VACES would deplete NH₃ in a manner similar to that seen for H₂O₂ (EF = 0.37 ± 0.25; see above) or for HNO₃ (EF = 0.12 ± 0.06; see below).

In the presence of particles the VACES system either modestly enriched gaseous ammonia levels or did not affect them. For example, experiments #7–10 with filtered air and added MgSO₄ particles, resulted in EF(NH₃) values in the range of 1.4–3.0. Similarly, experiments #11–12, which used filtered ambient air with added (NH₄)₂SO₄ particles, produced EF(NH₃) values of 0.95 and 1.7. As these experiments show, there was no distinguishable difference or trend between the NH₃ EF and the type of particles used, whether ambient PM, MgSO₄, or (NH₄)₂SO₄. Overall, the VACES system generally had a relatively small ammonia enhancement for both ambient and laboratory-generated particles, with an average (± 1σ) value for EF(NH₃) of 1.9 ± 0.82 (n = 10). However, as described above, we believe that NH₃ would be depleted under conditions where the saturator bath water was changed regularly or where there were lower levels of NH₃ in the air stream.

The relative humidity at the outlet of the VACES (RH_{out}) is another potentially important parameter that might affect the EFs of soluble gases. For example, in the case of ammonium sulfate the efflorescence relative humidity (ERH) is 40%. If evaporation of NH₃ during drying of the aqueous particles after the VACES virtual impactor increases the gas-phase NH₃ concentration, then one would expect higher enrichment of NH₃ when RH_{out} is smaller than ERH since this means all water, and all dissolved NH₃, should evaporate into the air stream. However, this effect was not observed in this study. For example, in experiment 12, where the relative humidity was below the ERH of ammonium sulfate (34.0 ± 0.3%), the EF(NH₃) value was below that of experiment 11 where the RH (45 ± 2.8%) was above the ERH. Taken together, all available data (Table 3) indicates that, within our uncertainties, the output relative humidity does not significantly affect the EF of ammonia. Similarly, EF(NH₃) appeared to be essentially independent of particle number concentration and particle number EF (Table 3).

In contrast to this modest effect of the VACES on ammonia levels, a strong depletion for gaseous nitric acid was observed. As shown by experiments #3, 4, and 13 (Table 3), the average EF for HNO₃ is 0.12 ± 0.06, i.e., the level of HNO₃ in the air after the VACES was nearly an order of magnitude less than the ambient level. HNO₃ may be dissolving in the water bath. However, because nitric acid is notoriously “sticky,” it is also possible that the depletion was caused by it diffusing and sticking to other components in the VACES, such as the drying tube after the virtual impactor.

TABLE 4
Properties of soluble gases used in this study

	H ₂ O ₂	NH ₃	HNO ₃
Physical Henry's law constant (M/atm)	1.0·10 ⁵	61	2.1·10 ⁵

Henry's law values are at 298 K; data from compilation of Sander (1999). Effective Henry's Law constants for NH₃ and HNO₃ will be higher than the physical values because of pH-dependent, acid-base chemistry that enhances aqueous partitioning. However, for the pH conditions expected in the VACES water bath in this study, the effective Henry's law constants will have the same order as the physical values listed here (NH₃ < H₂O₂ < HNO₃).

CONCLUSION

The VACES was chemically characterized at the University of California at Davis from December 2005 to March 2006 to examine the particle EF variation at various ambient conditions and operating parameters. In addition, potential gas phase concentration artifacts for the high solubility gases hydrogen peroxide (H₂O₂), ammonia (NH₃), and nitric acid (HNO₃) were investigated.

The three gases tested had different outcomes, ranging from modest enrichment of NH₃ in particle-laden air (EF(NH₃) = 1.9 ± 0.82), to strong depletion of gaseous HNO₃ (EF(HNO₃) = 0.12 ± 0.06). H₂O₂ fell in between, with EF(H₂O₂) ranging from 0.07 to 0.91 depending on the conditions. Detailed results for H₂O₂ indicate that there are two competing processes at play: 1) Soluble gases can be lost in condensed water in the VACES, particularly in the saturator water bath but also at other locations, and possibly to a small degree in the drying tube, depleting outlet gas-phase H₂O₂; 2) Soluble gases can also be taken up by the particles when they take up water in the saturator/condenser, concentrated when the wet particles pass through the virtual impactors, and re-released once particles are dried. The relative importance of processes 1) and 2) depend on the gas, and appear to follow in order of Henry's law solubilities (Table 4). Process 1) dominates for nitric acid (dry deposition may also contribute), competes for H₂O₂, and is a minor factor for ammonia under our conditions. In contrast, process 2) dominates for ammonia under our conditions, competes for hydrogen peroxide, and is less significant for nitric acid.

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