

## INTEGRATED AND REAL-TIME DIFFUSION DENUDER SAMPLERS FOR PM<sub>2.5</sub> BASED ON BOSS, PC AND TEOM TECHNOLOGY.

Delbert J. Eatough, Fida Obeidi, Yanbo Pang and Yiming Ding, Department of Chemistry and Biochemistry, Brigham Young University, Provo, UT 84602

Norman L. Eatough, Department of Chemistry, Department of Chemistry, California Polytechnic State University, San Luis Obispo, CA 93407

William E. Wilson, US Environmental Protection Agency, National Center for Environmental Assessment, Research Triangle Park, NC 27711

### ABSTRACT

Particulate matter (PM) is a complex mixture of stable condensed phases, adsorbed or dissolved gases, and semi-volatile materials, i.e. compounds that transfer between the gas and condensed phases. Fine particles in both rural and urban environments contain substantial quantities of semi-volatile material that can be lost from the particles during sample collection on a filter and during subsequent handling, storage and conditioning (or equilibration). These include ammonium nitrate, semi-volatile organic compounds and particle bound water. As a result, the concentrations of these species are often significantly in error for results obtained with a conventional single filter sampler. The accurate measurement of the mass and chemical components of fine particles will become more important as a result of the recent promulgation of fine particle standards by EPA and the additional monitoring that will be required for implementation of those standards as well as for additional research on the sources and effects of PM. Past organic compound diffusion-denuder samplers developed by us (BOSS, BYU Organic Sampling System) are not amenable to routine field use because of the need to independently determine the gas phase semi-volatile organic material breakthrough of the denuder for each sample. This problem has been eliminated in the Particle Concentrator - Brigham Young University Organic Sampling System (PC-BOSS) using a combined virtual impactor, particle-concentrator inlet to provide a concentrated stream of 0.1 - 2.5 micron particles. This is followed by a BOSS diffusion denuder and filter packs containing particle collecting and sorbent filters to collect particles, including any semi-volatile organic material or ammonium nitrate lost from the particles during sampling. The PC-BOSS contains a sequential sampler to allow for the routine collection of several samples. A second sampler, the Real-time Total Ambient Mass Sampler (RAMS), has been developed by combining the PC-BOSS with TEOM technology. In this

sampler, a diffusion dryer to remove gas phase water follows the diffusion denuder. The dried aerosol stream is then sampled with a "sandwich" (TX40 and sorbent) filter on the TEOM tapered element to collect particles, including any semi-volatile species. Laboratory and field validation data indicate the precision of determination of fine particulate material, including ammonium nitrate and semi-volatile organic material is better than  $\pm 10\%$ .

## INTRODUCTION

Human health endpoints associated with exposure to airborne particulate matter (PM) include increased mortality and morbidity from respiratory and cardiopulmonary disease (Vedal 1997, Schwartz 1996, USEPA 1996). These effects are observed with exposure to concentrations substantially below the U.S.  $PM_{10}$  ambient air quality standard. The observed exacerbation of health is believed to be associated more closely with exposure to fine particles than with exposure to coarse particles. As a result, the U.S. EPA has promulgated revised standards for PM. The revised PM standards maintain the  $PM_{10}$  standard (with a revision in the form of the 24-hour standard) to protect the public against the effects of coarse particles and establishes new annual and 24-hour fine particle standards with  $PM_{2.5}$  as the indicator. This recognition of fine and coarse particles as different classes of PM pollutants is an advance in the understanding and control of PM. However, ambient fine particulate matter is not a single pollutant, but is a mixture of many chemical species. Major components of fine particles include: sulfate, nitrate, ammonium, and hydrogen ions; trace elements (including toxic metals); organic material; elemental carbon (or soot); crustal components and water. Trace and crustal elements, and sulfate can be accurately measured by available technology. However, monitoring technologies for elemental carbon, organic carbon and nitrate are not as well established. Past studies have indicated that about one-fourth to one-third of the mass of fine particulate matter collected on filters in both the eastern and western U.S. is organic material and elemental carbon. The actual fraction of organic material in fine particles may be higher than indicated by these data, however. About half of the total fine particulate organic material is semi-volatile organic compounds (SVOC) and about 60-90% of the semi-volatile organic compounds are lost from particles during sampling on a quartz filter, a "negative" artifact (Cui 1997a,b, Eatough 1996, 1995, Tang 1994). As a result, fine particulate organic matter is expected to be significantly underestimated using the proposed EPA single filter Federal Reference Method. Previous studies (Cui 1997b, Eatough 1995, Fitz 1990, McDow 1990, Turpin 1994) have also indicated the presence of a "positive" artifact in the determination of particulate organic

compounds collected on a quartz filter due to the adsorption of gas phase organic compounds by the quartz filter and/or collected particles during sampling.

Several diffusion denuder samplers, such as the Harvard HEADS (Koutrakis 1988), the Brigham Young University Organic Sampling System (BOSS, Eatough 1993) and BIG BOSS (Tang 1994), have been developed to address the issues of both "positive" and "negative" artifacts in the sampling of the volatile components of particulate matter. The HEADS, and similar (Benner 1991) annular denuder samplers, quantitatively removes gas phase nitric acid in a base-coated denuder, and collects particulate nitrate, and any nitric acid and ammonia lost from the particles during sampling, with a filter pack containing both Teflon and sorbent filters. In the BOSS, most gas phase (>90%) organic compounds are removed by a charcoal impregnated filter, CIF, multi-channel, parallel plate diffusion denuder (Cui 1997a, Eatough 1993). Then the particles passing through the denuder are collected by a quartz filter, and any SVOC lost from the particles are collected by a sequential CIF sorbent filter or an XAD sorbent bed. The efficiency of the denuder decreases to less than 90% at a flow rate of 200 L/min in the high-volume BIG BOSS (Cui 1997b, Tang 1994). Since the concentration of gas phase SVOC is often an order of magnitude higher than the concentration of particulate phase SVOC, an extra system is required for each sample to determine the gas phase material breakthrough of the denuder. This requirement is not amenable to routine field use. High flow through the denuder also increases particle loss (Eatough 1997, Tang 1994). To maximize denuder efficiency and minimize particle loss, the gas flow through the denuder should be minimized. However, a useful particulate organic sampling system should have a flow rate sufficient to enable measurement of low concentrations of particulate components and to allow the detailed chemical characterization of particulate material.

The particle concentrator developed by Harvard University (Sioutas 1994a,b) provides technology which will allow decreasing the flow rate through the denuder while keeping the effective air sampling rate unchanged. The Harvard particle concentrator (PC) is a slotted virtual impactor with a 50% particle cut point at about 0.1  $\mu\text{m}$ . If the PC is preceded by a 2.5  $\mu\text{m}$  cut-point device, the concentrator separates fine particles from most of the gas phase material. Studies by Sioutas et al. (1994a,b) indicate there is no significant particle size distribution distortion by the concentrator and that the particle loss in the concentrator is from 10 to 20% when the concentration factor varies from 4-7.

This paper describes the development of two diffusion denuder sampling systems using a particle concentrator inlet with a high-volume, multi-system, multi-channel BOSS diffusion denuder.

## EXPERIMENTAL METHODS

### The PC-BOSS Sampling System

The combination of the technology used in the previously described BIG BOSS sampling system (Tang 1994) and the Harvard particle concentrator (Sioutas 1994a,b) results in the Particle Concentrator-Brigham Young University Organic Sample System (PC-BOSS) shown schematically in Figure 1. The system has been optimized to meet the following criteria; 1. Removal of at least 75% of the gas phase material before the sampled aerosol is passed through the diffusion denuder. 2. Efficiency >99% for the removal of SO<sub>2</sub>, HNO<sub>3</sub> and gas phase semi-volatile organic material. 3. Determination of particle mass, carbonaceous material and nitrate with a diffusion denuder sampler. 4. Operation on less than 20 amps of 110V power.

The inlet to the sampler is a Bendix cyclone with a particle cut of 2.3  $\mu\text{m}$  aerodynamic diameter at an inlet flow of 150 L/min (Chan 1977). The cyclone is followed by a virtual impactor particle concentrator. The design (Sioutas 1994b) and evaluation (Sioutas 1994a) of the particle concentrator has been previously described. The particle concentrator separates most of the gas phase material into the major flow and leaves particles larger than the cut point (about 0.1  $\mu\text{m}$ ) along with a significantly reduced fraction of the gas phase material in the minor flow. The performance of the particle concentrator for collection of ambient samples with the PC-BOSS was evaluated as a function of the minor to major flow ratio, and the distance between the accelerator and receiver slits of the virtual impactor. The optimum design uses a single particle concentrator with a 9.5 cm long slit and a distance between the accelerator and receiver slits 1.5 times the slit width of 0.32 mm. The minor flow (25% of the total 150 L/min flow) containing concentrated particles enters the BOSS diffusion denuder (Eatough 1993, Tang 1994). The denuder is comprised of 17 (4.5 x 58 cm) strips of Schleicher and Schuell charcoal impregnated filter paper which are separated at the long edges by 2-mm glass rods. The multi-parallel plate array of filter strips is contained within a (5 x 5 cm) square aluminum tube. The entire assembly is nominally 90 cm in length to accommodate the 58-cm sorbent filter strips and two nominally 15-cm long flow straightening sections ahead of and behind the denuding section. The denuder is followed by two parallel filter packs, Figure 1. The filter pack containing a 47 mm quartz filter (Pallflex,

prefired) followed by a 47 mm charcoal impregnated filter (3M EMPORE Carbon) is used to determine fine particulate carbonaceous material, including semi-volatile organic material lost from the particles during sampling. The second filter pack contains 47 mm Teflon (Gelman Zefluor) and nylon (Gelman Nylasorb) filters to determine mass, sulfate and nitrate, including any nitrate lost from particles during sampling.

#### **The RAMS Sampling System.**

A Real-time total Ambient Mass Sampler, RAMS, based on PC technology has also been developed and validated, and is being field tested for the real-time determination of total fine particulate mass, including volatile species. The RAMS measures total mass of collected particles, including volatile species with a TEOM® monitor (Rupprecht 1992, Patashnick 1991) using a "sandwich" filter containing a Teflon coated (R&P TX40) particle collection filter followed by a CIF (Schleicher and Schuell) to collect any volatile species lost from the particles during sampling. The sampler has the same design objectives as the PC-BOSS. However, since the instrument measures total mass collected by the "sandwich" filter, all gas phase compounds which can be adsorbed by a CIF must be removed from the sampling stream prior to the TEOM monitor.

The RAMS is shown schematically in Figure 2. The RAMS has a dual inlet system consisting of a 2.5  $\mu\text{m}$  elutriator-impactor (or virtual impactor or cyclone) inlet (University Research Glass) followed by a particle concentrator (Sioutas 1994a,b). Total inlet flow is 14.0 L/min. The major (discard) flow of the particle concentrator is 10.5 L/min, and the minor flow for the concentrated particle stream is 3.5 L/min, 25% of the total flow. This configuration was selected based on studies of the efficiency of the concentrator as a function of the flow ratio. The sampled aerosol is then passed through a citric acid/glycerine coated annular denuder (University Research Glass) to remove  $\text{NH}_3$ , and a NaI/glycerine coated annular denuder to remove  $\text{NO}_2$  and  $\text{O}_3$ . The concentrated particle stream then enters a BOSS denuder to remove gas phase organic material. Finally, the sample is passed through a 1 foot long, 200 element Nafion dryer (Perma Pure Inc., Model PD-750-12) to remove gas phase water. The minor flow is then monitored with the TEOM.

#### **Evaluation of the PC-BOSS and RAMS.**

**Characterization of the Particle Concentrator.** The performance of the particle concentrator is characterized by two parameters. The concentrator loss is the fraction of material entering the concentrator which is not present in either

the major or minor flow streams. The concentrator efficiency is the ratio of the mass in the minor flow stream to the sum of the mass in the minor and major flow streams. Both the efficiency and losses in the particle concentrator were determined for both one- and two-stage concentrators by measurement of sulfate and soot present in the major and minor flow streams, and in a filter pack sampler with a 2.5  $\mu\text{m}$  inlet cut for ambient air sampled in Provo, UT. The particle size distribution of the sampled fine particles was estimated from scanning electron microscopy analysis of particles on Nucleopore filters and from DMPS data for a few samples. The mass median diameter of the sampled fine particles was about 0.2  $\mu\text{m}$  at low relative humidities during the wintertime study. At higher (>70%) relative humidities, the particle diameter increased to about 0.3 to 0.4  $\mu\text{m}$ . The results of the efficiency experiments are given in Figure 3. The concentrator was operated with slit diameter to nozzle separation ratios of 1.0, 1.5 and 2.0 (Sioutas 1994a). The efficiency is comparable for sulfate and soot at low RH. The efficiency for sulfate increases with increasing relative humidity. The efficiency decreases with the use of a two stage concentrator, Figure 3, and increases with increasing separation of the nozzles of the concentrator, insert in Figure 3. It is anticipated that sample collection in environments with a more typical mass median diameter (e.g. 0.3 to 0.5  $\mu\text{m}$ ) for fine particles will result in a higher efficiency for the concentrator. The operational configurations for both the PC-BOSS and RAMS (a single concentrator with 25% minor flow, and a 1.5 slit diameter to nozzle separation ratio) should give efficiencies of about 90 to 95%. The fine particle sulfate loss in the concentrator was  $4\pm 8\%$  for a single stage concentrator and  $8\pm 8\%$  for a two stage concentrator at the chosen operational configuration. In general, increasing the ratio of minor to total concentrator flow increases the efficiency and decreases the losses. However, as the minor flow increases, the efficiency of the concentrator-denuder for the removal of gas phase organic material decreases. The compromise "best" parameters for operation of the PC-BOSS and RAMS were selected to balance concentrator-denuder efficiency and concentrator efficiency and losses.

**Denuder Efficiency.** The denuder efficiency for SVOC was determined by comparing the amounts of carbonaceous material collected in the concentrated particle stream by an EMPORE Carbon filter after a quartz filter but before a denuder, and by a 3M EMPORE carbon filter in the PC-BOSS with a quartz filter placed before the denuder. Data were obtained at a sample flow rate of 40 L/min. The collection efficiency over a six month period varied from 91 to 97% and averaged 95%. Since 75% of the gas phase organic material is removed by the particle concentrator, the

overall efficiency of the PC-BOSS for removal of gas phase organic compounds before the collection of concentrated particles averages 99%. The efficiency of removal of gas phase organic material in the RAMS will be >99% because of the reduced flow through the denuder (4 L/min) in this system.

The denuder breakthrough using the BIG BOSS (Cui 1997a,b, Tang 1994, Eatough 1995) is generally 20-50% of the SVOC lost from particles during sampling, which requires the correction of the data for the denuder inefficiency. In both the PC-BOSS and the RAMS the denuder breakthrough is negligible because of the high efficiency for removal of gas phase organic material with the combined particle concentrator and diffusion denuder. This is illustrated by the data in Figure 4.A. which compares the amount of gas phase material collected by a quartz filter for data obtained with the BIG BOSS and PC-BOSS. Similar results were obtained for EMPORE C filters.

The efficiency of the PC-BOSS for the removal of gas phase sulfur dioxide and nitric acid was also evaluated by comparing these species before and after the denuder. The efficiency is  $99\pm 2\%$  for the removal of both sulfur dioxide and nitric acid by the PC-BOSS denuder at a flow of 40 L/min. Thus, the removal of these species by the concentrator-denuder combination is essentially 100%.

**Fine Particle Loss.** Fine particle loss in the diffusion denuder of the PC-BOSS was evaluated by comparing sulfate collected before and after the denuder, Table 1. The bias in the comparison is only about 25% of the standard deviation, indicating there is no statistically significant loss of sulfate in the denuder. The standard deviation and relative standard deviation ( $\pm 0.36 \mu\text{g sulfate}/\text{m}^3$  and  $\pm 4.7\%$ ) in the results are about a factor of ten larger than the uncertainty in the blank data. Fine particle loss in the complete PC-BOSS system was evaluated by comparison of sulfate obtained in a fine particle filter pack sampler and with the PC-BOSS. The results, Table 1, indicate any particle loss is less than the precision of the measurements. Fine particle loss in the RAMS was evaluated by comparison of mass determined with a conventional TEOM monitor and with the RAMS with only the Teflon coated particle collection filter present. The results, Table 1, indicate any loss of fine particles in the RAMS is also within the uncertainty of the data. Particle loss in the denuder plus Nafion dryer is also within the uncertainty of the data,  $\pm 2 \mu\text{g}/\text{m}^3$  or  $\pm 5\%$ .

**Collection of Water by the RAMS Sandwich Filter.** The CIF used in the TEOM sandwich filter is cleaned with dichloromethane and dried at 200 °C before use (Tang 1994). This filter absorbs nitric acid, semi-volatile organic

compounds and water. Absorbed semi-volatile organic compounds are not lost from the charcoal sorbent below 100-150 °C. Absorbed nitric acid is lost at even higher temperatures. The absorbed water is, however, lost at temperatures of 30-70 °C. The effect of water absorption on TEOM data using a CIF sandwich filter is illustrated in Figure 5. In these experiments two filters were placed in front of the diffusion denuder to remove particles and the Nafion dryer was not present in the RAMS. Since the diffusion denuder removes all charcoal absorbing gases (e.g. HNO<sub>3</sub> and SVOC), the only gas phase species which should be absorbed by the "sandwich" filter in these experiments is water. As indicated by the data in Figure 5, the absorption and subsequent loss of water is evident in the data. The TEOM monitor "sandwich" filter for the data shown in Figure 5 was maintained at either 30°C or 50°C as indicated. Increasing the temperature of the "sandwich" filter dampens the effect, Figure 5. With the Nafion dryer in place the response to ambient water was negligible. The purge air to the dryer is either pure nitrogen or ambient air which is conditioned by passing through a commercial dehumidifier (HANKISON, Model PR5-115) to give a relative humidity less than 0.5%; the purge air is further treated by passing through a two DRIRITE cartridges; cleaned of organic compounds by passing through a charcoal bed; and then the humidity further reduced by passing the air through a filter to drop the pressure. The effect of dehumidification on the TEOM monitor response is shown in both ambient and chamber data in Figure 6. The response of the "sandwich" filter to ambient water is minimal and a stable, near-zero baseline is observed. Similar results are obtained in the chamber experiments with clean air at a relative humidity of 70 to 90%. The system is not able to respond to an instantaneous change in humidity but shows a transient response over about 30 minutes, Figure 6. If the purge air is not passed through the dryer, the uptake of water by the CIF in the "sandwich filter" is instantaneous and large, Figure 6. The average baseline under stable conditions for the data shown in Figure 6 is  $1.1 \pm 1.8 \mu\text{g}/\text{m}^3$ . Since the particles are concentrated three-fold by the impactor inlet, the uncertainty of the effect of water on the ambient concentration of particulate material collected on the sandwich filter should be less than  $0.5 \mu\text{g}/\text{m}^3$ .

**Collocated Sampling with the BIG BOSS, PC-BOSS and RAMS.** Collocated PC-BOSS results were in agreement, with a precision of  $\pm 4.4\%$ , for samples collected August through November 1996 on the Brigham Young University campus in Provo, UT, Table 1. BIG BOSS and PC-BOSS results were also in agreement, Table 1. The lower precision in this comparison, Table 1, is attributable to the lower precision of the BIG BOSS data, where precision is limited by



uncertainty in flow. Flow audit data obtained in field sampling with the PC-BOSS vary from 3 to 5%. Collocated TEOM and collocated RAMS data (with only a TX40 and no CIF filter) were both in agreement with comparable precision,  $\pm 3$  to 6%, Table 1. The precision of the mass data are not degraded by the presence of the particle concentrator and dryer in the RAMS.

**Quartz Filter Artifacts in the PC-BOSS.** Both "positive" and "negative" sampling artifacts are present when collecting organic particulate matter on a quartz filter. The loss of semi-volatile organic compounds from particles without subsequent collection by the filter is a "negative" artifact. A "positive" artifact may also be present in a quartz filter due to the adsorption of gas phase material. The PC-BOSS denuder removes essentially all gas phase compounds which can be collected by a quartz filter. In contrast, gas phase material which can be collected by a quartz filter passes the less efficient denuder of a conventional BIG BOSS, Figure 4A.

**Loss of Semi-Volatile Fine Particulate Organic Material During Sampling with the PC-BOSS.** The EMPORE Carbon sorbent filter in the PC-BOSS,  $C_1$  in Figure 1, collects all organic material still present in the gas phase after the diffusion denuder and quartz filter. The possible presence of gas phase organic material on  $C_1$  can be determined by collection of a collocated sample with a quartz filter before the BOSS denuder of the PC-BOSS. The EMPORE Carbon filter in this second sampler,  $C_2$ , measures the denuder breakthrough. The CIF filter in System 1 collects the breakthrough seen in  $C_2$  plus the semi-volatile organic material lost from particles during sampling. The semi-volatile organic material lost from particles during sampling is:

$$C_{SVOC\ Lost} = (C_1 - C_2)/E_C \quad (1)$$

where  $E_C$  is the efficiency of a CIF filter for the collection of gas phase material, 85% (Tang 1994). Values of both  $C_1$  and  $C_2$  were determined for the collocated PC-BOSS and BIG BOSS samples collected in Provo. For the BIG BOSS samples  $C_2$  averaged 20% of the  $C_1$  concentrations. However, for the PC-BOSS data, the  $C_2$  determined concentrations were all less than the  $0.4 \mu\text{g C/m}^3$  detection limit for the sampler. The amount of gas phase organic material not removed by the denuder was negligible for all PC-BOSS samples; the  $C_2$  term in equation 1 is not needed. Another significant difference between the BIG BOSS and PC-BOSS results was the SVOC lost from the particles during sampling, Figure 4B. The semi-volatile loss occurring in the BIG BOSS is substantially larger than that for the PC-BOSS. This can be attributed to the lower sample flow of the PC-BOSS, being only 15% of that in the BIG BOSS, and

the higher concentration of collected particles (Cui 1997c, Pankow 1994).

#### **Field Results Obtained With the RAMS.**

A comparison of the mass measured using a conventional TEOM monitor and the RAMS for collection of samples in Provo, UT and Riverside, CA is given in Figure 7. The difference in the two measurements reflects the retention of volatile fine particulate material by the "sandwich" filter of the RAMS. The Provo, UT data were obtained during winter when volatilization losses were expected to be small. The difference between the two measurements averaged  $7.0 \mu\text{g}/\text{m}^3$ , 24% of the TEOM result. The Riverside, CA samples were collected in September 1997. These samples were expected to have high concentrations of both particulate ammonium nitrate and SVOC. The difference between the two samplers is substantial, especially for the early morning period. This corresponds to the time when high concentrations of particulate nitrate and ammonia are transported from the west to the sampling site. High concentrations of SVOC are also expected in the sampled fine particles. The data given in Figure 7 indicate that an average of 72% of the fine particle mass was lost as volatile species during measurement with the conventional TEOM monitor. Two FRM  $\text{PM}_{2.5}$  monitors were also run over the time period of the Riverside data in Figure 7. The average mass obtained with the FRM samplers,  $12.3 \pm 0.5 \mu\text{g}/\text{m}^3$ , agreed with the TEOM monitor average of  $11.5 \mu\text{g}/\text{m}^3$ . Four one-hour PC-BOSS samplers were collected during the study period, Figure 7. Total  $\text{PM}_{2.5}$  obtained with the PC-BOSS and RAMS for these one-hour samples agreed. The PC-BOSS results indicate that about half of the material lost during sampling with either the TEOM or FRM monitor was ammonium nitrate and half was fine particulate SVOC. Additional experiments are now underway to further validate the RAMS measurement by comparison of RAMS and PC-BOSS results for both ambient  $\text{PM}_{2.5}$  and well-defined particles in chamber experiments.

#### **Conclusions**

A diffusion denuder sampling system combined with a particle concentrator (PC-BOSS) has been developed for the facile determination of fine particulate organic material without "negative" or "positive" artifacts. The PC-BOSS has a substantially enhanced denuder efficiency for removing gas phase material, compared to the BIG BOSS. The overall efficiency for the removal of gas phase organic material, nitric acid and sulfur dioxide is >99%. As a result, corrections for denuder breakthrough are negligible and fine particulate carbonaceous material and nitrate can be determined from analysis of only the filter packs after the PC-BOSS denuder. Particle loss in the PC-BOSS sampler

is also negligible. Because of the reduced flow rate and the increased concentration of particles, the loss of semi-volatile organic material from particles during sampling with the PC-BOSS is only about one fifth of that in the BIG BOSS. Finally, due to the decreased total flow and decreased total gas phase material passing through the denuder, the diffusion denuder is expected to have a prolonged life-time without significant degradation. Only the filter packs following the diffusion denuder in the sampling system need to be changed between sampling periods.

By addition of a Nafion dryer and a TEOM monitor to the PC-BOSS configuration, a total ambient mass sampler, RAMS, has been developed which is capable of real-time determination of  $PM_{2.5}$  mass, including volatile species such as nitrate and semi-volatile organic material. The instrument minimizes the effect of water on the measurement. Future research will further validate the RAMS by comparison with measurements made using the PC-BOSS for integrated measurements. In addition, experiments will be conducted to see if paradigms can be developed for the estimation of fine particulate water content with the RAMS.

#### Acknowledgments

The research reported here was supported by the U.S. Environmental Protection Agency, the Electric Power Research Institute, and Rupprecht and Patashnick, Inc. Although the research described in this article has been funded in part by the United States Environmental Protection Agency through grant number 825367010 to Brigham Young University, it has not been subjected to the Agency's required peer and policy review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred. The technical assistance of Wenxuan Cui, Jason Hill and Tim Pollock was appreciated.

#### References

- Benner C.L., Eatough D.J., Eatough, N.L. and Bhardwaja P. (1991) "Comparison of annular denuder and filter pack collection of  $HNO_3(g)$ ,  $HNO_2(g)$ ,  $SO_2(g)$  and particulate-phase nitrate, nitrite and sulfate in the Southwest Desert," *Atmos. Environ.* **25A**, 1537-1545.
- Chan T., and Lippmann M. (1977) "Particle collection efficiencies of air sampling cyclones: An empirical theory," *Env. Sci. Tech.* **11**, 377-382.
- Chow J.C. (1995) "Critical Review: Measurement methods to determine compliance with ambient air quality standards for suspended particles," *J. Air & Waste Manage. Assoc.* **45**, 320-382.
- Cui W., Machir J., Lewis L., Eatough N.L. and Eatough D.J. (1997a) "Fine particulate organic material at Meadview

Sioutas C., Koutrakis P. and Olson B.A. (1994b) "Development of evaluation of a low cutpoint virtual impactor," *Aerosol Sci. Tech.* 21, 223-235.

Tang H., Lewis E.A., Eatough D.J., Burton R.M. and Farber, R.J. (1994) "Determination of the particle size distribution and chemical composition of semi-volatile organic compounds in atmospheric fine particles," *Atmos. Environ.* 28, 939-947.

Turpin B.J., Huntzicker, J.J. and Hering S.V. (1994) "Investigation of organic aerosol sampling artifacts in the Los Angeles Basin," *Atmos. Environ.* 28, 3061-3071.

U.S. Environmental Protection Agency. "Air Quality Criteria for Particulate Matter," Environmental Protection Agency, Research Triangle Park, NC, 1996, EPA/600/P-95/001cF.

Vedal S. (1997) "Critical review. Ambient particles and health: Lines that divide," *J. Air & Waste Manage. Assoc.* 47, 551-581.

#### Figure Captions.

- Figure 1. Schematic of the PC-BOSS.
- Figure 2. Schematic of the Real-Time Ambient Mass Sampler, RAMS.
- Figure 3. Effect of minor/total flow ratio, humidity, number of stages and (lower plot) ratio of acceleration slit width to nozzle separation on the concentrator efficiency.
- Figure 4. Comparison of: A. Positive quartz filter artifacts after the denuder of the BIG BOSS and PC-BOSS. B. SVOC lost from particles during sampling for the PC-BOSS and BIG BOSS.
- Figure 5. Response of the RAMS to sampled air if two quartz filters are placed before the diffusion denuder and the Nafion dryer is not used. Data are for two collocated RAMS where the TEOM Monitor temperature is set at 30°C and 50°C for the two instruments. The measured mass is due to the uptake and release of water by the sorbent filter.
- Figure 6. Response of the RAMS to sampled air for ambient and chamber studies if two quartz filters are placed before the diffusion denuders and the Nafion dryer is used. TEOM monitor temperature = 50°C. The response to water seen in Figure 5 is not present unless a major step change in humidity occurs or the puge air for the dryer is stopped.
- Figure 7. Comparison of mass measurements with a RAMS and a collocated conventional TEOM monitor. For the Riverside CA study integrated PC-BOSS and FRM PM<sub>2.5</sub> sampler results are also given.

**Table 1.** Statistical Analysis of PC-BOSS and RAMS Data. Both regression calculated and "zero" intercept linear regression results are given.

Comparison	N	Slope	Intercept $\mu\text{g}/\text{m}^3$	$r^2$	Average $\mu\text{g}/\text{m}^3$	Bias $\mu\text{g}/\text{m}^3$	$\sigma$ , $\mu\text{g}/\text{m}^3$	$\sigma$ , %
Collocated PC-BOSS quartz carbon	7	0.99±0.02	0±1.49	0.99	21.5	0.32	0.93	4.4
		1.02±0.07	-0.75±1.59	0.98				
Sulfate before & after PC-BOSS denuder	20	1.01±0.01	0±0.53	0.99	7.7	0.08	0.36	4.7
		0.98±0.02	0.12±0.54	0.99				
Sulfate before & after PC-BOSS	30	0.98±0.03	0±0.2	0.65	0.9	0.01	0.12	13.
		0.89±0.12	0.1±0.2	0.66				
PM <sub>2.5</sub> C, PC-BOSS vs BIG BOSS	14	1.00±0.04	0±3.14	0.84	17.5	-0.62	2.05	11.7
		0.85±0.09	3.23±2.87	0.88				
Collocated TEOM PM <sub>2.5</sub> mass, 1 hr average	18	1.06±0.02	0±0.0	0.99	10.5	0.19	0.59	5.7
		1.09±0.02	-1.2±0.6	1.00				
Collocated RAMS TX40 mass, 1 hr average	19	1.03±0.01	0±0.8	0.99	12.4	-0.45	0.42	3.4
		1.02±0.02	0.2±0.8	0.99				
TEOM vs. RAMS TX40 mass, 1 hr average	17	0.98±0.04	0±2.3	0.77	14.7	0.19	1.6	10.6
		0.82±0.11	2.5±2.2	0.80				

**Keywords:** Fine Particulate Mass  
Fine Particulate Organic Material  
Carbonaceous Material  
Nitrate  
Sulfate  
Sampling Artifacts  
Denuder Sampler  
Filter Pack Sampler  
Real-Time Sampler

Figure 1

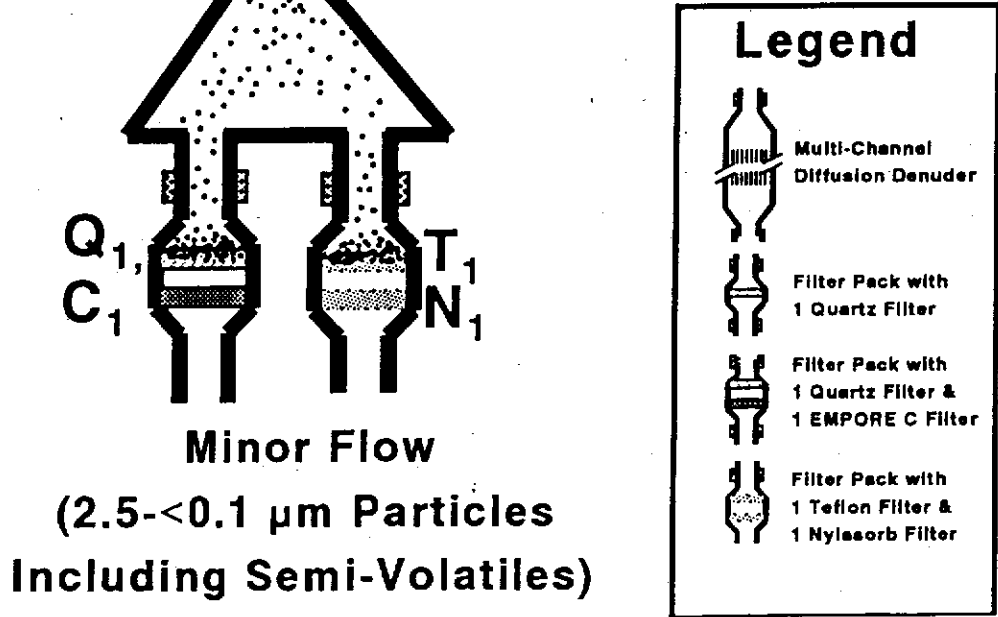
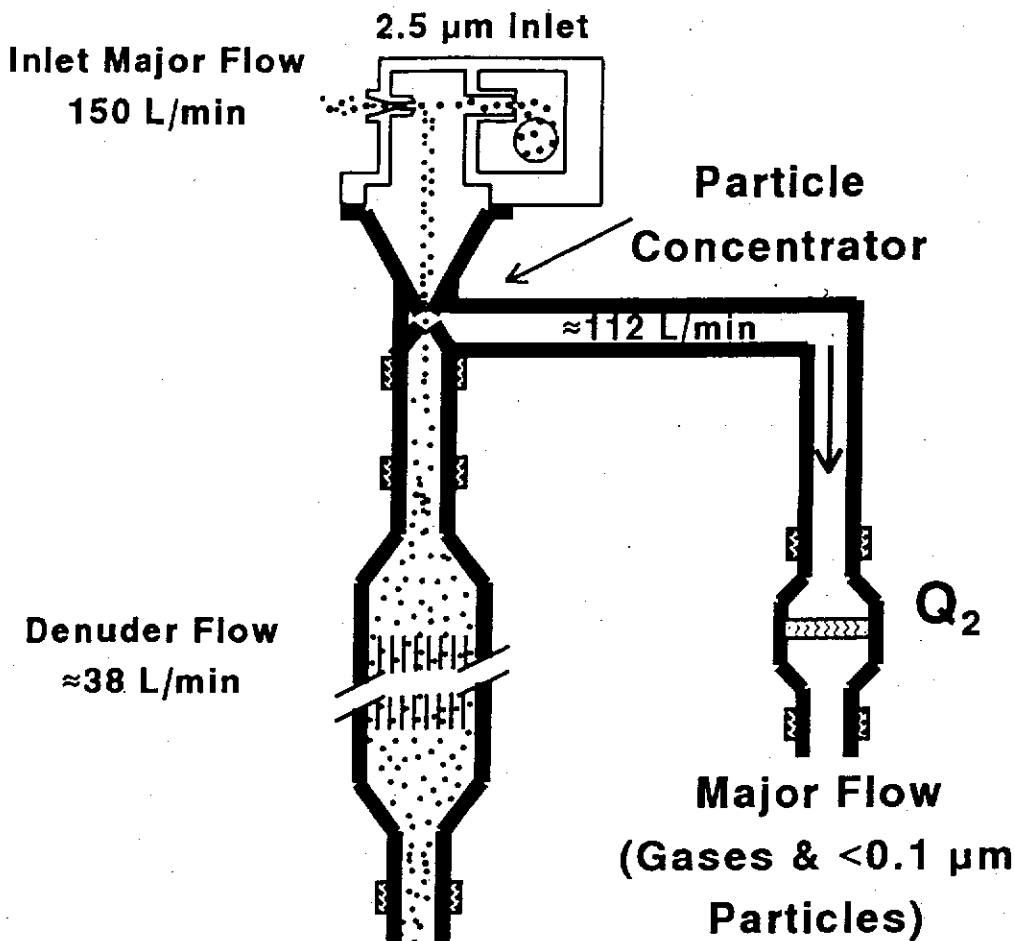


Figure 2

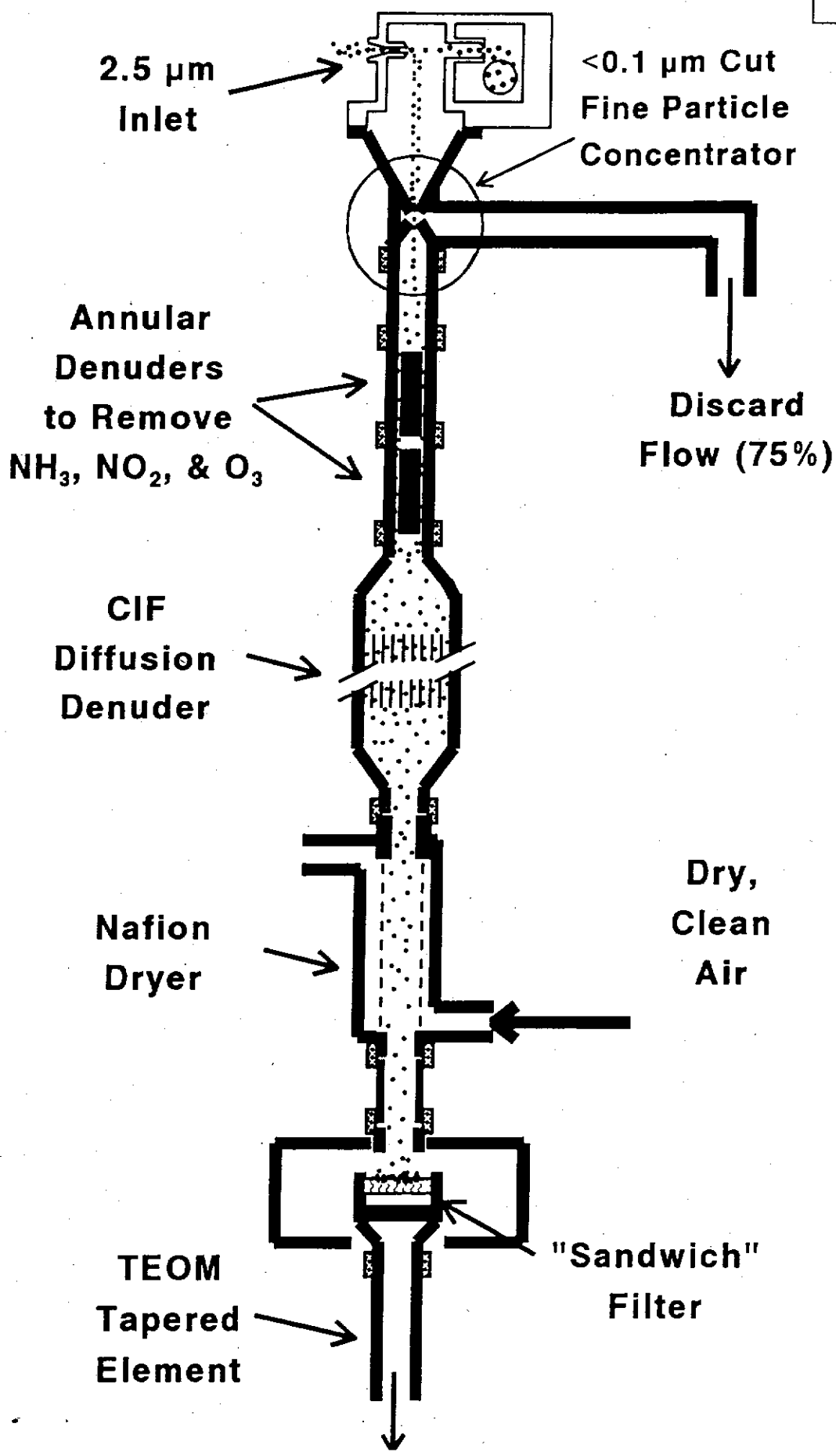




Figure 3

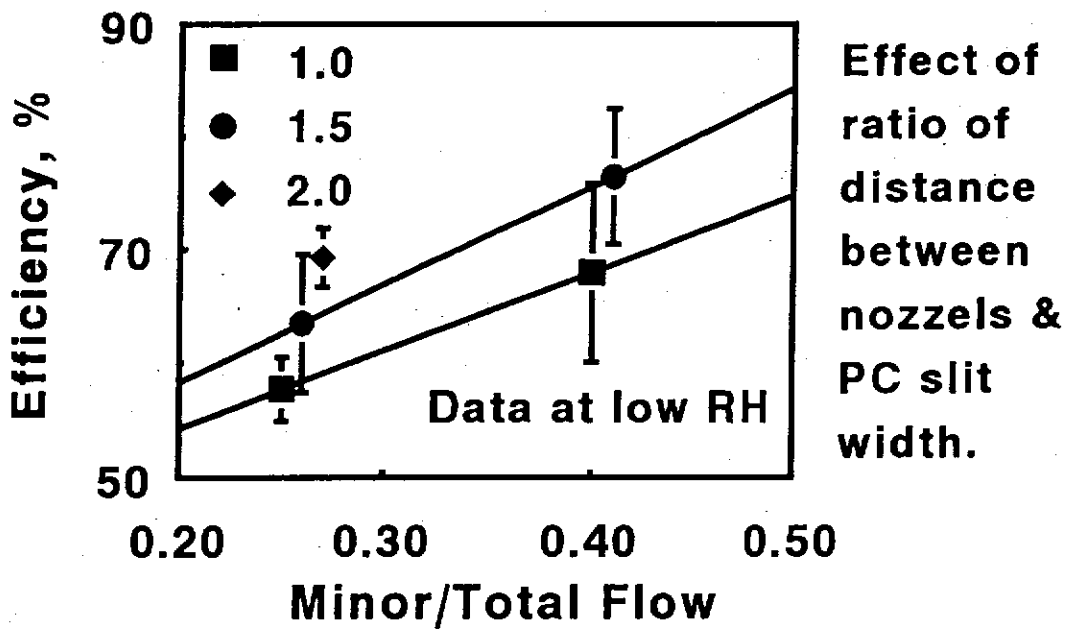
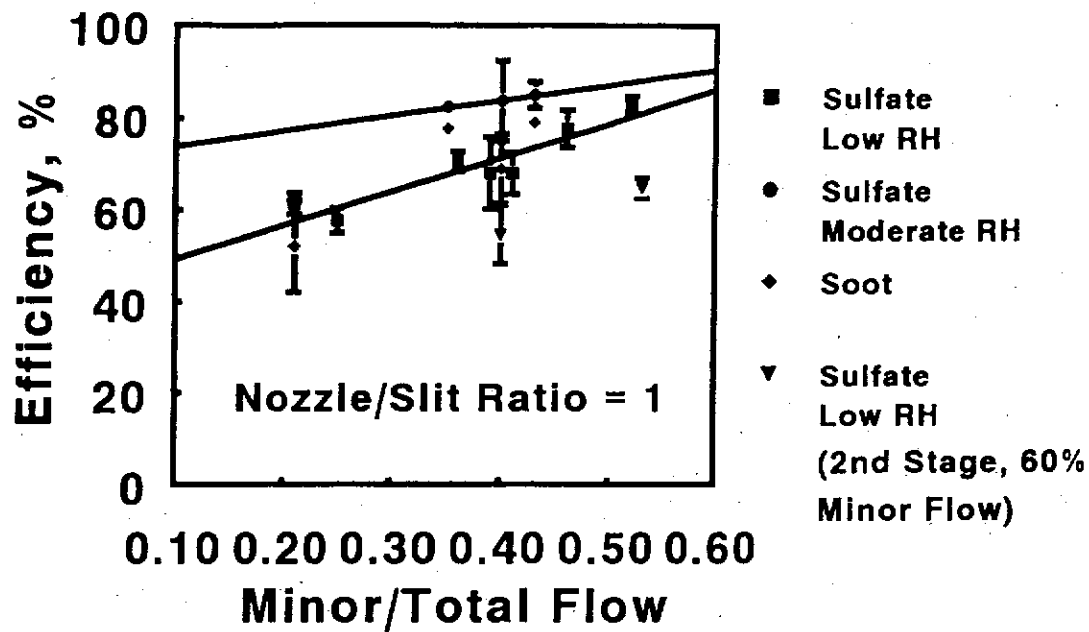


Figure 4

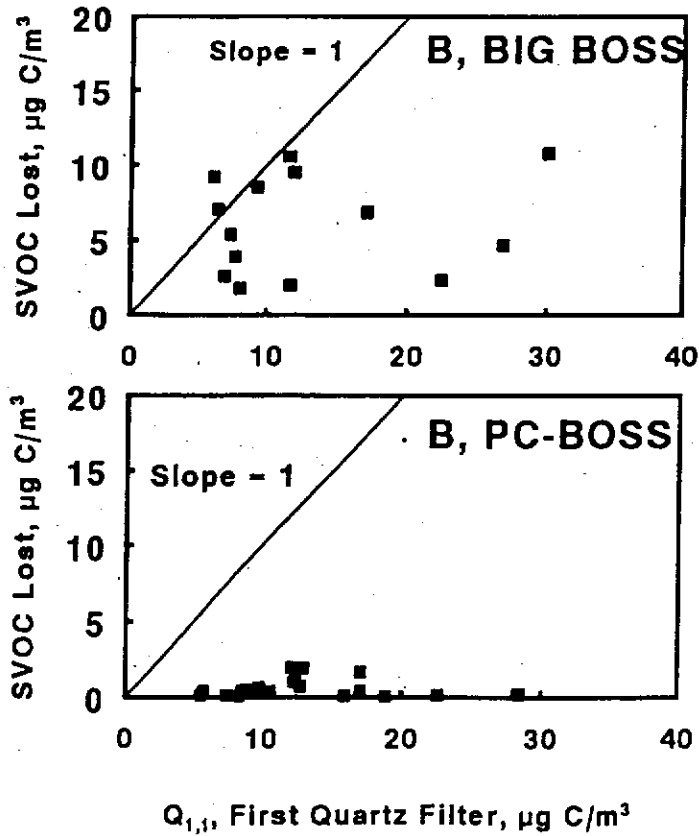
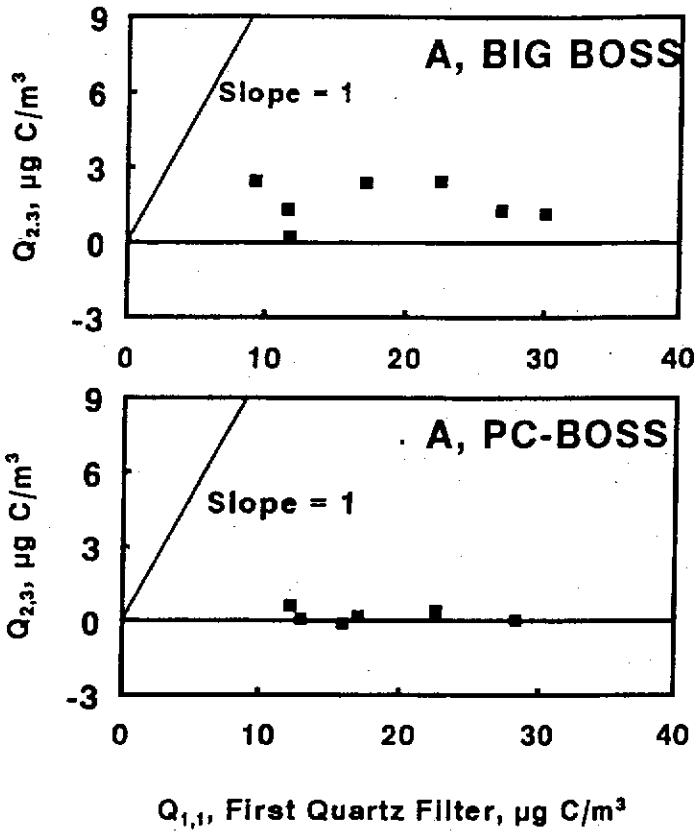


Figure 5

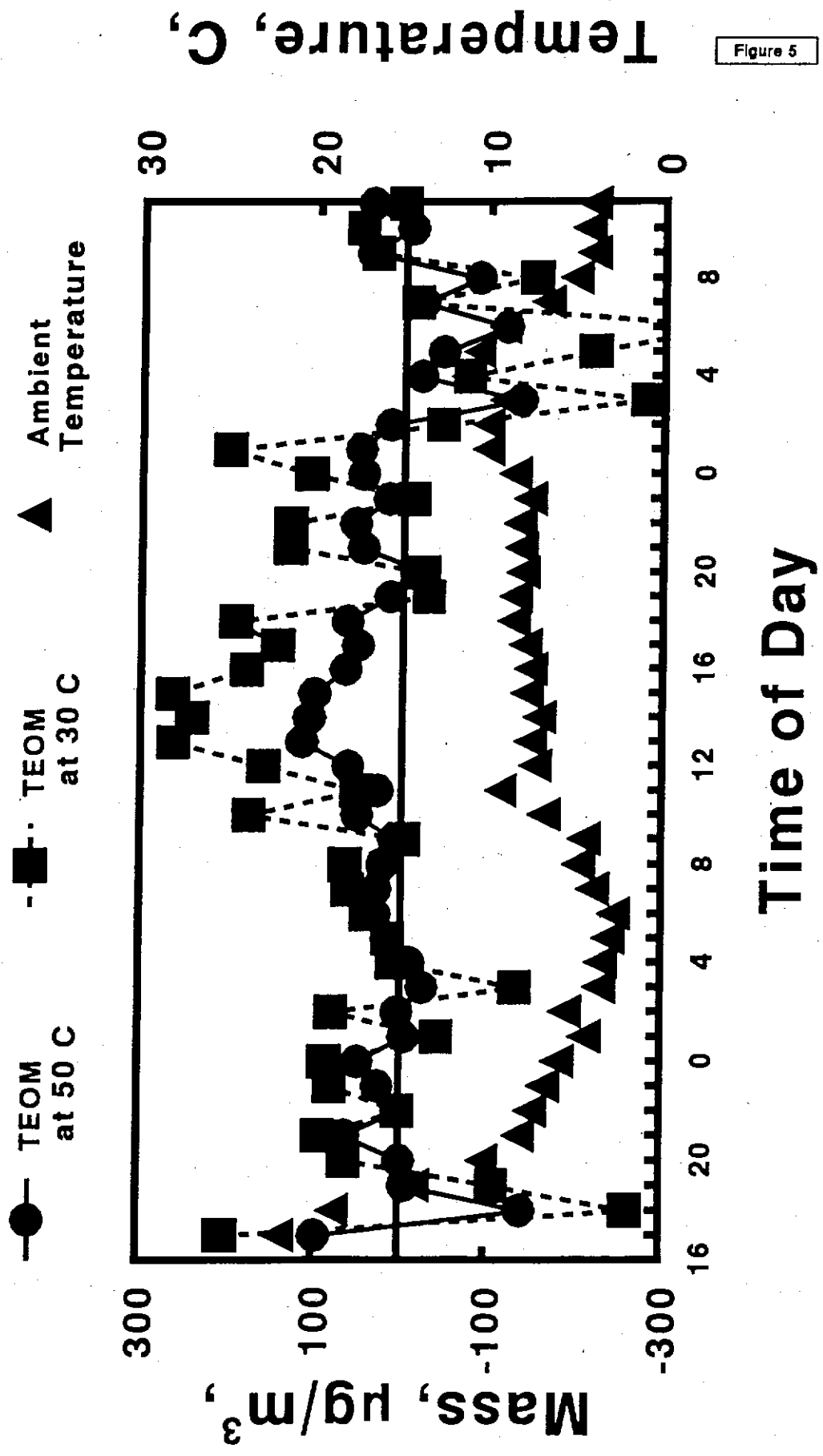


Figure 4

