

**Characterization and Improvement of the  
Versatile Aerosol Concentration Enrichment System  
(VACES)**

**Contract Number 04-332**

**Final Report**

Prepared for the California Air Resource Board  
and the California Environmental Protection Agency

**Submitted by the University of California, Davis and Los Angeles Campuses**

**January 13, 2010**

**Principal Investigators**

Anthony Wexler, University of California, Davis

Cort Anastasio, University of California, Davis

Susanne Paulson, University of California, Los Angeles

## Disclaimer

The statements and conclusions in this Report are those of the contractor and not necessarily those of the California Air Resources Board. The mention of commercial products, their source, or their use in connection with material reported herein is not to be construed as actual or implied endorsement of such products.

## Acknowledgments

This Report was submitted in fulfillment of ARB contract number 04-332, “Characterization of Versatile Aerosol Concentration Enrichment System” by the University of California, Davis and Los Angeles under the partial sponsorship of the California Air Resources Board. Work was completed as of December, 15, 2009.

## Table of Contents

<u>Section</u>	<u>Page</u>
<u>Front Matter</u>	
Title Page	i
Disclaimer	ii
Acknowledgements	iii
Table of Contents	iv
List of Figures	v
List of Tables	v
Abstract	vi
Executive Summary	vii
<u>Part I</u>	I-1
I-A. Introduction	I-3
I-B. Experimental Set-up and Procedures	I-8
I-C. Results and Discussion	I-15
I-D. Summary and Discussion	I-39
References	I-41
<u>Part II</u>	II-1
II-A. Background	II-3
II-B. iVACES system	II-5
II-C. Experimental Results	II-15
II-D. Conclusions and Discussion	II-20
References	II-22

## List of Figures

Figure	Page
I-1. Schematic diagram of VACES	I-9
I-2. Schematic diagram of experimental set-up	I-10
I-3. Coupled gas and aerosol phase H <sub>2</sub> O <sub>2</sub> sampling.	I-14
I-4. Daily averages of the VACES enrichment factors	I-16
I-5. Example of observation on January 25, 2006	I-17
I-6. Example of observations on January 27, 2006	I-18
I-7. Effect of concentration of ammonium sulfate particles on the VACES enrichment	I-19
I-8. Example of VACES enrichment at different sizes for oleic acid particles	I-20
I-9. Averages of VACES EFs at different sizes for four particle compositions	I-21
I-10. Enrichment factor of ammonia vs. total particle concentration at VACES outlet	I-24
I-11. Enrichment factor of ammonia vs enrichment of total particle number	I-25
I-12. Enrichment factor of ammonia versus the relative humidity at the VACES outlet	I-26
I-13. Aqueous phase H <sub>2</sub> O <sub>2</sub> concentration in the saturator region of VACES	I-29
I-14. Correlation between the gas-phase inlet and outlet H <sub>2</sub> O <sub>2</sub> and the VACES EF	I-38
II-1. Schematic diagram of iVACES	II-5
II-2. Diagram of the saturator	II-7
II-3. Diagram of the condenser	II-8
II-4. Photo of the virtual impactor	II-9
II-5. Photo of the air pump unit	II-11
II-6. Performance of the GAST vacuum/pressure pump	II-12
II-7. Diagram of the dryer	II-13
II-8. Two examples of iVACES enrichment for ambient particles	II-16,17
II-9. Example of iVACES enrichment in a new configuration	II-18
II-10. Effect of ambient RH on the humidification rate of the air samples	II-19

## List of Tables

Table	Page
I-1. Test matrix and results	I-23
I-2. Gas and aqueous phase H <sub>2</sub> O <sub>2</sub> , with outlet position post dryer	I-28
I-3. Gas and aqueous phase H <sub>2</sub> O <sub>2</sub> , with outlet position pre dryer	I-28
I-4. Gas Phase H <sub>2</sub> O <sub>2</sub> results	I-30
I-5. H <sub>2</sub> O <sub>2</sub> partitioning into the saturator	I-31
I-6. Aerosol Mass Data for Inlet and Outlet	I-33
I-7. Particle Phase H <sub>2</sub> O <sub>2</sub> and Field Blank Results	I-34
I-8. Outlet H <sub>2</sub> O <sub>2</sub> concentrations measured in 4 mL of extract solution	I-35
I-9. Enrichment Factors for Gas Phase H <sub>2</sub> O <sub>2</sub>	I-36
I-10. Enrichment Factors Measured During Gas and Aerosol H <sub>2</sub> O <sub>2</sub> Sampling	I-37
II-1. Specifications of the air pump	II-12

## **Abstract**

The Versatile Aerosol Concentration Enrichment System (VACES) was developed by Professor Costas Sioutas at the University of Southern California. It is used by numerous toxicologists for studies of the health effects of concentrated ambient particles in laboratory animals. Questions have been raised by these toxicologists as to the reliability of VACES and possible artifacts introduced by it. Part I of this study explored this reliability and a number of potential artifacts, finding that the artifacts were few and minor, and that reliability was a problem that could be solved by some redesign of the VACES. Part II of this study performed some of the redesign alleviating many but not all of the observed artifacts.

## Executive Summary

### Part I

The VACES was both physically and chemically characterized at the University of California at Davis from December 2005 to March 2007 to investigate the particle enhancement factor (EF) variation at various ambient conditions and operating parameters and the gas and particle phase concentration artifacts for the high volatility and high solubility compounds, such as hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), ammonia ( $\text{NH}_3$ ), and nitric acid ( $\text{HNO}_3$ ). The VACES EF for ambient particles, oleic acid, PSL, and ammonium sulfate varied from 5 to 25 in the typical northern California climate conditions during winter-spring, which depends not only on the ambient temperature and relative humidity but also VACES operational parameters. In order to maintain VACES in its optimum operation condition, operators need to be well trained and have substantial experience. Water accumulation in the virtual impactors affected VACES long-term performance. Generally, VACES functions well at normal ambient particle concentrations but performance decreases for high particle number loadings. The average ( $\pm \sigma$ ) value for the EF of  $\text{NH}_3$  in particle-loaded air was  $1.9 (\pm 0.82)$ , which indicates that VACES causes either no enrichment, or a relatively small enrichment, in gaseous  $\text{NH}_3$ . In contrast, a strong depletion for gaseous  $\text{HNO}_3$  was observed ( $\text{EF} = 0.12 (\pm 0.06)$ ), which can be caused by  $\text{HNO}_3$  dissolving in the water bath or sticking to other components in VACES, such as the drying tube after the virtual impactor. Overall gas phase  $\text{H}_2\text{O}_2$  is depleted as indicated by the average EF of  $0.40 (\pm 0.2)$ . Several points within the VACES are responsible for decreased gas phase  $\text{H}_2\text{O}_2$  levels at the outlet, among them water in the saturator region is responsible for a large part of uptake. Other locations include water and ice build up in virtual impactors and condenser tubes, respectively and silica gel used in diffusion dryers. These occurrences seem to be linked with a decline in VACES performance. The particle EF determined by mass during  $\text{H}_2\text{O}_2$  measurements was on average  $10 \pm 7$ . Particle phase  $\text{H}_2\text{O}_2$  levels at the outlet indicate Henry's Law was obeyed and are not indicative of any particle phase enhancement of  $\text{H}_2\text{O}_2$ .

### Part II

An improved Versatile Aerosol Concentration Enrichment System (iVACES) was built at UC Davis and primarily tested in laboratory. The EF was observed between 2 and 10. New iVACES components, such as the warm water supply, air pump unit, and Nafion tubing based dryer, work well and are more convenient for operation and maintenance than those in the original VACES. The porous pipe based saturator is expected to be more stable because the "water level" does not change during the operation. It can humidify the air samples up to 99% when the ambient air is not too dry, but performs poorly when the ambient air is dry. To solve this problem, it is necessary to increase the resident time of air samples inside the saturator by either increasing the length of the saturator or reduce the flow rate of the air samples. Adding additional water steam to the saturator, like the Harvard concentrator (*Demokritou et al., 2002 and Gupta et al., 2004*), would help with increasing the RH and reducing the dependence of iVACES performance on the ambient conditions. Up to now, the iVACES is still following the VACES general procedure, humidifying air samples in the saturator, growing up particles in the condenser, concentrating particle concentrations through the virtual impactor, and returning particles to their original size in the dryer. It may be more efficient to reverse the order of the saturator and the condenser, like the water-based condensational particle counters (*Hering and Stolzenburg, 2005a and Hering et al., 2005b*), where the air is cooled first and particles grow when they are warmed and humidified.

**Part I**

**Characterization of**

**Versatile Aerosol Concentration Enrichment System**

**(VACES)**

Yongjing Zhao, Heejung Jung, Cort Anastasio and Anthony Wexler

University of California, Davis

and

Chuaatemoc Arellanes and Suzanne Paulson

University of California, Los Angeles

November 15, 2007

**Progress Report to ARB**

## **Abstract:**

Experimental assessment on the Versatile Aerosol Concentration Enrichment System (VACES) was performed in the University of California at Davis from December 2005 to March 2007. Enrichment factor (EF) of the VACES was tested as a function of ambient conditions and operating parameters. Gas and particle phase concentration artifacts for the high volatility and high solubility compounds, such as hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), ammonia ( $\text{NH}_3$ ), and nitric acid ( $\text{HNO}_3$ ), were investigated. Results show that, for particles of oleic acid, polystyrene latex (PSL), ammonium sulfate, and ambient, the VACES EF changes between 5 and 25 in typical northern California climate conditions during winter-spring, which depends on the combination effects of ambient conditions (temperature and relative humidity) and VACES operational parameters. In the presence of particles the average ( $\pm \sigma$ ) value for the EF of  $\text{NH}_3$  and  $\text{HNO}_3$  were  $1.9 (\pm 0.82)$  and  $0.12 (\pm 0.06)$  respectively. Although the uncertainty on  $\text{NH}_3$  EF is fairly large, this result indicates that VACES causes either no enrichment, or a relatively small enrichment, in gaseous  $\text{NH}_3$ . In contrast to this lack of VACES effect on  $\text{NH}_3$  levels, a strong depletion for gaseous  $\text{HNO}_3$  is seen nearly an order of magnitude. We speculate that  $\text{HNO}_3$  may be dissolving in the water bath or diffusing and sticking to other components in VACES, such as the drying tube after the virtual impactor. The VACES also depleted gaseous  $\text{H}_2\text{O}_2$  levels, yielding an EF of  $0.40 \pm 0.2$ . Numerous measurements showed that a substantial amount of  $\text{H}_2\text{O}_2$  was taken up by water in VACES. Aqueous phase  $\text{H}_2\text{O}_2$  levels in the saturator ranged from 0.5 – 440  $\mu\text{M}$ , which indicates that most of the  $\text{H}_2\text{O}_2$  lost within the VACES is taken up by the saturator water. Measurements of aerosol phase  $\text{H}_2\text{O}_2$  were also conducted and based on limited data the VACES appears to not enhance aerosol  $\text{H}_2\text{O}_2$  levels.

## **A. Introduction**

Numerous epidemiological studies demonstrate that elevations in PM<sub>10</sub> and PM<sub>2.5</sub> are correlated to increases in acute morbidity and mortality in the population. Also epidemiological studies as part of the southern California Children's Health Study demonstrate that children growing up in more polluted environments experience reduced lung function, which may predispose these populations to acute effects. Yet, the vast majority of the human population and typical animal models do not elicit measurable physiological changes to normal levels of air pollutants. One approach to understand these health effects is to expose animal models to particle concentrations greatly in excess of ambient. One way to do this is to generate particles in laboratory combustion processes, but these particles do not represent the full spectrum of compositions and sizes that humans inhale from the atmosphere. Another way is to increase the concentration of ambient particles. Most ambient aerosol concentrators employ virtual impactors where high pressure drops are needed to concentrate the ultrafine particles that are thought to have significant health effects, but animal models cannot survive at low pressures without special care, and these low pressures are expensive to establish and maintain. Research groups at Harvard University and University of Southern California (USC) have developed a means for concentrating ambient particles with a modest pressure drop in the virtual impactor by first growing the particles by water condensation. Large particles need only a small pressure drop to concentration the particles 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 USC group is portable and relatively inexpensive so is very popular with toxicologists and others investigating the health effects of ambient PM.

Previous studies by the USC group [Kim *et al.* 2000, 2001a, and 2001b and Geller *et al.* 2002] show that the VACES artifacts tested to date are insignificant. In this paper we report on additional work on characterization of the VACES by groups at University of California at Davis (UC Davis) and the University of California at Los Angeles (UCLA). Below we summarize results previous to the current investigations.

### **A.1. Coupling VACES with Rapid Single-particle Mass Spectrometers (RSMS)**

Evaluation of the VACES was conducted in the field at an EPA supersite in Pittsburgh, PA in March 2001 and in a laboratory on the UC Davis Campus in September 2003 using RSMS-3 and RSMS-2. Our field evaluation of coupling VACES and RSMS-3 resulted in the following conclusions [Zhao *et al.*, 2005]: (a) By coupling with the VACES concentrator, hit rates of the RSMS-3 single particle mass spectrometer increased by 5-20 times except when RSMS-3 sampled the smallest and largest particle sizes where its flow rate was off the optimum configuration of the VACES concentrator. (b) Small differences in chemical composition were observed between samples with and without the VACES particle concentrator. The shift of 8-10% particles from one class to another could be caused by the changes in the composition of ambient air, or due to statistical variation in RSMS measurements, or spectrum classification. There was no evidence showing that the VACES particle concentrator introduced the particle shift.

### **A.2. Investigating the VACES impact on hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) concentrations in Particles**

A pilot study to investigate the impact of the VACES on particulate peroxide concentrations was performed in 2004 at the Southern California Supersite Particle Instrumentation Unit when it was located just downwind of the 110 Freeway near downtown Los Angeles [Arellanes *et al.*, 2006]. In this study, peroxide generation by particles in the extraction

solution was monitored [Arellanes *et al.*, 2006]. Because these measurements found that particles generate far more peroxide, by a factor of about 700, than 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.

Fine mode PM was collected using a virtual impactor followed by a filter in parallel with samples collected on filters after passing through the VACES. The results of the comparison between UCLA virtual impactor sample train and the VACES show reasonable agreement (within about 30%) between the VACES and virtual impactor based samples when both instruments were operated with the same size cut. For all but one of the runs, the peroxides were higher in the VACES samples. A portion of this difference is likely due to inaccuracies in the size cuts and flow rates of the two instruments, although how much is not known.

### **A.3. The investigations performed for this Study**

The study described in this current work is to experimentally assess possible artifacts generated by the VACES, focusing on a number of potential physical and chemical characteristics. One artifact relates to possible time variations in the concentration factor, especially near the cut point of the virtual impactor. A number of investigators have observed fluctuations in the VACES EF over time, and this EF fluctuation may be a subtle function of operating and ambient conditions. A second set of artifacts involves the possible concentration enhancement of high volatility, highly soluble vapors, such as hydrogen peroxide, nitric acid and ammonia. These species may partition primarily to the gas phase under "dry" ambient conditions, that is when the relative humidity (RH) is substantially less than saturation but may partition primarily to the particle phase under the high humidity, high liquid water content conditions in and downstream of the saturator. Thus, VACES may also concentrate these species in the gas phase.

Consider a water soluble compound that is highly volatile, such as  $\text{H}_2\text{O}_2$ , so that it partitions primarily to the gas phase when fog and cloud are not present. Many organo-peroxides and other organic and inorganic compounds fit this description. Consider what transpires as air containing  $\text{H}_2\text{O}_2$  and other gas and particulate pollutants enters the VACES. The air first encounters the water bath that warms and humidifies the air. Just as water evaporates from the bath into the air,  $\text{H}_2\text{O}_2$  may condense into the bath water, creating a negative artifact. Next the air is rapidly cooled, supersaturating water in the air and causing the particles to grow rapidly into aqueous drops. Gas to particle conversion of water vapor is likely accompanied by the same for  $\text{H}_2\text{O}_2$  since the particles become dilute droplets in the process. The particles are now concentrated in the virtual impactor and dried, evaporating any  $\text{H}_2\text{O}_2$  that condensed. Thus any  $\text{H}_2\text{O}_2$  that is present upon supersaturation is concentrated along with the particles, creating a possible positive artifact. Thus there are two potential VACES artifacts. The first, the negative artifact, is a reduction in the concentration of high volatility, high solubility compounds because of dissolution into the water bath and/or loss to other surfaces in VACES. The second, a positive artifact, is a potential increase in concentration of volatile, soluble gases that occurs during concentration of the particles. The magnitude of the negative artifact is unknown, but the positive artifact may be as high as the EF of the particles, i.e., a factor of 10 – 30 depending on how VACES is operated.

When using VACES in biosampler mode, that is to collect particle samples in water for instillation exposures, the high volatility, highly soluble compounds may be concentrated in the liquid phase. The biosampler collects particles by first growing them in the saturator and then concentrating them in the virtual impactor, but it omits the diffusion dryer and instead collects the particles with their associated water. In this process there is potential for the particles collected in the biosampler to retain soluble gases that may have collected during the growth and

concentration steps of the process. Assessment on the VACES in biosampler mode was not a part of this study.

The aims of this work include: a) an exploration of the VACES EF as a function of ambient conditions and operating parameters and b) an identification of gas and particle phase concentration artifacts for the high volatility, high solubility compounds with the eventual goal of improving the VACES, if necessary.

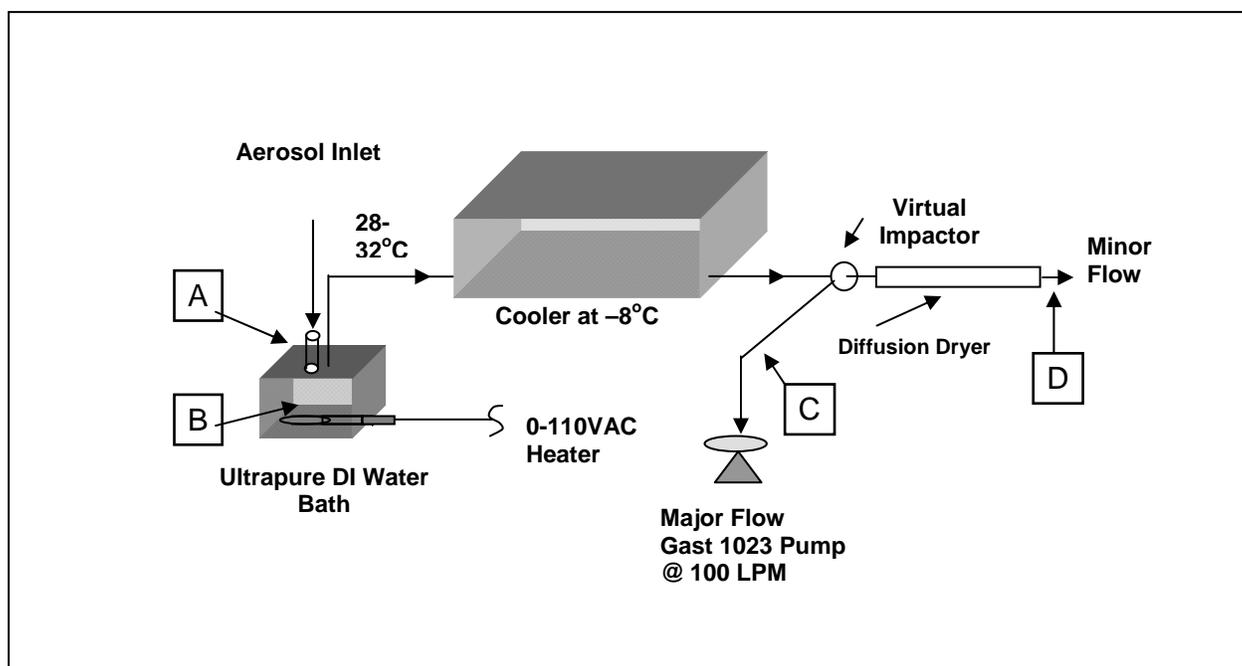
## **B. Experimental set-up and procedures**

### **B.1. VACES principles of operation**

VACES has been described in detail in previous work [*Sioutas et al.*, 1999, *Kim et al.*, 2001a and 2001b, *Zhao et al.*, 2005]. The major components of particle concentration in VACES are briefly summarized here. Schematic diagram of VACES is shown in Figure 1 in which monitoring points A, B, C, and D are also indicated.

Ambient air is drawn at 100 lpm into a saturator, consisting of a tank containing a layer of warm water with air flowing above it. As ambient air passes over the water surface, it is warmed and humidified by heat and mass transfer from the water surface. The warm, humid air now passes through three cylindrical pipes that are cooled by a liquid-air refrigeration unit. The air cools in these pipes, supersaturating and thereby causing water vapor to condense on the aerosol particles resulting in rapid growth. The droplet-laden air then passes through three virtual impactors (built at the University of Southern California under the direction of C. Sioutas) where particles are concentrated in the minor flow air. Finally the air passes through diffusion dryers returning the particles to their original sizes.

Inlet temperature (T) and RH were measured at point A, water and air temperature inside the saturator were measured at point B, the major flow rate was measured at point C, and at point D minor flow rate, outlet air T, and RH were monitored. Points A and D were also the points of up-stream (inlet) and down-stream (outlet) samples, respectively.

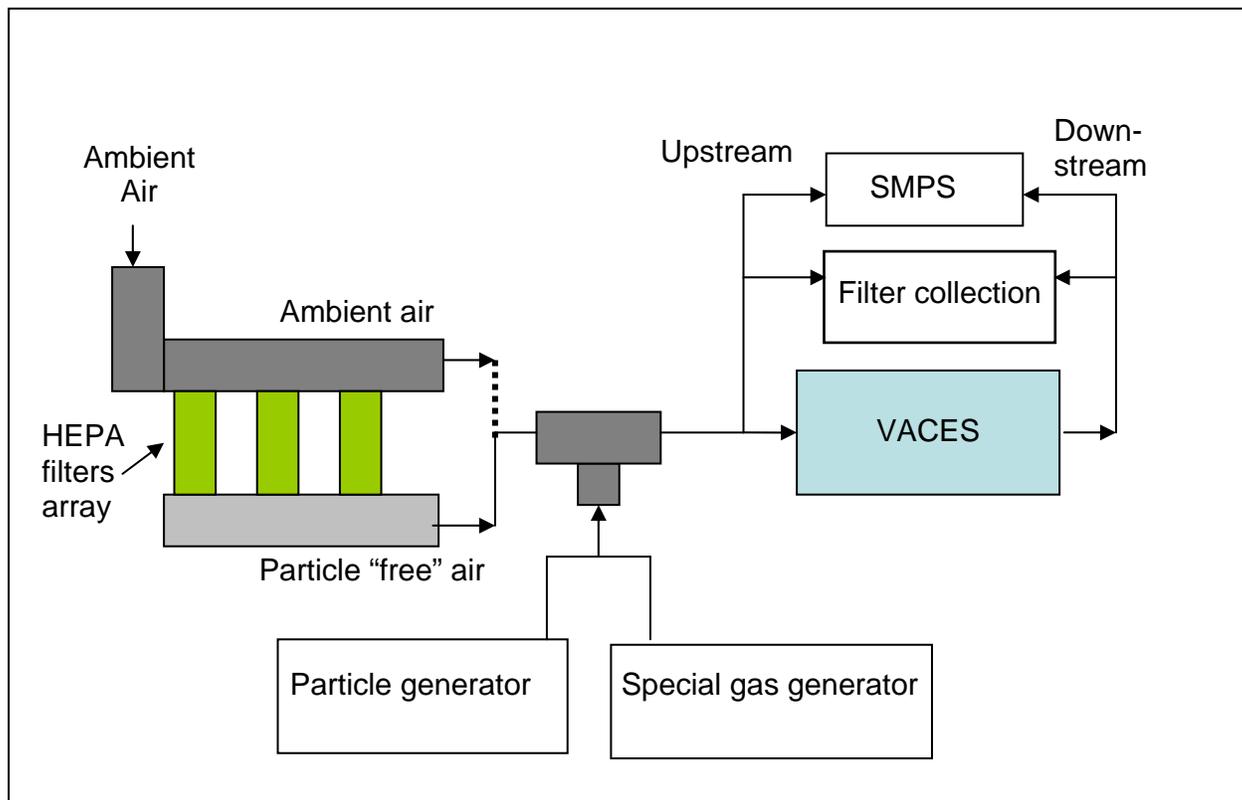


**Figure 1.** Schematic diagram of VACES

## B.2. Instrumental set-up

Set-up of the instruments to characterize the VACES is shown in Figure 2. 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, PN#1602300) was installed before the VACES to remove ambient particles with 99.99% efficiency ( $>300$  nm). Laboratory generated particles (such as PSL and oleic acid) and special gases (such as  $\text{H}_2\text{O}_2$  and  $\text{HNO}_3$ ) were mixed with the inlet ambient air (either particle “free” or not) in a 1-1/4” ID Tee shape stainless steel tubing and then further mixed in a 1-1/4” ID, 180 cm long Teflon tube before entering the VACES. Up-stream and down-stream air/particle samples were sequentially collected from points A and D (see Figure 1) by SMPS (Scanning Mobility Particle Sizer, TSI, Model 3936L25) to measure the VACES EF or by filter-based particle collectors for further mass and composition analysis. An automated stainless steel ball valve switched samples between up-stream and down-stream about every 10 minutes. The VACES EF was experimentally determined by the ratio of down-stream

total particle counts (or mass) to the up-stream value. Physical characterization on the VACES was conducted from mid-December 2005 to mid-March 2006. The chemical characterization schedule is described below in detail.



**Figure 2.** Schematic diagram of experimental set-up

### **B.3. Testing VACES perturbations of gas and particle phase ammonia and nitric acid**

In experiments examining the effect of VACES on gaseous  $\text{NH}_3$  and  $\text{HNO}_3$ , concentrations of these species, and of the corresponding ions in the particles, 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%  $\text{K}_2\text{CO}_3$  to collect  $\text{HNO}_3$ , and the next coated with a 1.5% solution of citric acid (w/v) in methanol to collect  $\text{NH}_3$ . To coat each, 10 mL of solution was pipetted into the denuder, which was then capped, gently agitated for 1 minute, and drained. The denuder was then dried using zero air. In order to minimize contamination, denuders were prepared within 24 hours 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  $\mu\text{m}$  pore, Pall) followed by a Nylon filter (Nylasorb, 1  $\mu\text{m}$  pore, Pall). 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, and 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 up both upstream and downstream of VACES. VACES was run with an upstream flow rate of 325 lpm, of which 15 lpm were pulled through the upstream DFP connected 15 cm in front of the VACES water bath. We used two of the channels downstream of VACES, each with a flow of 5 lpm: one for particle number measurements using the SMPS, and one for the downstream DFP. Both DFP flows were controlled with a critical orifice and flow rates were measured before and after every experiment while VACES was running. DFP sampling times ranged from 1 to 3 hrs depending on the aerosol and gas concentrations at the inlet and outlet of the VACES. The silica gel in the VACES diffusion drier was replaced at the beginning of each experiment day and was used at most for two experiments, the maximum number of DFP experiments that could be done in a day. Before sampling, VACES was run 1 to 2 hrs to reach steady state operation condition (determined by monitoring the outlet temperature and relative humidity). We used ambient air as the default input airstream into VACES, in some cases with a HEPA particle filter upstream of the VACES inlet. In some experiments we added aerosol from the diluted output of a nebulizer containing a solution of either magnesium sulfate or ammonium sulfate. In a few experiments we also added gaseous nitric acid upstream of VACES by using a temperature-controlled permeation source.

After each experimental day the DFPs were removed and denuders were extracted within 1 hour 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  $\mu\text{L}$  of ethanol, adding 8.0 mL of Milli-Q, shaking for 3 hours, and pouring the extract into a Nalgene bottle that was refrigerated until analysis. Concentrations of cations and anions in the denuder and filter extracts were determined using a Dionex DX-120 Ion Chromatograph as described by *Zhang and Anastasio* (2001).

Limits of detection (LODs) for IC measurements of  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ , and  $\text{Mg}^{2+}$  were in the range of 0.1~0.2  $\mu\text{M}$  depending on the species, which is equivalent to 0.6 to 1.6 nmol

in our 6.0 or 8.0 ml extraction volume. A separate DFP for a blank was prepared by the same procedure as for the sample DFP at the same time. The blank DFP was 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 twice the blank level for a given experiment are not reported, while sample values that are between 2 – 3 times the blank level for the analyte are reported but qualified.

#### **B.4. Testing VACES perturbations of gas and particle phase hydrogen peroxide**

The effects of the VACES on  $\text{H}_2\text{O}_2$  in the gas, aqueous and particulate phases are investigated. The effects of the VACES on  $\text{H}_2\text{O}_2$  was monitored by measuring gas and particulate  $\text{H}_2\text{O}_2$  levels just before entering the VACES (inlet) and immediately after exiting the final VACES stage (outlet). Aqueous phase  $\text{H}_2\text{O}_2$  was monitored in the saturator water before and after sampling. Sample collection techniques (gas and particle phase) and  $\text{H}_2\text{O}_2$  quantification have been described in detail (*Arellanes 2006 and Hasson 2003*)

Initial experiments focused on the impact of the VACES on the gas phase concentration of  $\text{H}_2\text{O}_2$ . Gas phase  $\text{H}_2\text{O}_2$  was generated by passing zero generated air through a bubbler containing approximately 200 mL of 1.0 M  $\text{H}_2\text{O}_2$  at a flow of 1 Lpm. This was then mixed with the VACES inlet flow, which was unfiltered ambient air at 315 Lpm. Gas samples were collected at the VACES inlet located approximately 15 cm above the water saturator region and outlet which was located just before or following one of the two diffusion dryers (as noted). Gas sampling was achieved by attaching two independent stripping coils, connected via black conducting tubing, to both inlet and outlet positions. Stripping coils sampled from the VACES at a flow rate of 4.5 Lpm, which was monitored continuously to ensure a constant flow.

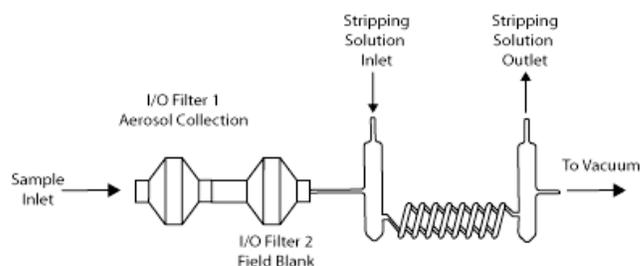
Sampling times were kept at 20 minutes throughout the gas sampling runs. In between runs, the stripping coils were flushed for 10 min. with stripping solution to prevent sample cross contamination. In addition to gas phase sampling, the water in the saturator was also analyzed for  $\text{H}_2\text{O}_2$  by drawing off an aliquot before and after runs. VACES EF was determined by an SMPS which alternately sampled the inlet and outlet flows at the start of each 20 minute run.

The first eight sample runs were conducted with the outlet position situated at the exit of one silica gel diffusion dryer (3/16 and 17). For the next seven sampling runs the outlet position was moved just upstream of the dryer, so that the gas did not come into contact with the silica gel (3/18). The relative humidity was continuously measured at both inlet and outlet. After 3/18 the outlet sampling position was moved to its original position (the exit of a diffusion dryer) and remained there for the remainder of the campaign.

Four experiments per day were conducted on 3/16 and 3/17 and saturator water was sampled at the onset, then after the second and fourth runs. In some cases more doubly distilled water had to be added to the saturator since the level had dropped due to evaporation. On 3/18 a total of seven runs were completed with the new outlet location. Saturator water was analyzed at the onset, then after the fourth and the last run. More water was added after the fourth run, and the new water was also analyzed. From 3/22 to 4/06 aerosols were also collected at both inlet and outlet and analyzed for  $\text{H}_2\text{O}_2$ . Additionally, gas and aqueous phase  $\text{H}_2\text{O}_2$  concentrations were monitored during this period.

Particle phase  $\text{H}_2\text{O}_2$  content was measured at the VACES inlet and outlet with the outlet located at the exit of one of two diffusion dryers. Particles collected were either ambient or generated by an atomizer or nebulizer. The nebulizer (BGI Inc.) contained a 0.5% (w/v) ammonium sulfate (AS) solution and produced particles with a size distribution centered at 420 nm. The atomizer (TSI, Model 3076) was used to generate AS aerosols from a 200 mM AS

solution with a size distribution centered at 40 nm, and was used only on 3/27. Generated AS particles were added to incoming HEPA filtered air at the same point that gas phase  $H_2O_2$  was introduced. The gas and aerosol streams were allowed to mix in a 180 cm corrugated Teflon tube (to enhance mixing) before they reached the inlet. During the first tests (3/24-3/26), gas and particle phase  $H_2O_2$  samples were collected simultaneously by connecting two filter housings in series followed by the stripping coil to the inlet/outlet positions (Figure 3). Because the stripping coil requires a relatively low flow (4.5 lpm), and this limits the quantity of particles collected for analysis, gas and particle sampling was decoupled for subsequent experiments.



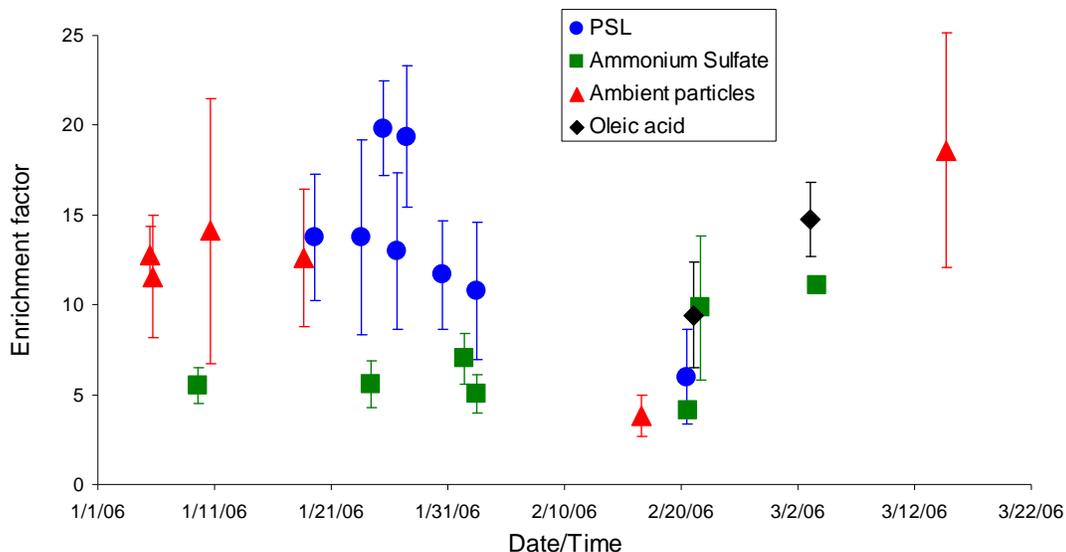
**Figure 3.** Coupled gas and aerosol phase  $H_2O_2$  sampling.

For the next set of experiments, particle samples were collected at 30 Lpm for 2 to 3 hrs. Gas phase  $H_2O_2$  was monitored for 5 min prior to, at midpoint (while particle sampling was stopped) and immediately after sampling was completed. Gas phase  $H_2O_2$  concentrations presented below are an average of these three samples. Saturator water was analyzed for  $H_2O_2$  prior to sampling (new water) and when all sampling had been stopped.

## **C. Results and Discussion**

### **C.1 The effects of VACES on particle concentration and size distribution**

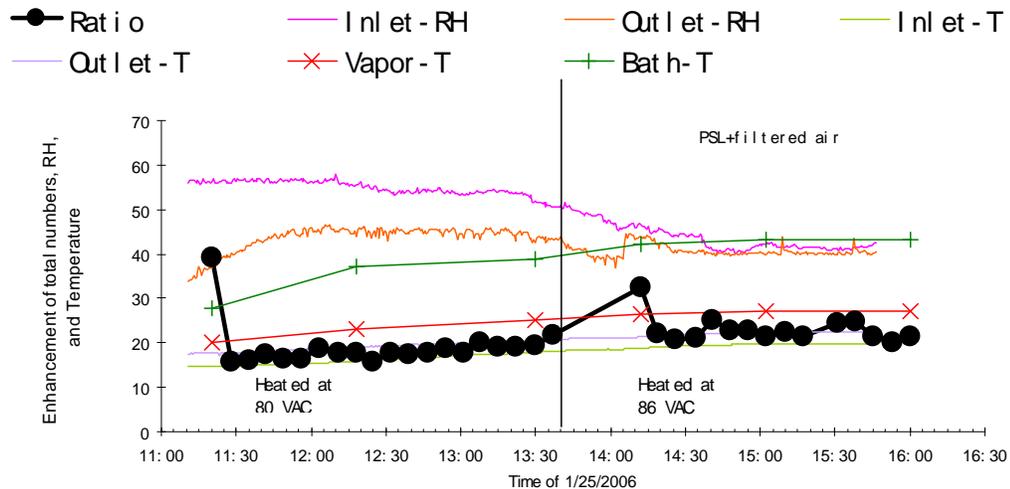
Physical assessment on the VACES was conducted from January to mid-March 2006, focusing on temporal variations in its performance, EF being a key performance indicator. VACES EF here was determined by the ratio of downstream total particle counts to upstream as measured by the SMPS, see Figures 1 and 2. Figure 4 shows daily averages of the VACES EFs observed between January and mid-March 2006 with lab generated particles of PSL, ammonium sulfate, and oleic acid and ambient particles as well. Vertical bars represent standard deviation of the daily values. Generally, the daily averaged VACES EFs varied from 5 to 20. Daily standard deviation in the EF changed from less than 10% to more than 100%. Difference in the EF among the PSL, oleic acid, and ambient particles was not significant. For ammonium sulfate particles, the achieved EFs were below 10, lower than other three particles. Based on our observations, the VACES performance depends on many factors, such as ambient (inlet) T and RH, the setting of heating power that affects water and air temperature inside the saturator, aging of the silica gel in the diffusion dryer, amounts of water accumulated inside the virtual impactor, the inlet particle concentration, and possibly other factors. Several examples of the measurements are presented and discussed below to demonstrate how VACES enrichment changed with time and operating parameters.



**Figure 4.** Daily averages of the VACES enrichment factors.

Figure 5 shows variations in the VACES EF observed on January 25, 2006. The particles were laboratory generated PSL with diameters centered at 90 nm. The PSL concentration from generator was not monitored with the SMPS because it overflowed the upper range of the SMPS CPC. The PSL was diluted by mixing with filtered ambient air before entering the VACES. In this experiment, inlet T and RH, outlet T and RH, major and minor flow rates, and water and air temperatures inside saturator were observed, as indicated in Figures 1 and 2. Up-stream and down-stream samples were measured with the SMPS, also see Figures 1 and 2, to obtain total particle counts and size distributions. The VACES EF was calculated by the ratio of total particle counts from outlet to those from inlet. Major and minor flow rates were very stable during the experimental period from 11:00 to 16:00 on that day. The saturator heating element voltage was initially set at 80 VAC and adjusted to 86 VAC during the middle of the experiment in order to increase the water temperature, but temperatures of water and air inside the saturator are nearly unresponsive to the sudden heater power changes. The VACES EF increased from 15 to 25 as the temperatures of inlet air, water and air inside the saturator increased. Then, the EF

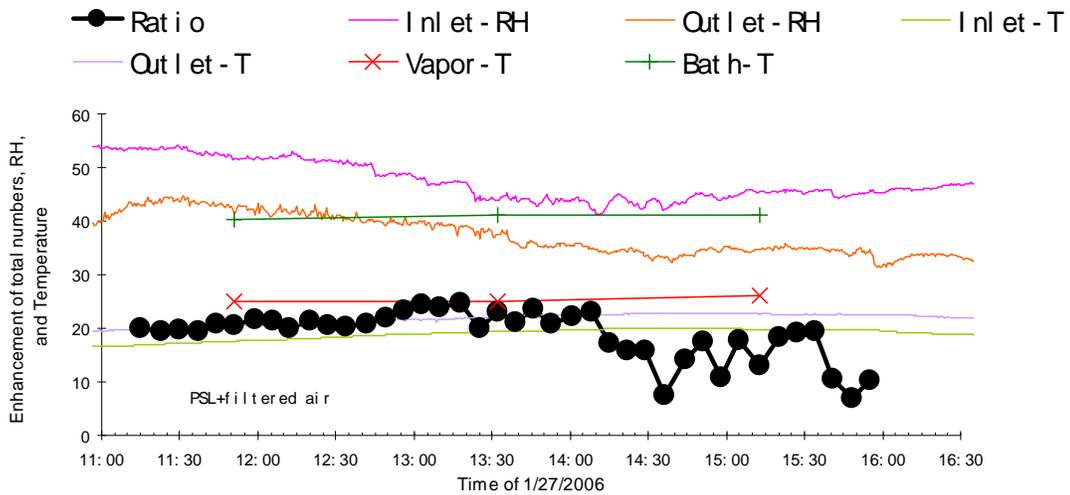
decreased very little before the experiment ended. The VACES EF did not appear to correlate with inlet RH in this experiment although we assumed it could be affected by inlet RH.



**Figure 5.** Example of observation on January 25, 2006.

Figure 6 is another example of the measurement on January 27, 2006 to test the long-term performance of the VACES. Similar to Figure 5, inlet and outlet air temperature and RH and saturator water and air temperature were recorded and shown in the figure. Heating power was not adjusted during the experiment. PSL particles mixed with filtered ambient air were used. EF was calculated by dividing the total outlet particle counts by the total inlet counts that were measured by SMPS. In the first three hours of the experiment, from 11:00 to 14:00, the EF increased slowly from 20 to 25 as the inlet T and saturator T increased. But, the EF suddenly dropped to below 10 at 14:30. As can be seen in Figure 6, the recorded parameters did not change substantially at that point; water accumulation inside the virtual impactor degraded VACES performance. The accumulation rate of water inside the virtual impactor was proportional to the saturator temperature. Increasing the saturator temperature favors the VACES EF but, at the same time, increases water deposition in the virtual impactors reducing

the length of time when VACES performance is optimal. Therefore, the saturator temperature must be set at a reasonable range. Removing accumulated water inside the virtual impactor during VACES operation prolongs optimal performance. Automation in a VACES redesign is recommended.

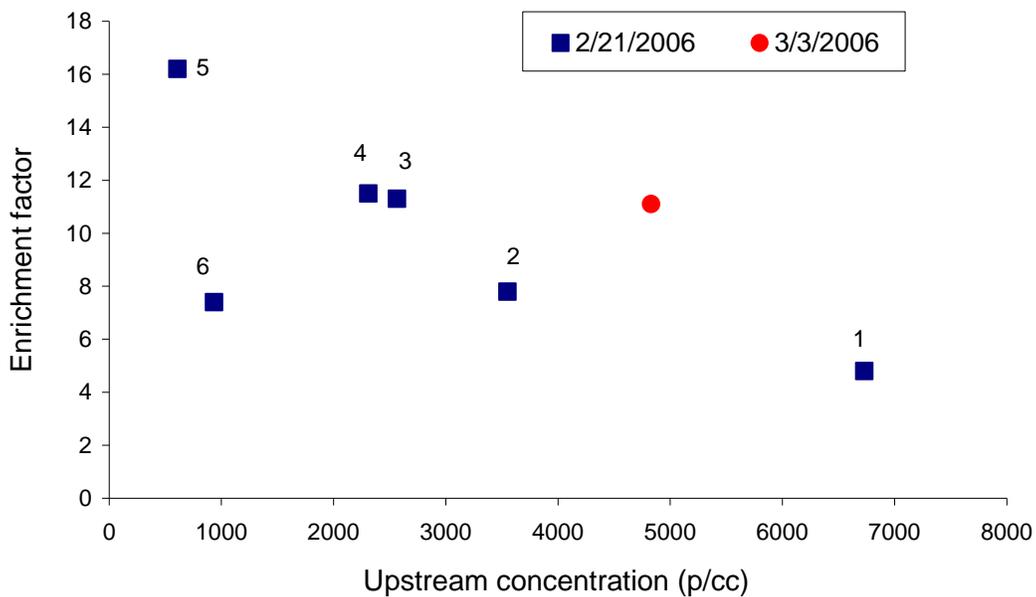


**Figure 6.** Example of observations on January 27, 2006.

As seen in Figure 4 that the VACES enriched of ammonium sulfate particles was not as high as the other three particle compositions. VACES has a finite amount of water in the vapor phase that may condense on the particles to grow them, before the virtual impactor. Here, the AS particle concentration was so high that there was insufficient water vapor to grow the particles. A test was conducted on February 21, 2006 to evaluate the VACES EF as a function of upstream particle concentration (Figure 7). VACES EF decreased from 16 to 5 as the concentration of ammonium sulfate particles increased from 600 to 7000 p/cc. Numbers marked near each data points in Figure 7 indicate time sequence order of the measurements. Data No.1 was collected first and Data No. 6 was last. It took about 2 hours to complete this test. Note

that Data Point 6 is anomalous due to water accumulation in the virtual impactor, as mentioned previously.

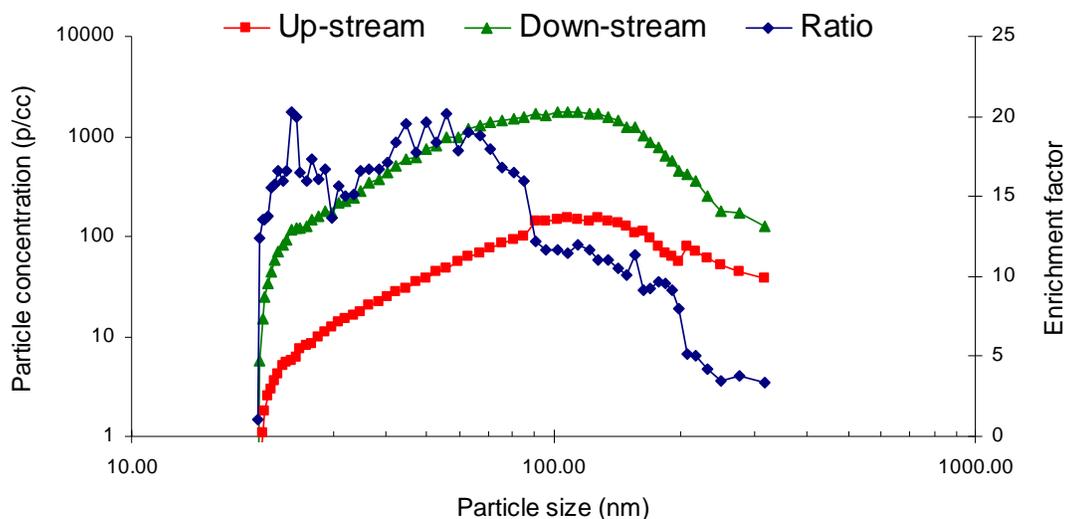
For all the experiments with ammonium sulfate particles, a high outlet RH was always observed (data are not presented), which may be due to the hygroscopic nature of these particles. In this case, water accumulated faster in the virtual impactor than experiments with less hygroscopic particles. Water accumulation in the virtual impactors degrades their performance and is another reason why the daily averaged EFs for ammonium sulfate particles were lower than other particles (see Figure 4).



**Figure 7.** Effect of upstream concentration of ammonium sulfate particles on the VACES enrichment factors. The VACES EFs were determined by total particle counts covering 40-1000nm size range.

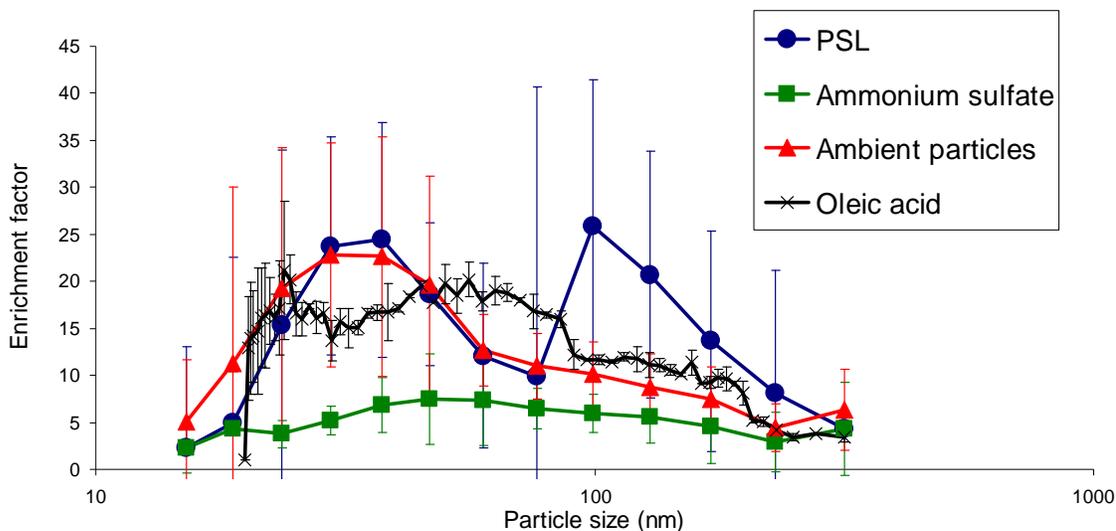
So far, the VACES performance has been presented using the ratio of upstream to downstream total particle counts. Below we show and discuss some results of VACES EF measurements as a function of particle size. In order to avoid artifacts associated with differences between SMPSs, the particle size distributions at both down- and up-stream were measured with a single SMPS and samples were collected by a three-way stainless steel ball valve. The switching time between up-stream and down-stream measurements was about 20 minutes with inlet sampled first and outlet second.

Figure 8 shows an example of size distributions of oleic acid particles before (inlet) and after (outlet) the VACES, and their ratio. The size distributions are similar by the ratio elucidates a size dependence on particle size. The EFs were about 20 at particle sizes below 70 nm and then decreased to below 5 at 300 nm. Since the outlet RH was not the exactly same as the inlet, particles after the diffusion dryer (after VACES concentration) do not necessarily return to their original size. The outlet particle size may shift to larger or smaller sizes relative to the inlet depending on the inlet and outlet RH.



**Figure 8.** Example of VACES enrichment at different sizes for oleic acid particles.

Figure 9 is a summary of the VACES enrichment at different particles for PSL, ammonium sulfate, oleic acid, and ambient air observed from January to mid-March 2006. The EFs at both larger and smaller sizes were lower than those at the middle sizes. At smaller sizes, VACES could not concentrate particles as much as desired due to diffusional loss of particles to the walls. For larger particles, the cut point of the virtual impactor may affect VACES EF, a similar phenomenon observed with our RSMS-3 instruments [Zhao *et al.*, 2005].



**Figure 9.** Averages of VACES EFs at different sizes for four particle compositions.

### C.2. The effects of VACES on gaseous and particulate ammonia and nitric acid

We investigated whether the concentration of gas species such as nitric acid or ammonia can be enriched or depleted inadvertently in the VACES as we previously hypothesized in the section A.3. Prior studies (Zhao *et al.*, 2005; Kim *et al.*, 2001) evaluated performance of VACES in terms of particle number, particle mass and particle composition but not the gas species. In this study we investigated whether VACES affects concentrations of gas species. This is an important question to be answered since VACES are used to enrich particle concentrations to

reduce sampling time for particle health effect studies [De Vizcaya-Ruiz *et al.*, 2006; Kim *et al.*, 2001b].

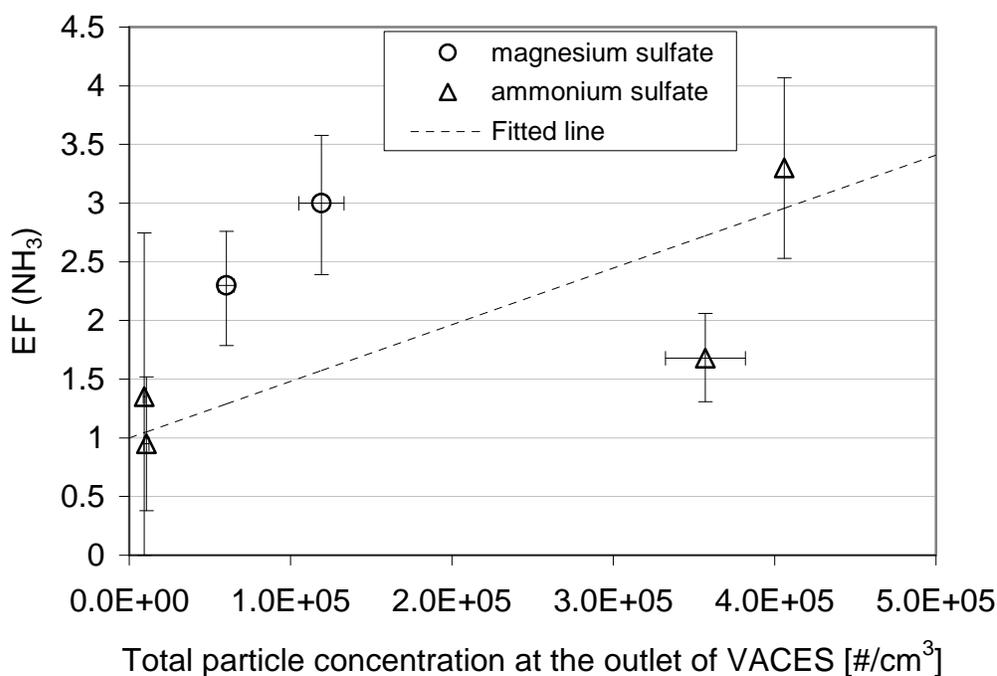
In the absence of particles we expect that VACES should not affect the concentrations of gas species in the sampled air. This expectation is confirmed by experiments (# 5 and 6 in Table 1) where we used particle free, filtered air and the EFs for NH<sub>3</sub> (EF(NH<sub>3</sub>)) are nearly one. However, we also find that there is very little enrichment or depletion of gaseous ammonia even in the presence of particles. For example, experiments #7-10 with filtered air and added MgSO<sub>4</sub> particles, resulted in EF(NH<sub>3</sub>) values in the range of 1.4 to 3.0. Similarly, experiments #11-12, which used filtered ambient air with added (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> particles, produced EF(NH<sub>3</sub>) values of 0.95 and 1.7. As these experiments show, we found no distinguishable difference or trend between the NH<sub>3</sub> EF and the type of particles used, whether ambient PM, MgSO<sub>4</sub>, or (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. Ambient concentrations of gas species of our interest during this test were as follows. NH<sub>3</sub> = 284 ± 109 nmol/m<sup>3</sup> (from 11 data points, Jan-Mar 2006, Davis, CA), HNO<sub>3</sub> = 29.2 ± 4.2 nmol/m<sup>3</sup> (from 3 data points, Jan-Mar 2006, Davis, CA). These results show that the VACES system generally has either no effect, or only a relatively small enhancement, on the levels of gaseous ammonia in the outflow when sampling air with abundant ambient NH<sub>3</sub>. However, it is possible that the VACES water bath would deplete gaseous ammonia in the air stream if the water is not near equilibrium with the gas stream. For example, this could occur if the water had just been changed. In Davis air, which has abundant ammonia levels, we expect that the water bath reaches equilibrium with gaseous ammonia fairly quickly and thus is not a sink for subsequent experiments.

**Table 1.** Test matrix and results.

Expt #	Date	Particle filter	Aerosol	HNO <sub>3</sub> source	RH <sub>out</sub> (%)	EF(N)	EF(NH <sub>3</sub> )	EF(HNO <sub>3</sub> )	N <sub>inlet</sub>
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	0.075	--
4	13-Feb	N	ambient	N	15.6	--	1.7	0.19	--
5	28-Mar	Y	N	N	26.5	--	1.0	--	--
6	15-Mar	Y	N	N	33.4	--	0.90	--	--
7	21-Mar	Y	MgSO <sub>4</sub>	N	--	7.0	3.0	--	1.7E+04
8	21-Mar	Y	MgSO <sub>4</sub>	N	--	4.7	2.3	--	1.3E+04
9	7-Mar	Y	MgSO <sub>4</sub>	N	33.5	11	1.4	--	8.8E+02
10	7-Mar	Y	MgSO <sub>4</sub>	N	28.8	8.6	--	--	9.1E+02
11	28-Feb	Y	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	N	44.5	4.9	1.7	--	7.3E+04
12	28-Feb	Y	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	N	34.0	4.2	0.95	--	2.5E+03
13	24-Jan	Y	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	Y (70°C)	47.4	4.9	--	0.10	--
14	12-Jan	N	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	Y (60°C)	--	7.2	3.3	--	--

Footnotes: Temperature in HNO<sub>3</sub> 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.

While VACES has no large effect on gaseous ammonia levels, our expectation is that any effect might be more apparent under high particle number concentrations. Our working hypothesis is that higher number particles should provide more particle surface area where condensed water coating can dissolve and evaporate surrounding gas species. As shown in Figure 10 we see a modest positive correlation ( $R^2 = 0.29$ ) between EF(NH<sub>3</sub>) and total particle concentration measured at the outlet of VACES. However, due to relatively large uncertainties, the scatter of the data, and the modest range of EFs, we cannot draw any firm conclusions from these results.

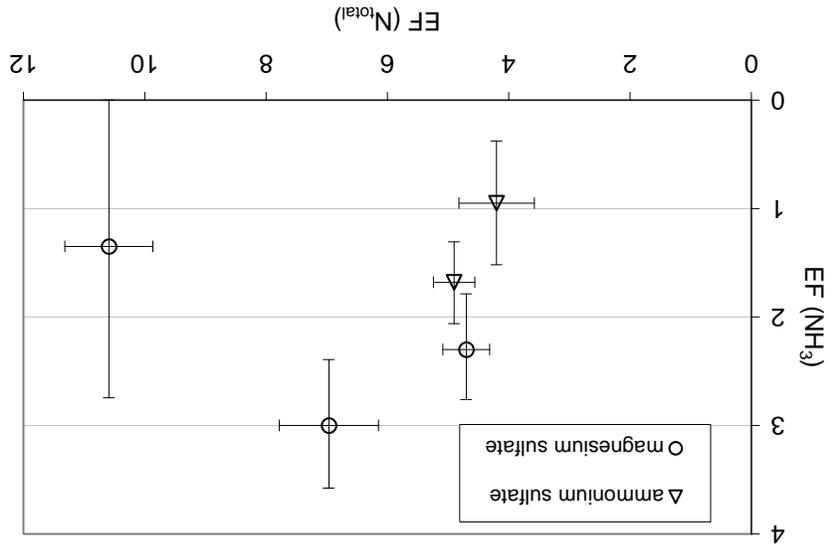


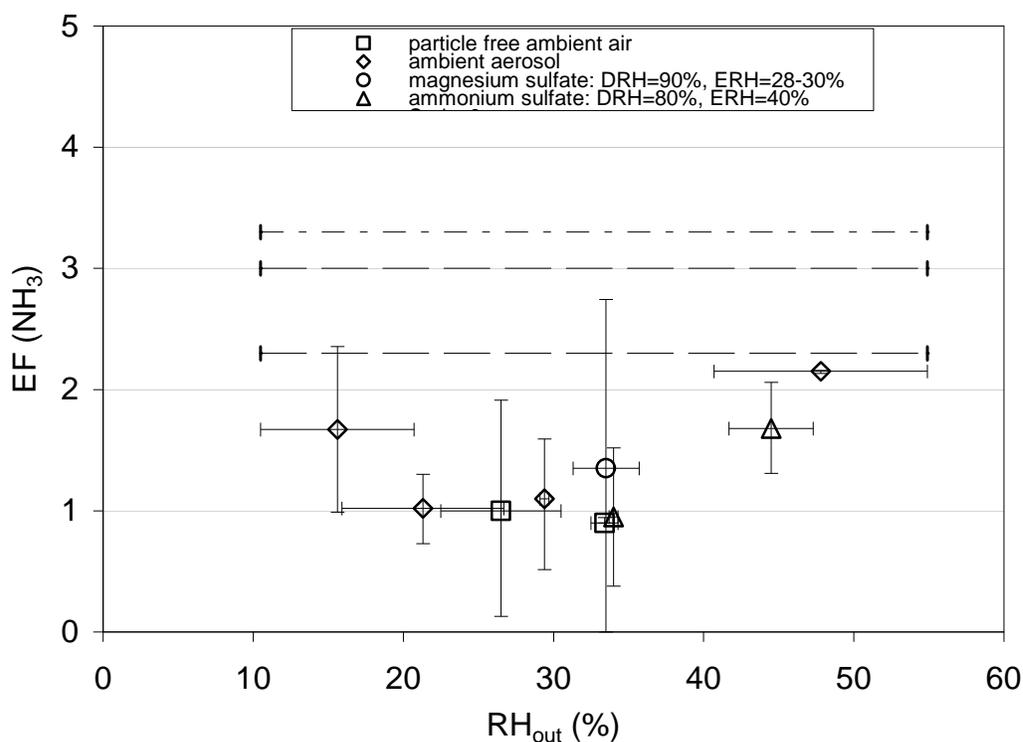
**Figure 10.** Enrichment factor of ammonia vs. total particle concentration at VACES outlet. Dotted line is fitted line:  $R^2=0.29$ ,  $Y=A+Bx$  where  $A=1.00$  and  $B=4.82 \cdot 10^{-6}$

Similarly, we see no good relationship between  $EF(NH_3)$  and  $EF(N_{total})$ , the EF for total particle number concentration. If our hypothesis above was correct, we expect higher values of  $EF(NH_3)$  with higher  $EF(N_{total})$  since a greater wet particle loading is a greater opportunity for  $NH_3$  and other gas-phase species to dissolve then evaporate after particle enrichment through VACES. However, we do not see a clear relationship between these variables, as shown in Figure 11. With the exception of the point at  $EF(N_{total})=10.6$  there is a strong relationship, but this data point has large uncertainty and there are only 5 data points. Thus it is difficult to tell whether there is positive correlation.

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  $NH_3$  during drying of the aqueous particles after the VACES virtual impactor increases the gas-phase  $NH_3$  concentration, then one would expect higher enrichment of  $NH_3$  when  $RH_{out}$  is smaller than ERH since this means all water, and all dissolved  $NH_3$ , should evaporate into the sampled air stream. However, we do not see this effect in our data. For example, in experiment 12, where the relative humidity was below the ERH of ammonium sulfate ( $34.0 \pm 0.3\%$ ), the  $EF(NH_3)$  value was below that of experiment 11 where the RH ( $45 \pm 2.8\%$ ) was above the ERH. Looking at all of the available data in Figure 12 shows that, within our uncertainties, there is no significant effect of the output relative humidity on the EF of ammonia.

**Figure 11.** Enrichment factor of ammonia vs enrichment of total particle number ( $EF(N_{total})$ )





**Figure 12.** Enrichment factor of ammonia versus the relative humidity at the outlet of VACES ( $RH_{out}$ ). X-error bars show  $\pm$  one standard deviation of the measurement, while y-error bars are  $\pm$  one blank value. There are three data with no  $RH_{out}$  data available. These are drawn as three dotted lines extending over the range of RH values from the other experiments. - - line: ammonium sulfate aerosol, - - - line: magnesium sulfate aerosol.

In addition to the variables described above, we have also examined whether the EF for gaseous ammonia is related to total particle concentration measured at the inlet of VACES vs  $EF(NH_3)$  and  $EF(N)$ . In none of these cases was there a significant correlation. In experiments with ambient or laboratory-generated particles the average ( $\pm 1\sigma$ ) value for  $EF(NH_3)$  is  $1.9 \pm 0.82$  ( $n = 10$ ), while the average value is  $0.95 \pm 0.07$  for the two experiments with no particles. While the uncertainties on our ammonia EFs are fairly large, this result indicates that, typically, VACES causes either no enrichment, or a relatively small enrichment, in gaseous ammonia in particle-containing air and that this was essentially independent of particle number concentration, particle number EF, or output relative humidity.

In contrast to this lack of effect of VACES on ammonia levels, we do see a strong depletion for gaseous nitric acid. As shown by experiments #3, 4, and 13 in Table 1, the average EF for  $\text{HNO}_3$  is  $0.12 \pm 0.06$ , i.e., the level of  $\text{HNO}_3$  in the air after VACES is nearly an order of magnitude less than the ambient level. We speculate that  $\text{HNO}_3$  may be dissolving in the water bath and that the bath is an enormous sink for  $\text{HNO}_3$  because its concentration is much lower than ambient ammonia. However, because nitric acid is notoriously “sticky”, it is also possible that the depletion is caused by it diffusing and sticking to other components in VACES, such as the drying tube after the virtual impactor.

### **C.3. The effects of VACES on $\text{H}_2\text{O}_2$ in the gas, aqueous and particle phases**

#### **C.3.1 Gas and Aqueous Phase $\text{H}_2\text{O}_2$ Results**

On 3/16 and 3/17, outlet gas phase  $\text{H}_2\text{O}_2$  was measured downstream of the diffusion dryer. On 3/18, the position of the gas phase sampler was moved upstream of the dryer to provide some insight into the losses associated with the diffusion drier vs. the body of the VACES. Gas and aqueous phase  $\text{H}_2\text{O}_2$  levels for 3/16 and 3/17 are shown in Table 2. The outlet gas phase  $\text{H}_2\text{O}_2$  was consistently lower than the inlet levels, by  $58 \pm 15\%$ , indicating  $\text{H}_2\text{O}_2$  uptake by the VACES. Gas and particle phase  $\text{H}_2\text{O}_2$  levels for 3/18 are shown in Table 3. Similar to the previous outlet location, the gas phase concentration of  $\text{H}_2\text{O}_2$  is reduced by  $50 \pm 9\%$  at the outlet. While removing the diffusion dryer results in slightly lower average  $\text{H}_2\text{O}_2$  uptake, the effect is well within VACES performance variation (see also below) and  $\text{H}_2\text{O}_2$  collection and measurement uncertainty.

**Table 2.** Gas and aqueous phase H<sub>2</sub>O<sub>2</sub>, with outlet position post dryer.

Date	Run #	[H <sub>2</sub> O <sub>2</sub> ] Inlet (ppb)	[H <sub>2</sub> O <sub>2</sub> ] Outlet (ppb)	Outlet/Inlet	Percent Decrease	[H <sub>2</sub> O <sub>2</sub> ] Saturator (μM)
16-Mar	1	4.5	1.2	0.27	73	0.0006
	2	93.3	35.1	0.38	62	13.5
	3	49.5	33.4	0.67	33	10.4*
	4	51.2	28.2	0.55	45	5.9
17-Mar	1	129.6	55.9	0.43	57	7.5
	2	135.1	30.5	0.23	77	44
	3	45.3	21.5	0.48	52	-
	4	73.7	25.5	0.35	65	52.8
Ave				0.42 ± 0.1	58 ± 15	

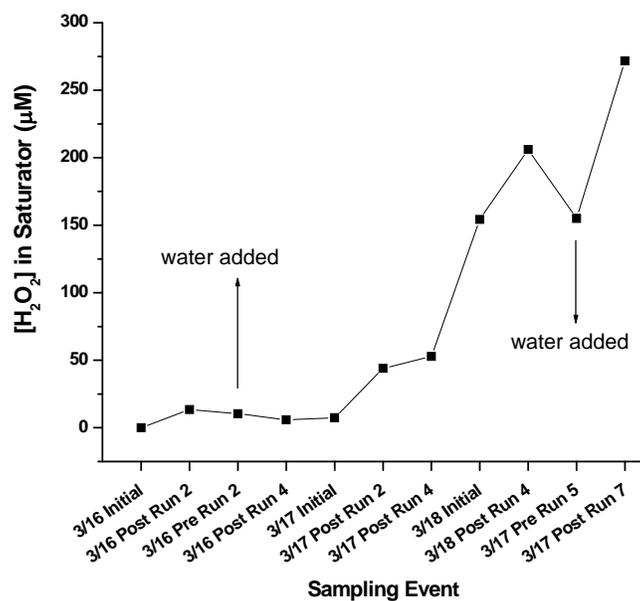
\*Indicates double distilled water was added to existing water.

**Table 3.** Gas and aqueous phase H<sub>2</sub>O<sub>2</sub>, with outlet position pre dryer.

Date	Run #	[H <sub>2</sub> O <sub>2</sub> ] Inlet (ppb)	[H <sub>2</sub> O <sub>2</sub> ] Outlet (ppb)	Outlet/Inlet	Percent Decrease	[H <sub>2</sub> O <sub>2</sub> ] Saturator (μM)
18-Mar	1	77.4	48.4	0.63	37	154
	2	97.6	49.6	0.51	49	-
	3	124.0	66.3	0.53	47	-
	4	163.7	69.5	0.42	58	206
	5	133.6	67.6	0.51	49	155*
	6	136.8	78.1	0.57	43	-
	7	165.9	57.5	0.35	65	272
Ave				0.50 ± 0.1	50 ± 9	

\*H<sub>2</sub>O<sub>2</sub> was allowed to flow through VACES for 2 hrs before this sample was collected.

Figure 13 shows the concentration of H<sub>2</sub>O<sub>2</sub> in the saturator over the 3 sampling days (3/16-3/18) during which the saturator water was not changed (this is the standard VACES operating procedure). Hydrogen peroxide in the saturator increased from less than 0.50 μM on 3/16 to close to 300 μM on 3/18. These initial results prompted a change in protocol, in which the saturator water was drained and the saturator rinsed with doubly distilled water each day and allowed to dry overnight. In the morning approximately 5 L of doubly distilled water was added.



**Figure 13.** Aqueous phase H<sub>2</sub>O<sub>2</sub> concentration in the saturator region of VACES

Table 4 shows gas and aqueous phase results for 3/22-4/6. Overall, similar trends i.e., lower gas phase H<sub>2</sub>O<sub>2</sub> levels at the VACES outlet and uptake of H<sub>2</sub>O<sub>2</sub> by saturator water, are observed. Particles were also sampled at the inlet and outlet during this phase, these results will be discussed in a later section. Gas phase results continue to show substantial H<sub>2</sub>O<sub>2</sub> uptake by the VACES, averaging  $65 \pm 30\%$  (Table 4).

**Table 4.** Gas Phase H<sub>2</sub>O<sub>2</sub> results

Date	run	[H <sub>2</sub> O <sub>2</sub> ] Inlet (ppb)	[H <sub>2</sub> O <sub>2</sub> ] Outlet (ppb)	Gas Phase H <sub>2</sub> O <sub>2</sub> Outlet/Inlet	[H <sub>2</sub> O <sub>2</sub> ] in Saturator water
22-Mar	1	162	5	0.03	29
26-Mar	1	27	2	0.07	-
26-Mar	2	17	4	0.24	40
27-Mar	1	17	12	0.71	26
29-Mar	2	12	2	0.17	-
29-Mar	3	5	2	0.40	34
30-Mar	1	26	4	0.15	-
30-Mar	2	25	2	0.08	25
2-Apr	1	61	61	1.00	57
3-Apr	2	83	71	0.86	176
4-Apr	2	35	16	0.46	108
5-Apr	1	199	69	0.35	-
5-Apr	2	164	55	0.34	438
6-Apr	1	117	23	0.20	-
6-Apr	2	139	28	0.20	322
<b>Ave</b>				<b>0.35</b>	
<b>SD</b>				<b>0.29</b>	

Data in gray shading indicates ambient aerosols sampled using the coupled sampling protocol. Hydrogen peroxide concentration for saturator water is the final measurement of day.

Gas and aqueous phase measurements indicate that the majority of H<sub>2</sub>O<sub>2</sub> has become incorporated into the saturator water. We can roughly compare the total number moles of H<sub>2</sub>O<sub>2</sub> lost in the VACES with the saturator uptake of H<sub>2</sub>O<sub>2</sub> (Table 5). To make these calculations two assumptions are made. 1) It is assumed that the H<sub>2</sub>O<sub>2</sub> bubbler and VACES were operated 7 hrs a day (includes 1 – 1.5 hr VACES warm-up time and idle time between samples). 2) Volume of water in saturator at end of day was 2.5 (about half of original volume). 3) Gas phase H<sub>2</sub>O<sub>2</sub> levels at inlet are an average for the whole day. Using the average measured gas-phase inlet and outlet H<sub>2</sub>O<sub>2</sub> concentrations we can calculate the H<sub>2</sub>O<sub>2</sub> that is lost in the VACES. This can be compared to the quantity of H<sub>2</sub>O<sub>2</sub> collected in the saturator, calculated from the H<sub>2</sub>O<sub>2</sub> concentration measured at the end of the day. The average amount of gas phase H<sub>2</sub>O<sub>2</sub> passing through the VACES that became trapped in saturator water is 70 ± 50% (note this is not the fraction of the H<sub>2</sub>O<sub>2</sub> taken up in the VACES that is observed in the saturator). However, it is noted that on 3/26

and 4/3 the degree of H<sub>2</sub>O<sub>2</sub> uptake by the saturator exceeds 125% (the theoretical limit of 100% plus the uncertainty of ± 25%) yet H<sub>2</sub>O<sub>2</sub> is still detected at the outlet. This is likely an error due to the above assumptions made regarding bubbler and VACES operation time since these parameters were not closely monitored.

**Table 5.** H<sub>2</sub>O<sub>2</sub> partitioning into the saturator

Date	Ave [H <sub>2</sub> O <sub>2</sub> ] Inlet (ppb)	Ave [H <sub>2</sub> O <sub>2</sub> ] Outlet (ppb)	End of Day Saturator [H <sub>2</sub> O <sub>2</sub> ] (μM)	Moles of H <sub>2</sub> O <sub>2</sub> passing saturator	Moles of H <sub>2</sub> O <sub>2</sub> in Saturator	Degree of H <sub>2</sub> O <sub>2</sub> uptake by saturator
16-Mar <sup>1</sup>	50	24	10	2.68E-04	3.96E-06	0.1
17-Mar <sup>1</sup>	96	33	53	5.17E-04	2.11E-05	0.3
18-Mar <sup>1,2</sup>	128	62	272	6.93E-04	1.09E-04	1.0
22-Mar <sup>3</sup>	162	4	29	8.77E-04	7.25E-05	0.1
26-Mar <sup>3</sup>	22	3	39	1.20E-04	1.00E-04	0.8
27-Mar <sup>3</sup>	17	12	27	9.38E-05	6.75E-05	0.7
27-Mar	17	2	4	9.17E-05	1.68E-06	0.1
29-Mar	10	2	34	5.52E-05	1.38E-05	1.6
30-Mar	26	3	25	1.39E-04	9.96E-06	0.4
31-Mar	17	0.1	11	9.33E-05	4.44E-06	0.3
2-Apr	61	61	57	3.28E-04	2.30E-05	0.4
3-Apr	62	92	176	3.44E-04	7.02E-05	1.3
4-Apr	41	27	108	2.21E-04	4.31E-05	1.2
5-Apr	181	62	438	9.79E-04	1.75E-04	1.1
6-Apr	128	25	322	6.90E-04	1.29E-04	1.2
Estimated Uncertainty	10% <sup>4</sup>	10% <sup>4</sup>	5% <sup>4</sup>	15% <sup>5</sup>	10% <sup>5</sup>	25% <sup>5</sup>
<b>AVE</b>						<b>0.71</b>
<b>SD</b>						<b>0.5</b>

<sup>1</sup>Only gas phase H<sub>2</sub>O<sub>2</sub> was monitored.

<sup>2</sup>The outlet position bypassed the diffusion dryer.

<sup>3</sup>These samples were taken in the coupled sampling configuration described in text. After this date a decoupled sampling configuration was used.

<sup>4</sup>Estimated uncertainty is based on prior experiences in measuring h<sub>2</sub>o<sub>2</sub> in aqueous and gas phases using a stripping coil and HPLC-fluorimeter.

<sup>5</sup>Estimated uncertainty in time of VACES and bubbler operation

Based on measurements and comparing gas phase inlet to aqueous phase H<sub>2</sub>O<sub>2</sub> levels the majority of H<sub>2</sub>O<sub>2</sub> taken up by the VACES ends up in water in the saturator. Other locations also appear to take up H<sub>2</sub>O<sub>2</sub>, and presumably other highly soluble species, including the diffusion dryers, condensers and virtual impactors. After a prolonged period of use a build of water in the virtual impactors through condensation along with substantial ice build up in the condensing

tubes. During our experiments up to 15 mL of water was removed from the VI's daily. This water was tested once and found to have an H<sub>2</sub>O<sub>2</sub> concentration of 27 μM. Ice (12 mL) from a single condensation tube was collected and allowed to melt. Analysis for H<sub>2</sub>O<sub>2</sub> revealed a concentration of 7.8 μM. The uptake of H<sub>2</sub>O<sub>2</sub> from these two points is likely vary from day to day, depending on the length of operation, the relative humidity of the sample, and possibly other factors as well. Finally the diffusion dryers packed with silica gel, may also take up some H<sub>2</sub>O<sub>2</sub> (above).

### **C.3.2 Filter Field Blanks: Mass Analysis**

For every aerosol sample run a field blank was collected simultaneously, shown as inlet/outlet (I/O) filter 2 in Figure 3. Filter Field blank mass gain data is shown in Table 6. The accuracy of the mass measurement is about ± 8 - 10 μg, thus any filter blanks that gained more than 10 μg may indicate a leak and aerosol data for these runs are not reported. Data in this category are inlet filter blanks collected on 3/22, 3/27, 3/29, 3/30 and 4/3 1<sup>st</sup> sample, and 3/31, and outlet filter blanks on 3/26, 3/31 and 4/4 1<sup>st</sup> sample. A total of four ambient aerosol samples were collected spanning 3/22 to 3/27. We had hoped to do more ambient sampling however it rained almost constantly during the measurements, thus particle levels were too low to provide meaningful results. Ambient aerosols were sampled using the coupled method (above), hence the filter mass gain at the inlet was below the accuracy of the mass measurement and is not reported; data for 3/29 sample 2 also had too little mass gain to be reliable and are omitted.

**Table 6.** Aerosol Mass Data for Inlet and Outlet.

Date	run	Inlet mass gain ( $\mu\text{g}$ )	Inlet FB mass gain ( $\mu\text{g}$ )	Inlet % FB mass	Outlet mass gain ( $\mu\text{g}$ )	Outlet FB mass gain ( $\mu\text{g}$ )	Outlet % FB mass
22-Mar	1	Low <sup>1</sup>	-	-	148	0	0
26-Mar	2	Low <sup>1</sup>	-	-	17	0	0
27-Mar	1	Low <sup>1</sup>	-	-	132	5	4
27-Mar	1	-	-	-	44	1	2
29-Mar	1	Low <sup>1</sup>	-	-	32	3	9
29-Mar	2	44	5	11	12	0	0
30-Mar	1	-	-	-	38	4	11
30-Mar	2	47	0	0	17	0	0
2-Apr	1	64	0	0	177	2	1
3-Apr	1	-	-	-	58	7	11
3-Apr	2	58	3	5	231	0	0
4-Apr	1	56	10	18	-	-	-
4-Apr	2	58	0	0	102	0	0
5-Apr	1	55	0	0	122	0	0
5-Apr	2	58	0	0	156	0	0
6-Apr	1	69	7	10	94	0	0
6-Apr	2	58	0	0	124	6	5

<sup>1</sup>The mass on the inlet filter was below the mass detection limit for these runs.

### C.3.3 Filter Field Blanks: H<sub>2</sub>O<sub>2</sub> Analysis

Field blank filters were extracted and analyzed for H<sub>2</sub>O<sub>2</sub> in the same manner as filters loaded with particles. In addition, H<sub>2</sub>O<sub>2</sub> in the stripping solution was monitored daily. Peroxide signal from the stripping solution was low and fairly consistent throughout the campaign, averaging  $2.3 \pm 1 \times 10^{-8}$  M. Filter field blanks were reasonably low and reproducible, averaging  $0.35 \pm 0.14$  and  $0.34 \pm 0.14$  nanomoles H<sub>2</sub>O<sub>2</sub> in 4 mL of solution at the inlet and outlet positions, respectively. About a quarter of this signal is due to stripping solution. However, H<sub>2</sub>O<sub>2</sub> signals associated with the generated ammonium sulfate solutions were also small, and on average inlet signals did not exceed the field blanks, and for outlet filters the H<sub>2</sub>O<sub>2</sub> signals exceeded field blanks by about 35% (not shown), and by 55 % for filters with mass gains greater than 120  $\mu\text{g}$ , shown in Table 7. It should be noted that generated ammonium sulfate particles register much

lower H<sub>2</sub>O<sub>2</sub> signals (by factors of 100-1000) than do ambient particles collected in Southern California.

**Table 7.** Particle Phase H<sub>2</sub>O<sub>2</sub> and Field Blank Results.

Date	Outlet Nanomoles H <sub>2</sub> O <sub>2</sub>	Outlet Field Blank Nano-moles H <sub>2</sub> O <sub>2</sub>	Outlet % H <sub>2</sub> O <sub>2</sub> from Inlet Field Blank
2-Apr	0.98	0.12	12
3-Apr	0.50	0.30	59
3-Apr	1.07	0.29	27
5-Apr	0.34	0.24	69
6-Apr	0.56	0.34	61
<b>AVE</b>		0.26	46
<b>SD</b>		0.08	22

Nano-moles of H<sub>2</sub>O<sub>2</sub> observed in 4 mL of extract solution.

### C.3.4 Henrys Law Comparison

The amount of aerosol phase H<sub>2</sub>O<sub>2</sub> measured can be compared to expected uptake predicted by Henrys Law. Using recorded gas phase H<sub>2</sub>O<sub>2</sub> measurements, liquid water content and Henrys law constant for H<sub>2</sub>O<sub>2</sub> (1 X 10<sup>5</sup> M atm<sup>-1</sup>) the aerosol phase concentration of H<sub>2</sub>O<sub>2</sub> can be found. In addition, it is known that the presence of AS in aerosols will increase Henrys Law constant for H<sub>2</sub>O<sub>2</sub> by about a factor of 2, and this is roughly accounted for in the data presented below. The expected H<sub>2</sub>O<sub>2</sub> concentration is determined by first computing the mass fraction of water based relative humidity using the following empirical equation (*Li et al.*, 2000):

$$\begin{aligned} \text{Mass Fraction of Water} = & 2.27515 - 11.147(\text{RH}) + 36.3369(\text{RH})^2 - 64.2134(\text{RH})^3 \\ & + 56.8341(\text{RH})^4 - 20.0953(\text{RH})^5 \end{aligned} \quad (\text{Eqn. 1})$$

Using the total aerosol mass gain and expected mass fraction of water, the amount of water collected is calculated. Overall, the mass fraction of water is low, not exceeding 0.31 which is expected since relative humidities were low as a result of the diffusion dryer. Once the volume of water is determined the number of expected H<sub>2</sub>O<sub>2</sub> moles is calculated and a molarity in 4 mL of extract solution can be found. The expected molarity is compared to the measured H<sub>2</sub>O<sub>2</sub> molarity. Because ammonium sulfate aerosols appear to take up H<sub>2</sub>O<sub>2</sub> approximately according to Henry's Law, H<sub>2</sub>O<sub>2</sub> content on particles collected on filters was only detectable for runs with both relatively high particle concentrations and high gas-phase H<sub>2</sub>O<sub>2</sub> concentrations. The experiments where both conditions were met are the outlet filters on the dates shown in Table 8.

**Table 8.** Outlet H<sub>2</sub>O<sub>2</sub> concentrations measured in 4 mL of extract solution, a comparison of expected to measured values.

Date	RH	Water Mass Fraction	Henry's Law Prediction [H <sub>2</sub> O <sub>2</sub> ] nM	Measured [H <sub>2</sub> O <sub>2</sub> ] nM	Measured to predicted H <sub>2</sub> O <sub>2</sub> comparison
2-Apr	42.1	0.25	169	217	1
3-Apr	49.3	0.31	131	51	0.4
3-Apr	39.8	0.23	237	196	1
5-Apr	38.2	0.21	104	26	0.3
6-Apr	32.5	0.15	19	30	2
6-Apr	32.2	0.15	29	54	2
<b>Ave</b>		<b>0.22</b>			<b>1.1</b>
<b>SD</b>		<b>0.06</b>			<b>0.7</b>

### C. 3.5 Enrichment Factor

The EF was determined using two methods: particle number and mass. Particle number concentrations at the inlet and outlet were determined using an SMPS. EF by mass is determined by weighing the tared filters used for particle collection.

Table 9 summarizes gas phase H<sub>2</sub>O<sub>2</sub> and the EF determined by particle number concentration for initial tests run from 3/16 to 3/18. As indicated above, on 3/18 the outlet position was situated to sample the VACES airstream before it entered the diffusion dryer. For

gas phase samples collected on 3/16 and 17 the EF determined by particle number concentration varies from 1 to 10 and averages  $4 \pm 3$ . On 3/18 the average EF is  $5 \pm 1$ , which slightly higher and was less variable. An EF determined by mass was not possible as aerosols were not collected in this stage of testing. The gas phase inlet/outlet  $\text{H}_2\text{O}_2$  ratio is uncorrelated with the EF base on particle number for this data.

**Table 9.** Enrichment Factors for Gas Phase  $\text{H}_2\text{O}_2$

Date	Run #	Gas Phase $\text{H}_2\text{O}_2$ Outlet/Inlet	EF by Particle Number Concentration
16-Mar	1	0.27	10
	2	0.38	5
	3	0.67	2
	4	0.55	1
17-Mar	1	0.43	7
	2	0.23	2
	3	0.48	2
	4	0.35	2
<b>Ave</b>		<b><math>0.40 \pm 0.1</math></b>	<b>4</b>
18-Mar	1	0.63	6
	2	0.58	6
	3	0.61	6
	4	0.48	3
	5	0.58	6
	6	0.65	4
	7	0.39	3
<b>Ave</b>		<b><math>0.50 \pm 0.1</math></b>	<b>5</b>

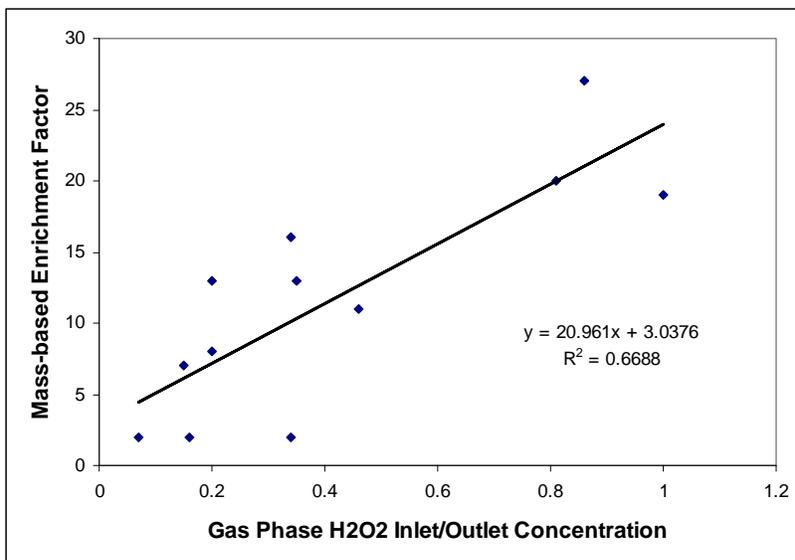
Table 10 summarizes all gas and aerosol phase outlet to inlet ratios as well as EFs determined by particle number concentration and mass. After Apr 2<sup>nd</sup> particle number concentrations were not recorded due a problem with the SMPS. The EF determined by mass is, on average,  $10 \pm 7$  with a range of 2 to 27. On average the gas phase  $\text{H}_2\text{O}_2$  concentration at the outlet is 54% less than at the inlet. A ratio that is very similar to the initial gas phase only  $\text{H}_2\text{O}_2$  during testing.

**Table 10.** Enrichment Factors Measured During Gas and Aerosol H<sub>2</sub>O<sub>2</sub> Sampling.

Date	run	Gas Phase H <sub>2</sub> O <sub>2</sub> Outlet/Inlet	Outlet RH	Inlet RH	EF (Mass)	AVE EF (particle number concentration)
22-Mar	1	0.028	31.6	37.7	- <sup>1</sup>	8
26-Mar	1	0.071	29.7	31.8	- <sup>1</sup>	10
26-Mar	2	0.242	27	30.5	- <sup>1</sup>	3
27-Mar	1	0.699	36.2	49.6	- <sup>1</sup>	1
29-Mar	2	0.16	37.6	42.3	2	4
29-Mar	3	0.34	37.7	49.3	2	5
30-Mar	1	0.15	37.5	47.2	7	5
30-Mar	2	0.07	37.3	48.3	2	6
2-Apr	1	1.00	39.8	52.5	19	6
3-Apr	2	0.86	42.2	55.4	27	
4-Apr	1	0.81	34.4	41.1	20	
4-Apr	2	0.46	38.2	49	11	
5-Apr	1	0.35	32.5	38.1	13	
5-Apr	2	0.34	32.2	35	16	
6-Apr	1	0.20	31.6	37.7	8	
6-Apr	2	0.20	29.7	31.8	13	
<b>AVE</b>		<b>0.46</b>			<b>10</b>	<b>5</b>
<b>SD</b>		<b>0.2</b>			<b>8</b>	<b>3</b>

<sup>1</sup>The inlet mass concentration was below the mass detection limit. Gray shading indicates gas and aerosol H<sub>2</sub>O<sub>2</sub> were sampled simultaneously, and that ambient aerosols rather than generated ammonium sulfate aerosols, were sampled.

The data in Table 10 suggest little relationship between the EFs calculated based on particle numbers and from mass collected on filters. Further, there is no correlation between number based particle EF and the loss of gas-phase H<sub>2</sub>O<sub>2</sub> in the VACES. There is, however, interestingly, a reasonably strong correlation between the mass-based EF and the uptake of H<sub>2</sub>O<sub>2</sub> in the VACES, shown in Figure 14. The mass-based EF and both the inlet and the outlet relative humidity are at most weakly correlated.



**Figure 14.** Correlation between the gas-phase inlet and outlet H<sub>2</sub>O<sub>2</sub> and the VACES EF calculated from inlet and outlet aerosol masses.

## D. Summary and discussion

The VACES was both physically and chemically characterized at the University of California at Davis from December 2005 to March 2007 to investigate the EF variation at various ambient conditions and operating parameters and the gas and particle phase concentration artifacts for the high volatility and high solubility compounds, such as hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), ammonia ( $\text{NH}_3$ ), and nitric acid ( $\text{HNO}_3$ ). The VACES EF for ambient particles, oleic acid, PSL, and ammonium sulfate varied from 5 to 25 in the typical northern California climate conditions during winter-spring, which depends not only on the ambient temperature and relative humidity but also VACES operational parameters. In order to maintain VACES in its optimum operation condition, operators need to be well trained and have substantial experience. Water accumulation in the virtual impactors affected VACES long-term performance. Generally, VACES functions well at normal ambient particle concentrations but performance decreases for high particle number loadings. The average ( $\pm \sigma$ ) value for the EF of  $\text{NH}_3$  in particle-loaded air was  $1.9 (\pm 0.82)$ , which indicates that VACES causes either no enrichment, or a relatively small enrichment, in gaseous  $\text{NH}_3$ . In contrast, a strong depletion for gaseous  $\text{HNO}_3$  was observed (EF =  $0.12 (\pm 0.06)$ ), which can be caused by  $\text{HNO}_3$  dissolving in the water bath or sticking to other components in VACES, such as the drying tube after the virtual impactor. Overall gas phase  $\text{H}_2\text{O}_2$  is depleted as indicated by the average EF of  $0.40 (\pm 0.2)$ . Several points within the VACES are responsible decreased gas phase  $\text{H}_2\text{O}_2$  levels at the outlet, among them water in the saturator region is responsible for a large part of uptake. Other locations include water and ice build up in virtual impactors and condenser tubes, respectively and silica gel used in diffusion dryers. These occurrences seem to be linked with a decline in VACES performance. The particle EF determined by mass during  $\text{H}_2\text{O}_2$  measurements was on average  $10 \pm 7$ . Particle

phase  $\text{H}_2\text{O}_2$  levels at the outlet indicate Henry's Law was obeyed and are not indicative of any particle phase enhancement of  $\text{H}_2\text{O}_2$ .

## References

- Arellanes, C., S.E. Paulson, P.M. Fine and C. Sioutas, Exceeding of Henry's Law by Hydrogen Peroxide Associated with Urban Aerosols. *Envir. Sci.Tech.* (2006), DOI: 10.1021/es0513786.
- De Vizcaya-Ruiz, A.; Gutierrez-Castillo, M. E.; Uribe-Ramirez, M.; Cebrian, M. E.; Mugica-Alvarez, V.; Sepulveda, J.; Rosas, I.; Salinas, E.; Garcia-Cuellar, C.; Martinez, F.; Alfaro-Moreno, E.; Torres-Flores, V.; Osornio-Vargas, A.; Sioutas, C.; Fine, P. M.; Singh, M.; Geller, M. D.; Kuhn, T.; Miguel, A. H.; Eiguren-Fernandez, A.; Schiestl, R. H.; Reliene, R.; Froines, J. Characterization and in vitro biological effects of concentrated particulate matter from Mexico City. *Atmospheric Environment* (2006), 40 (Suppl. 2), S583-S592
- Geller, M.D., S. Kim, C. Misra, C. Sioutas, B.A. Olson, and V.A. Marple, A methodology for measuring size-dependent chemical composition of ultrafine particles *Aerosol Sci. & Tech.* (2002), 36, 748-762.
- Hasson, A.S. and S.E. Paulson, An Investigation of the Relationship between Gas-phase and Aerosol-borne Hydroperoxides in Urban Air. *J. Aerosol Sci.* (2003), 34: 459-468.
- Kim, S., M.C. Chang, D. Kim, and C. Siouats, C, A new generation of portable coarse, fine, and ultrafine particle concentrators for use in inhalation toxicology, *Inhal Toxicol* (2000), 12, 121-137.
- Kim, S., P. Jaques, M.C. Chang, J.R. Froines, and C. Sioutas, A versatile aerosol concentrator for simultaneous *in vivo* and *in vitro* evaluation of toxic effects of coarse, fine and ultrafine particles: Part I: Laboratory evaluation, *J. Aerosol Sci.* (2001a), 32, 1281-1297.
- Kim, S., P. Jaques, M.C. Chang, C. Xiong, S.K. Friedlander, and C. Sioutas, A versatile aerosol concentrator for simultaneous *in vivo* and *in vitro* evaluation of toxic effects of coarse,

- fine and ultrafine particles: Part II: Field evaluation, *J. Aerosol Sci.* (2001b), 32, 1299-1314.
- Sioutas, C., S. Kim, and M.C. Chang, Development and evaluation of a prototype ultrafine particle concentrator, *J. Aerosol Sci.* (1999), 30, 1001-1017.
- Zhang, Q. and Anastasio, C., Chemistry of Fog Waters in California's Central Valley. Part 3. Concentrations and Speciation of Organic and Inorganic Nitrogen, *Atmospheric Environment* (2001), 35(32), 5629-5643.
- Zhao, Y., Bein, K.J., Wexler, A. S., Misra, C., Fine, P. M., Sioutas, C., Field evaluation of the versatile aerosol concentration enrichment system (VACES) particle concentrator coupled to the rapid single-particle mass spectrometer (RSMS-3), *Journal of Geophysical Research* (2005), 110, D07S02, doi:10.1029/2004JD004644

## **Acknowledgements.**

This project was supported by the California Air Resources Board (CARB) on agreement number 04-332. Authors would like to thank UC Davis and USC colleagues for their assistance operating the VACES.

# **Part II**

## **Improved Versatile Aerosol Concentration Enrichment System (iVACES)**

**(March 2007 – March 2010)**

By

Yongjing Zhao and Anthony S. Wexler

Air Quality Research Center

University of California-Davis

One Shields Ave. Davis, CA 95616

October 27, 2009

**Abstract:**

Based on our finding in the first part of this project, Part I. Characterization of Versatile Aerosol Concentration Enrichment System (VACES) from December 2005 to March 2007, an improved Versatile Aerosol Concentration Enrichment System (iVACES) was developed and tested at the University of California, Davis from March 2007 to October 2009. Laboratory tests were performed to characterize the enrichment factor (EF) of the iVACES at different ambient conditions and operating parameters. The iVACES EF changes between 2 and 10 in typical northern California climate conditions during summer-fall seasons, depending on the combined effects of ambient conditions (temperature and relative humidity) and iVACES operational parameters. The remaining problems are discussed and further improvements are suggested.

## **A. Background**

Versatile Aerosol Concentration Enrichment System (VACES) was tested experimentally at UC Davis from December 2005 to March 2007. Major findings include:

### **Engineering Problems**

- 1) A reduction in inlet flow may cause collapse of the water bath from the drop in pressure in the system.
- 2) The water in the water bath may completely evaporate, and destroy the heater and/or cause a fire, without continuous oversight.
- 3) The ceramic bath heater is highly susceptible to breakage.
- 4) Water in the bath evaporates and must be replaced manually.
- 5) Water accumulates in the virtual impactor, which must be removed and emptied periodically (limiting continuous operation time).

### **Functional Problems**

- 6) The concentration enrichment factor depends on ambient temperature and relative humidity and the bath temperature and does not reach values greater than 10 for a wide range of conditions.
- 7) High particle inlet concentrations are not further concentrated well, because there was insufficient condensed water to grow all particles large enough to pass the virtual impactor.
- 8) The optimum bath temperature depends on the temperature and relative humidity of the input and output air masses.
- 9) The silica gel dryer saturates and must be replaced daily.

Solutions to the above set of nine problems were proposed which involve construction of and/or replacement upgrades to VACES. As requested by the California Air Resources Board, these modifications and additions to the system will be tested over a wide range of ambient

conditions to ensure that uniform concentration enrichment factors are achievable and independent of ambient relative humidity, temperature and particle concentration and that the system returns the outflow to back to ambient temperature and relative humidity.

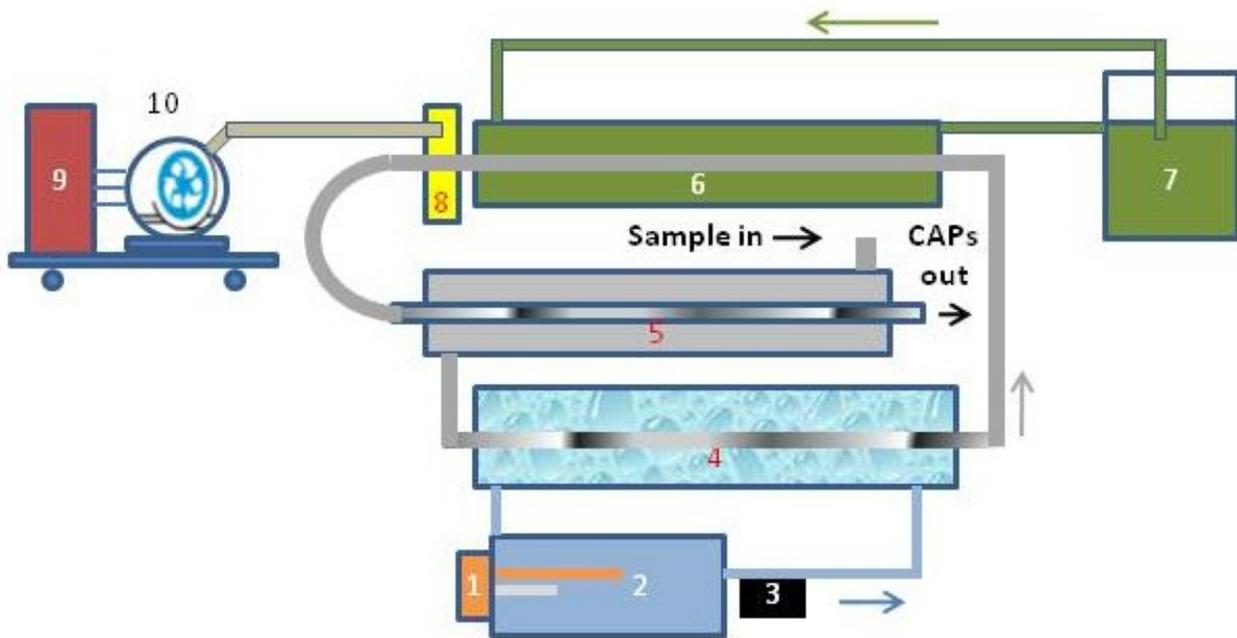
The goal of this study is to design a new particle enrichment system, iVACES, that overcomes as many of the above problems as possible and therefore improves the VACES performance to make it more stable and easy to operate over a wide range of ambient conditions. Ideally, the improved system concentrates particles uniformly over the range 30nm to 500 nm.

Details of the improved VACES (iVACES) design are described and test results are presented in this report.

## B. iVACES system

### B.1. Schematic diagram of iVACES

The schematic diagram of iVACES is shown in [Figure 1](#). The iVACES consists of the following major components that are also part of the VACES system: saturator, condenser, virtual impactor, and dryer. In addition, the iVACES system contains a warm water supply that



**Figure 1.** Schematic diagram of iVACES. 1-Heater with thermostat, 2-Water reservoir, 3-water pump, 4-saturator, 5-dryer, 6-condenser, 7-Chiller, 8-Virtual Impactor, 9-VFD, 10-Vacuum pump. In general, air path is shown in gray where the gradient indicates the changes in air humidity, warm water in light in blue, coolant path in green, and arrows show the flow direction.

includes a water reservoir, heater with thermostat, and water pump to provide temperature controlled warm water to the saturator. The Chiller circulates the cold coolant to and from the condenser. The air pump unit draws major air flow through the iVACES.

Operation principles of the iVACES is the same as VACES which has been described in detail in previous work [*Sioutas et al.*, 1999, *Kim et al.*, 2001a and 2001b, *Zhao et al.*, 2005] and also summarized in the Part I of this report.

All of the iVACES components are described in the following sections.

## **B.2. Warm water supplier**

The warm water supply was added to the VACES system to overcome engineering problems (2)-(4).

The warm water supply includes a heater with thermostat, a water reservoir, and a water pump. It provides temperature controlled warm water to the saturator. The water reservoir is made of a 3" CPVC pipe. The pipe plug immersion heater (P/N=PD451-OMC37, OGDEN) has a thermostat to control the water temperature from 60 to 250°F. The heater element is immersed in the water reservoir to directly heat the water and the temperature sensor of the heater is also inside the water reservoir to monitor the water temperature and feed back the signal to the thermostat to control the water temperature. The water pump (Model 809 series, March Pumps) supplies warm water to the condenser with a maximum capacity of 3.1 GPM at 1.8 psi pressure.

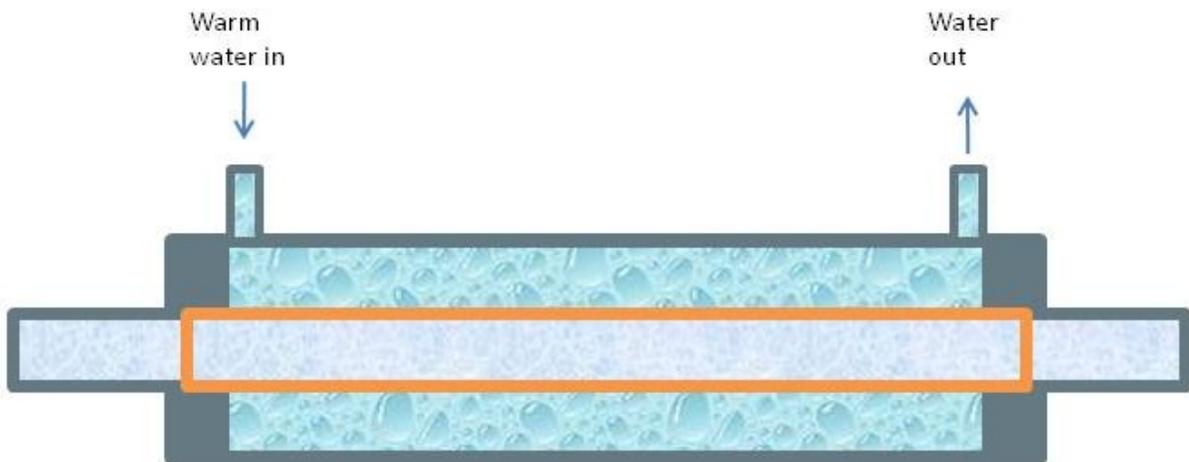
The warm water supply has a drain valve at the bottom of the reservoir which makes it easier to replace the DI water. The water reservoir stores more water to enables the iVACES to operate longer than VACES. It is easy to add additional water to the reservoir at any time during the experiment because it has an open port. The heat element is made of stainless steel tubing so it is hard to physically break. The thermostat on the heater not only controls the water temperature but also prevents the water from overheating.

## **B.3. Saturator**

Unlike the VACES, the saturator in iVACES is separated from the water supply. This design, together with the use of a porous pipe in the saturator, is to overcome engineering problems (1) – (4).

**Figure 2** is a diagram of the saturator. The outer tube is a 3 foot long 3” diameter CPVC pipe and the inside one is a 2.5 foot long 1” diameter porous pipe with 25-40 micron pore size. Warm water flows between the CPVC and porous pipes, wetting the inside of the porous pipe. Air samples flowing inside the porous pipe exchange heat and mass with the water vapor and becoming warm and humidified when they exit from the saturator.

Because the porous pipe is made of Nylon and the wall thickness is  $\frac{1}{4}$ ”, it will not collapse in the event that the pressure drops inside the porous pipe due to reduction in inlet flow caused by inlet blockage. Because the water “surface level” never changes in the iVACES saturator and water temperature is controlled, the heat and water vapor exchange to the air sample does not vary substantially during an experiment.



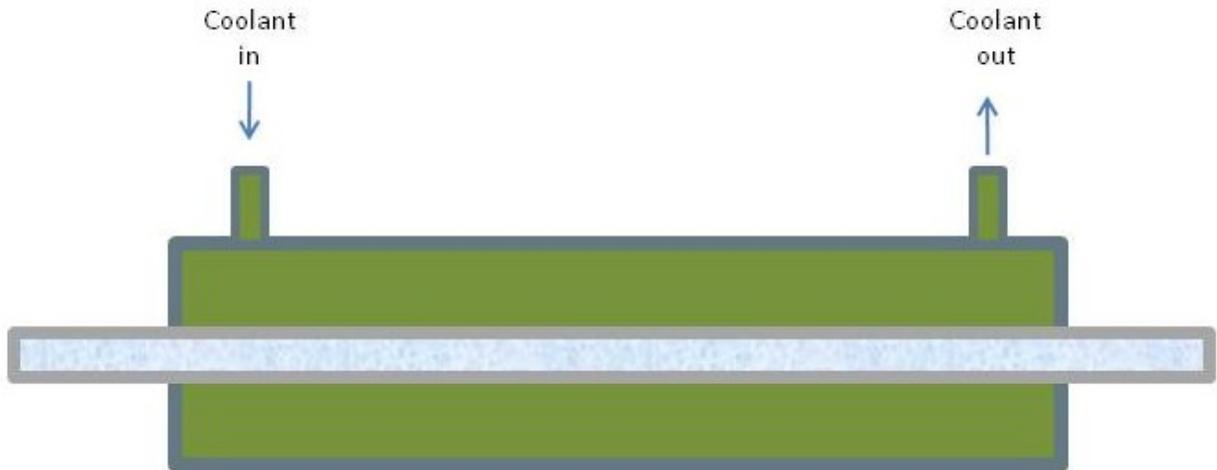
**Figure 2.** Diagram of the saturator. The porous pipe is shown in orange color.

#### B.4. Chiller

The chiller is a commercial refrigerator (2095 Bath & Circulator model, Forma Scientific) with 7.5 gallon coolant capacity that can be cooled down to -20°C.

### B.5. Condenser

**Figure 3** shows a diagram of the condenser consisted of a 2" PVC pipe outsider and a 1" OD stainless steel (SS) tube, whose inside tube is 3 feet long. This condenser is nearly the same as that in VACES except for the brass Swagelok fittings used for the couplings between the PVC pipe and the SS tubing to prevent the leak of high pressure coolant. A smaller size SS tubing of ¾" OD was tested to compare with the 1" OD SS tubing. The results show that 1" OD tubing had caused less water accumulation problem, possibly because the air flow is less turbulence.



**Figure 3.** Diagram of the condenser. Outsider is a 2" PVC pipe and insider is a 1" OD SS tubing of 3 feet long. Swagelok fittings are used between at the joins between PVC pipe and the SS tubing.

### B.6. Virtual impactor

The virtual impactor is nearly the same as that in VACES except for the improved engineering construction. Instead of using glue for the joints, SS pipe adapter for the major flow is connected to the main body with NPT threads and the SS tubing for the minor flow is attached to the main body with flange fittings. A photo of the new virtual impactor is illustrated in **Figure 4**. The cut point of the virtual impactor is about 2.3 micron when the major flow rate is 100 L/min which means that particles above 2.3 micron in size go to minor flow stream (5 L/min) and those below the cut point are removed with the major flow stream. If all particles in the air sample can be grown to larger than 2.3 micron after the saturation-condensing procedure, the particle concentration in the minor flow stream would be 20 times higher than that in the air samples, which is called the enrichment factor (EF) of the iVACES:

$$EF = \frac{\text{Concentration in minor flow}}{\text{Concentration in samples}} = \frac{100}{5} = 20$$



**Figure 4.** Photo of the virtual impactor. Its cut point is 2.3 micron.

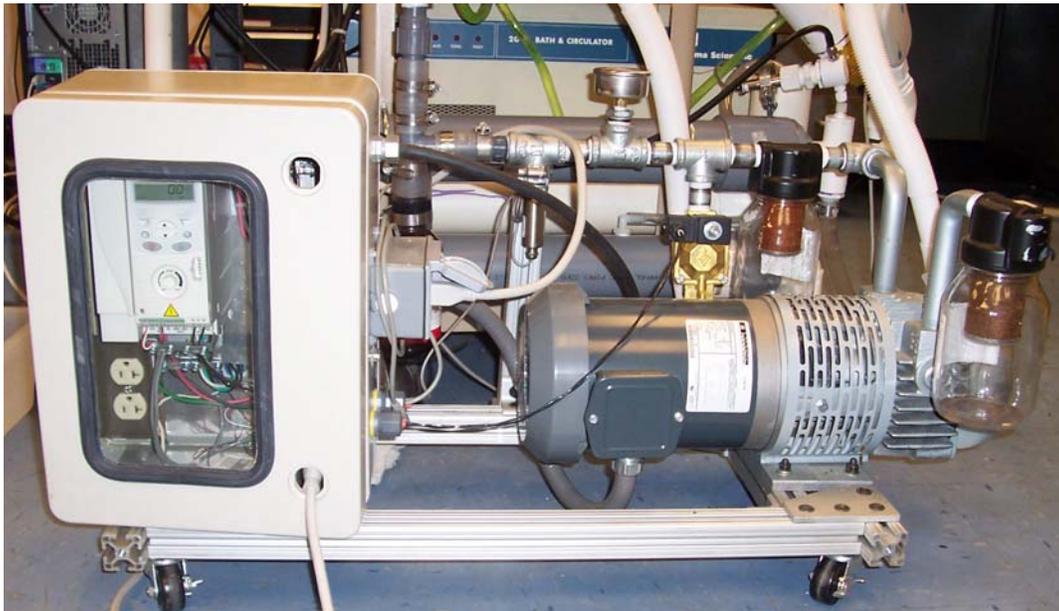
In order to fix engineering problem (5), a drain port with a shut-off is installed on the bottom of the virtual impactor (not shown in the photo), so that accumulated water can be removed quickly. We are still trying to understand the cause of water accumulation so we can reduce or remedy this problem.

## **B.7. Air pump unit**

The air pump unit includes a pump (P/N=2567-V107-G471, GAST), a variable frequency drive (VFD) (P/N=ACS150-01U-07A5-2, ABB, Inc.) installed inside a fiberglass watertight cabinet enclosure (P/N=22406000, Rose+Bopla Enclosures), a vacuum gauge, a vacuum transducer (P/N=PX209-015A5V, Omegadyne, Inc.), and normal open brass ball valve (P/N=SV6004-NO, Omega Engineering, Inc.), a flow meter (P/N=40241, TSI, Inc.), and 1” steel pipes. All these components are mounted on a small (15 “x 32”) rolling cart made of 80/20 frames, see a photo of the unit in [Figure 5](#).

The air pump is a GAST rotary van vacuum/pressure pump with specifications listed in Table 1 and the pump performance is shown in [Figure 6](#). The VFD converts a single-phase 60Hz 200-240V line power to a three-phase and variable frequency electricity power to drive the air pump. The VFD frequency can be up to 500Hz adjustable to change the output voltage from 0V to input voltage corresponding to power range of 0.5-3 HP. The pump rotation rate and therefore the air flow rate can be adjusted by changing the 3-phase power frequency. So, the air pump can be operated at lower speed when its loading is low to save energy which is important in the field when the power capacity is limited but the power demand is high; this also aids in the scaling up the system to multiple conditioning and impactor equipment since the VFD can control the pump to meet the needed load. In addition to housing the VFD, the fiberglass watertight enclosure also services as a power panel to provide single-phase 110VAC electricity for iVACES. The mass flow meter monitors airflow rate of the iVACES major flow. In theory, the major flow rate can be controlled by the VFD based on the mass flow meter signal after adding an optional proportional–integral–derivative controller (PID controller) to the VFD. But this does not seem necessary, because the major flow rate is determined by the virtual impactor’s orifice where the

airflow is choked. The mass flow meter is used only in the prototype iVACES for testing purposes and will not be a part of the iVACES. The signal from the pressure transducer is directly sent to the VFD. When the pressure in the vacuum line drops below a pre-set value, the VFD opens the brass ball valve to prevent the pump from overloading also protecting other parts of iVACES. The pressure gauge is used to visually monitor the pressure in vacuum line. The 1” steel pipes are used to build the air path and vacuum lines.



**Figure 5.** Photo of the air pump unit.

Table 1. Specifications of the air pump

Rotation rate	1725 RPM at 60Hz
Power	1.5 HP (1.1kW)
Air flow rate	21 CFM (at 0 PSI)
Maximum vacuum	28" HG
Maximum pressure	15 PSI

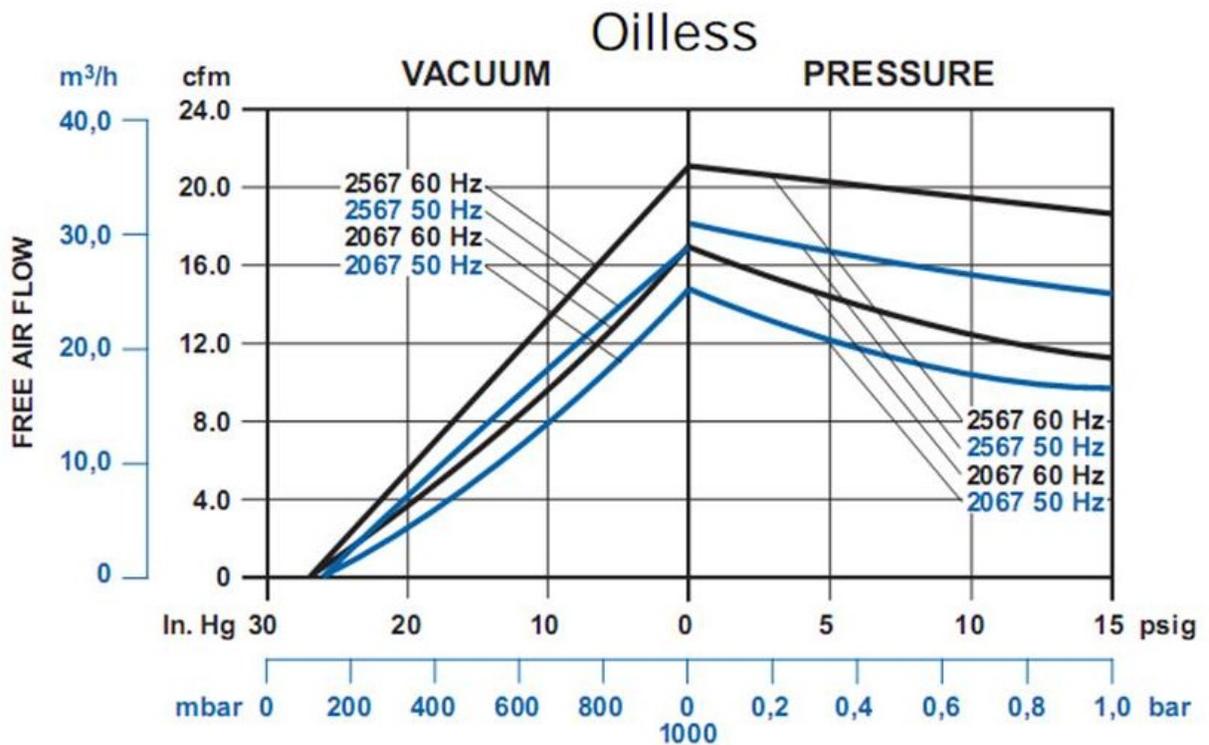


Figure 6. Performance of the GAST vacuum/pressure pump

### B.8. Dryer

In order to fix functional problem (9), the silica gel based dryer in the VACES was replaced by a Nafion tube based dryer in the iVACES.

The Nafion based dryer is actually a heat and humidity exchanger (see [Figure 7](#)). The outside tube is a 2” PVC pipe and the inside ones are 1 mm ID and 2.5 foot long Nafion tubing (P/N=TT-110, Perma Pure LLC). The entrance and exit ports of the dryer are made of 1” PVC pipes. SS 3/8” Swagelog fittings are used to couple the Nafion tubing to the 2” PVC pipe. In total 5 Nafion tubes are installed inside the dryer. Because the Nafion tubing allows vapor transfer from the higher humidity side to the lower side through its wall, the incoming air flow into the iVACES system (100 L/min) from the ambient exchanges humidity and heat with the minor flow air (5 L/min) where both humidity and particle concentration are high after coming out from the virtual impactor. So, the temperature and humidity in the minor flow stream are returned close to ambient conditions resulting in decrease of particle sizes and finally returning them close to their originally sizes.

Silica gel in the VACES drier needed to be changed frequently when the silica became saturated. In iVACES, the Nafion tubing does not “saturate” or become used up in any way, so there is no need to change it. In addition, the humidity exchange between the dry inlet air and the wet minor flow air increases RH in the inlet air which is important for humidifying and growing particles.



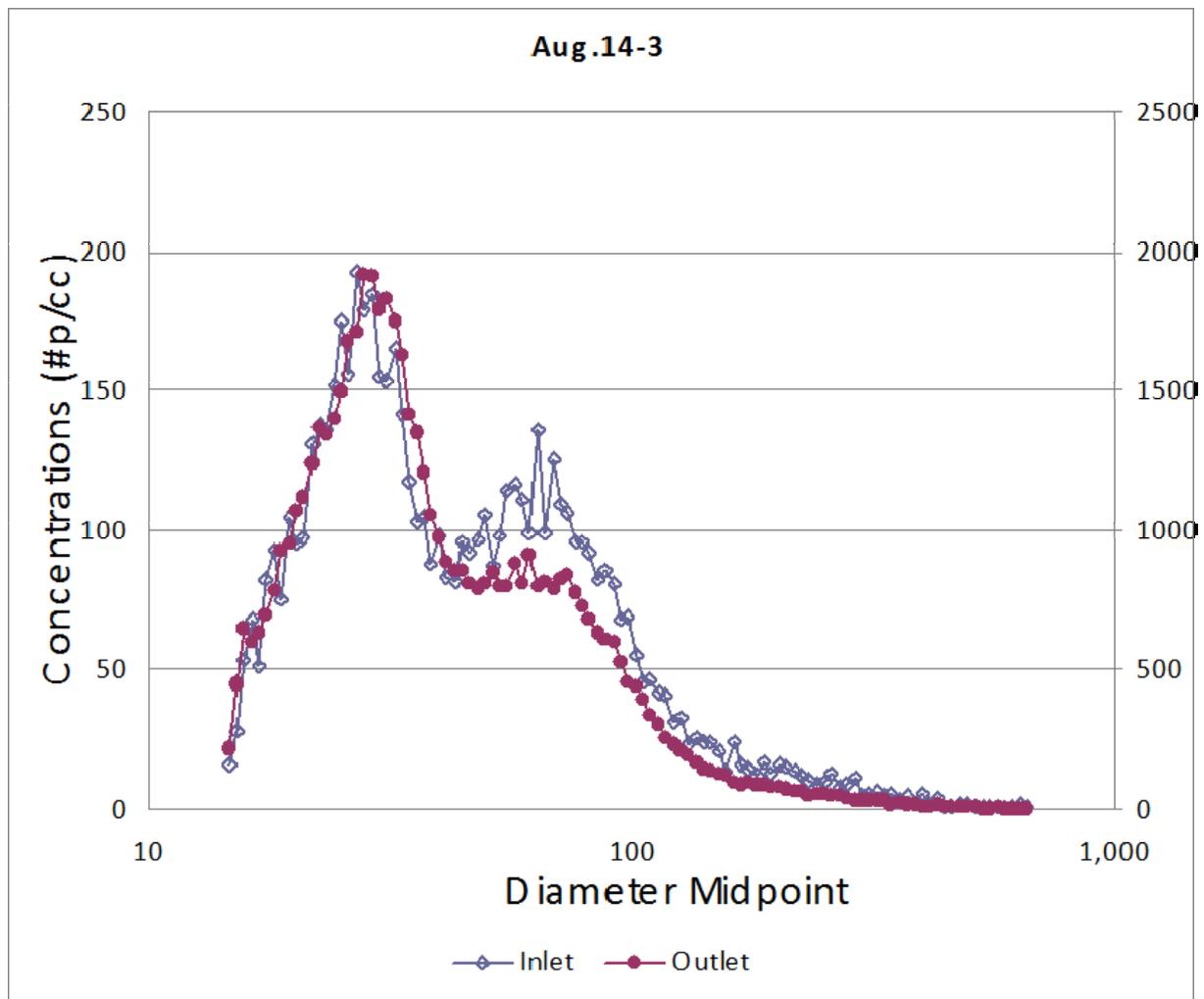
**Figure 7.** Diagram of the dryer. Outsider is a 2” PVC pipe and the insiders are five 1-mm ID nafion tubing. Entrance and exit ports are 1” PVC pipes.

## C. Experimental results

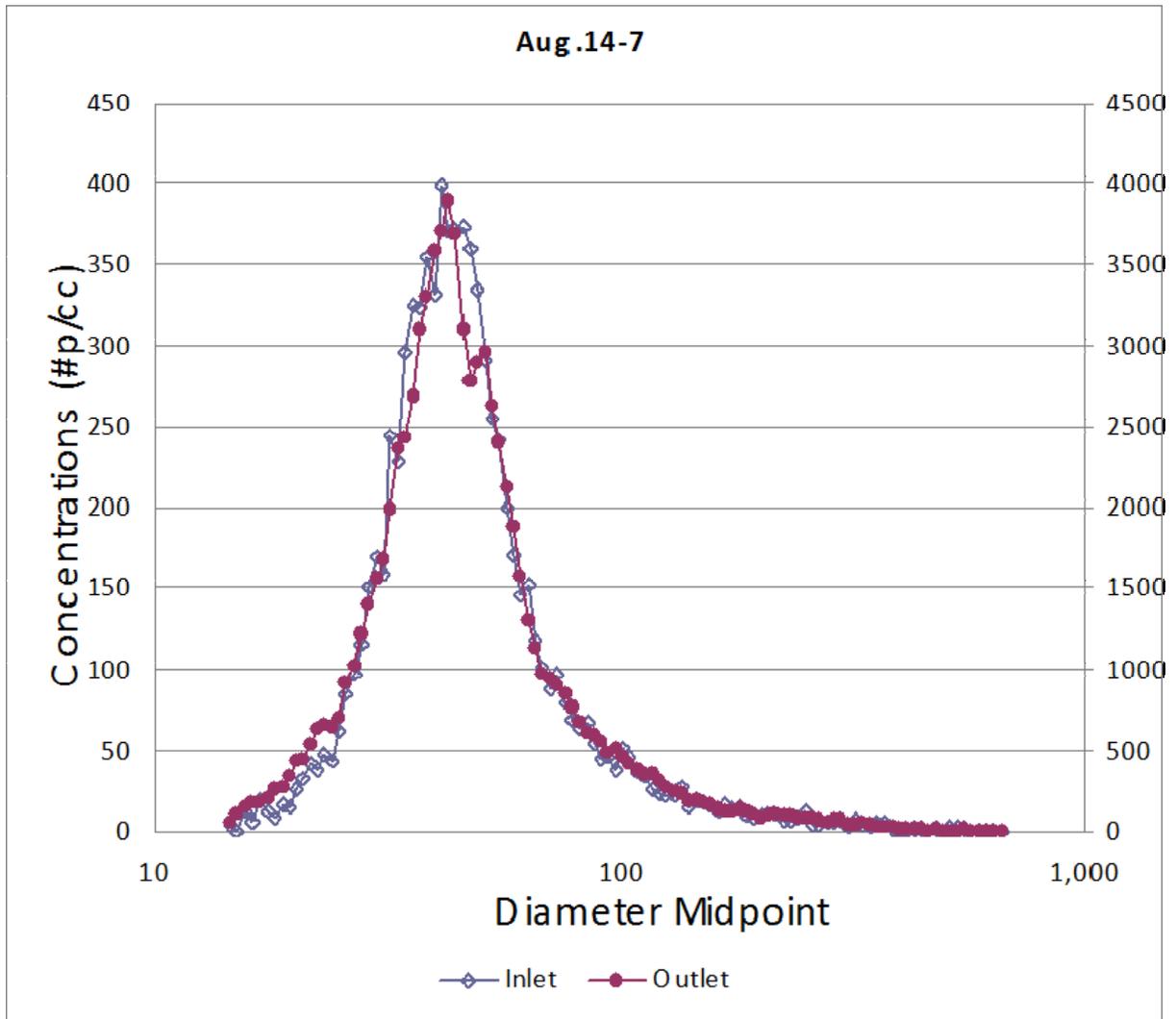
### C.1. Enrichment of ambient particles by iVACES.

The iVACES was primarily tested in laboratory using ambient particles. Due to numerous unexpected problems discovered during the construction, mainly water accumulation in the virtual impactor that affects iVACES performance significantly, systematic experiments have not been done to completely characterize iVACES performance. In order to overcome the discovered problems and improve the performance, the orientation of the iVACES components was rearranged several times.

Overall, the iVACES EF was observed between 2-10 under different ambient conditions (RH, temperature, and particles size distribution) and operating parameters (warm water temperature and coolant temperature). But, no relationship between these conditions/parameters and the EF was found so far. **Figure 8** shows two examples of the ambient particles enrichment by iVACES obtained on August 14 under same ambient RH (33%), ambient temperature (23.8°C), warm water temperature (36°C), and coolant temperature (-2.5°C), but different size distribution. It can be seen from the figure of example A that the ambient particle distribution has double peaks, one at about 28 nm and the other at about 64nm. The iVACES enriched the particles in small sizes about 10 times which is better than those in larger sizes (7-8 times), resulting in a change in the geometric diameter mean from 44nm before air samples entering iVACES to 39.5 nm after the iVACES processing and a 9.1 times enrichment in total particle numbers. In the figure of example B, the ambient particle size distribution has a single peak at about 43 nm. This particles size distribution was preserved well by the iVACES enrichment process as the particle diameter means did not change. The enrichment of total particle numbers was almost 10.



	Inlet	Outlet
<b>Median (nm)</b>	39.2	34.2
<b>Mean (nm)</b>	57.0	49.0
<b>Geo. Mean (nm)</b>	44.1	39.5
<b>Geo. Std. Dev.</b>	1.9	1.8
<b>Total Concentration (#/cc)</b>	6463	58675

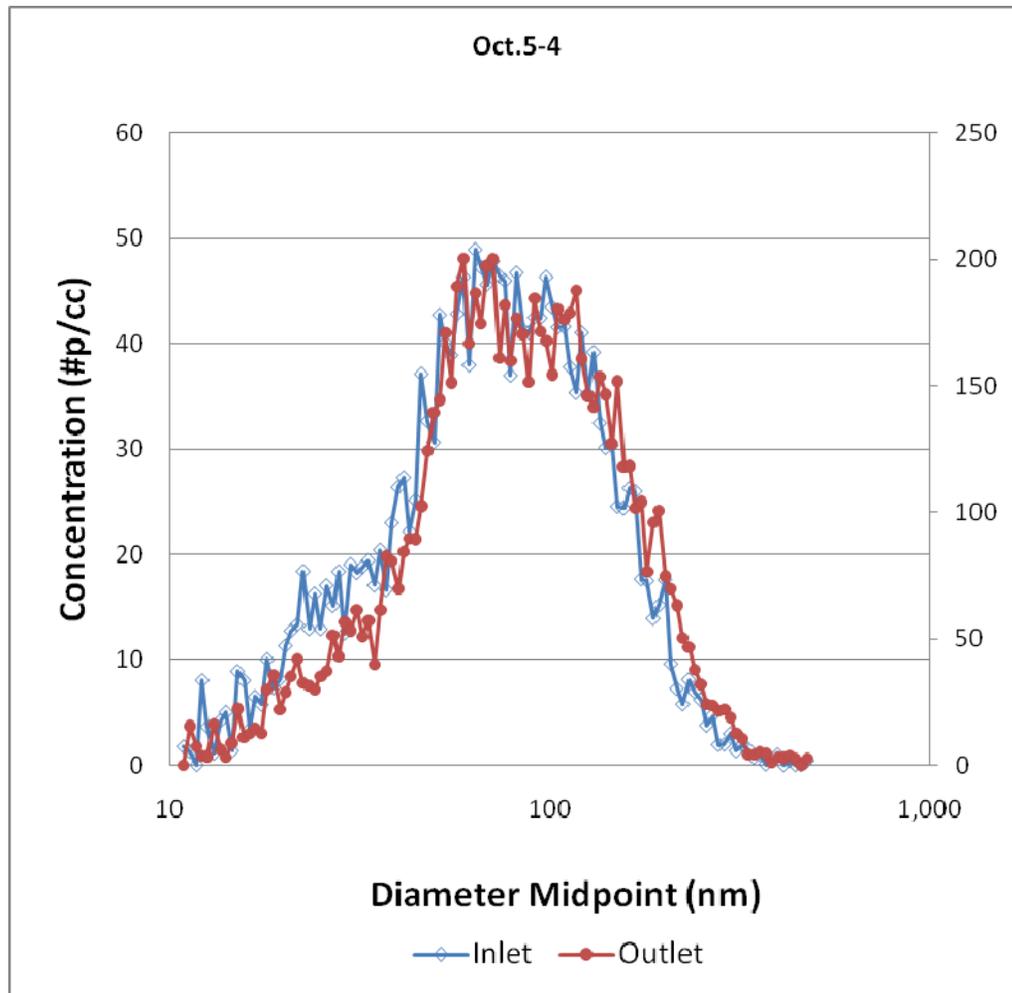


	Inlet	Outlet
<b>Median (nm)</b>	<b>44.3</b>	<b>44.0</b>
<b>Mean (nm)</b>	<b>53.8</b>	<b>53.8</b>
<b>Geo. Mean (nm)</b>	<b>47.2</b>	<b>46.8</b>
<b>Geo. Std. Dev.</b>	<b>1.6</b>	<b>1.6</b>
<b>Total Concentration (#/cc)</b>	<b>8344</b>	<b>82601</b>

**Figure 8.** Two examples of iVACES enrichment for ambient particles.

The lower enrichment for large size particles in example A of [Figure 8](#) indicated possible losses of the large size particles when the air stream making turns in iVACES. To test this hypothesis, the system components were rearranged to reduce the number of bending sections

and an example of the test is shown in **Figure 9**. The enrichment of particles in larger sizes was improved compared to those in small sizes. But particle diameter means were shifted about 10 nm towards large size and the enrichment of total particle number was only about 4. We did a lot of troubleshooting again to fix the problem with water accumulation in the new configuration, but were not able to further improve the EF.



	Inlet	Outlet
<b>Median (nm)</b>	<b>72.7</b>	<b>81.1</b>
<b>Mean (nm)</b>	<b>85.3</b>	<b>95.9</b>
<b>Geo. Mean (nm)</b>	<b>69.7</b>	<b>79.1</b>
<b>Geo. Std. Dev.</b>	<b>1.9</b>	<b>1.9</b>
<b>Total Concentration(#/cc)</b>	<b>2086</b>	<b>8302</b>

**Figure 9.** Example of iVACES enrichment in a new configuration

## C.2. Effect of ambient RH on iVACES enrichment

Although the relationship between iVACES EF and ambient conditions (RH and temperature) has not been established yet, the effect of ambient RH on iVACES enrichment was observed. Usually when the ambient RH is low, it is hard to achieve a high iVACES EF. Figure 10 shows the RH of air samples exiting from the saturator as a function of warm water temperature at different ambient RH and air flow rate. It can be seen that when the ambient air was dry (22%), the maximum RH of air samples after the saturator was only about 90% when the water was heated to 43°C. After that point, the RH of air samples stopped increasing. By contrast, when the ambient air was wet (40-50%), the air samples could be humidified over 99% when the water was heated higher than 50°C. This confirms that when the ambient air is dry, it is more difficult than wet to achieve a higher iVACES EF. It can also be seen that reducing the air flow rate (increasing the resident time of air samples in the saturator) from 100 L/min to 50 L/min helps with increasing the RH of air samples at low water temperature (<40°C).

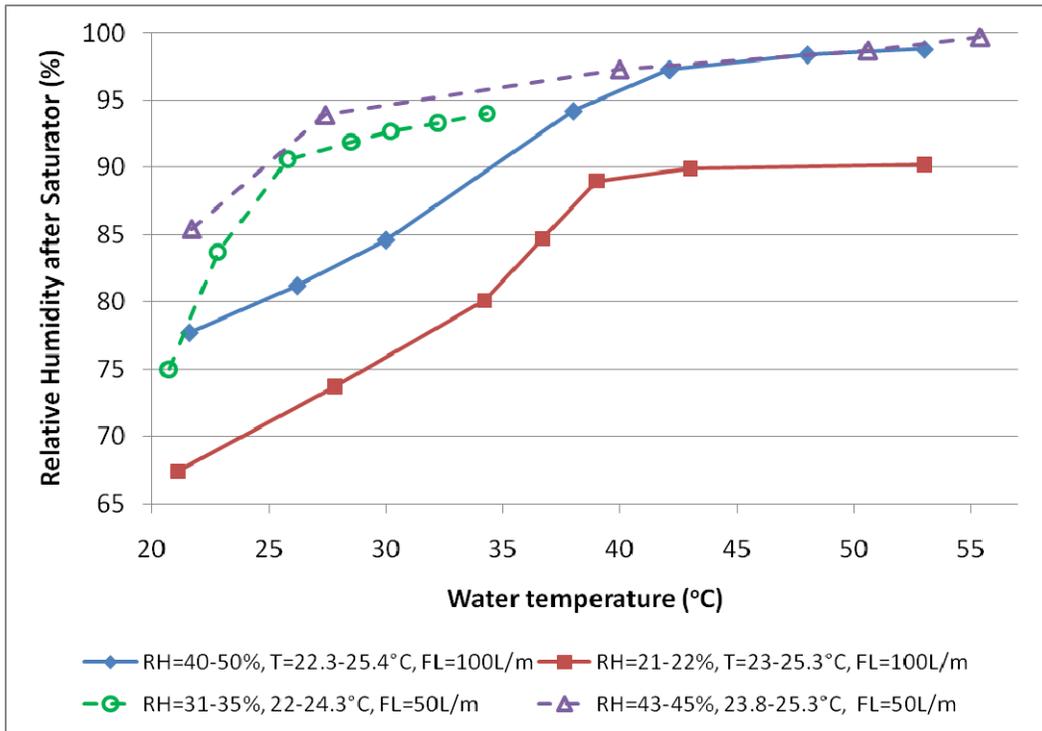


Figure 10. Effect of ambient RH on the humidification rate of the air samples

## D. Conclusion and discussion

- An improved Versatile Aerosol Concentration Enrichment System (iVACES) was built at UC Davis and primarily tested in laboratory. The EF was observed between 2 and 10.
- New iVACES components, such as warm water supply, air pump unit, and Nafion tubing based dryer work well and are more convenient for operation and maintenance than those in the original VACES.
- The virtual impactor and condenser in iVACES are nearly the same as those in VACES, except for improved engineering in construction.
- The porous pipe based saturator is expected to be more stable because the “water level” does not change during the operation. It can humidify the air samples up to 99% when the ambient air is not too dry, but performs poorly when the ambient air is dry. To solve this problem, it is necessary to increase the resident time of air samples inside the saturator by either increasing the length of the saturator or reduce the flow rate of the air samples. Adding additional water steam to the saturator, like the Harvard concentrator (*Demokritou et al., 2002 and Gupta et al., 2004*), would help with increasing the RH and reducing the dependence of iVACES performance on the ambient conditions.
- Up to now, the iVACES is still following the VACES general procedure, humidifying air samples in the saturator, growing up particles in the condenser, concentrating particle concentrations through the virtual impactor, and returning particles to their original size in the dryer. It may be more efficient to reverse the order of the saturator and the condenser, like water based condensational particle counters (*Hering and Stolzenburg, 2005a and Hering et al., 2005b*), thus, the air is cooled first and particles grow when they are warmed and humidified.

- Engineering problems (1)-(5) and functional problem (9) have been fixed in the iVACES, but functional problems (6-8) have not. We are working on them now.

## E. References

- Demokritou, P., T. Gupta, and P. Koutrakis, A High Volume Apparatus for the Condensational Growth of Ultrafine Particles for Inhalation Toxicological Studies, *Aerosol Science and Technology* (2002), 36, 1061–1072
- Gupta, T., P. Demokritou, and P. Koutrakis, Effects of Physicochemical Properties of Ultrafine Particles on the Performance of an Ultrafine Particle Concentrator, *Aerosol Science and Technology* (2004), 38(S2), 37–45.
- Hering, S. V. and M.R. Stolzenburg, Method for Particle Size Amplification by Water Condensation in a Laminar, Thermally Diffusive Flow, *Aerosol Sci. Technol* (2005a), 39, 428-436.
- Hering, S. V., M.R. Stolzenburg, F.R. Quant, D.R. Oberreit and P.B. Keady, A Laminar-Flow, Water-Based Condensation Particle Counter (WCPC). *Aerosol Sci. Technol* (2005b), 39, 659-672.
- Kim, S., P. Jaques, M.C. Chang, J.R. Froines, and C. Sioutas, A versatile aerosol concentrator for simultaneous *in vivo* and *in vitro* evaluation of toxic effects of coarse, fine and ultrafine particles: Part I: Laboratory evaluation, *J. Aerosol Sci.* (2001a), 32, 1281-1297.
- Kim, S., P. Jaques, M.C. Chang, C. Xiong, S.K. Friedlander, and C. Sioutas, A versatile aerosol concentrator for simultaneous *in vivo* and *in vitro* evaluation of toxic effects of coarse, fine and ultrafine particles: Part II: Field evaluation, *J. Aerosol Sci.* (2001b), 32, 1299-1314.
- Sioutas, C., S. Kim, and M.C. Chang, Development and evaluation of a prototype ultrafine particle concentrator, *J. Aerosol Sci.* (1999), 30, 1001-1017.
- Zhao, Y., Bein, K.J., Wexler, A. S., Misra, C., Fine, P. M., Sioutas, C., Field evaluation of the versatile aerosol concentration enrichment system (VACES) particle concentrator

coupled to the rapid single-particle mass spectrometer (RSMS-3), *Journal of Geophysical Research* (2005), 110, D07S02, doi:10.1029/2004JD004644

## **Acknowledgements.**

This project was supported by California Air Resources Board (CARB) on a contract #: 04-332