

## **Appendix C**

# Progress of work on development of a passive sampler for particulate matter and gases

Pamela Padgett and Michel Arbaugh

## Rationale and significance

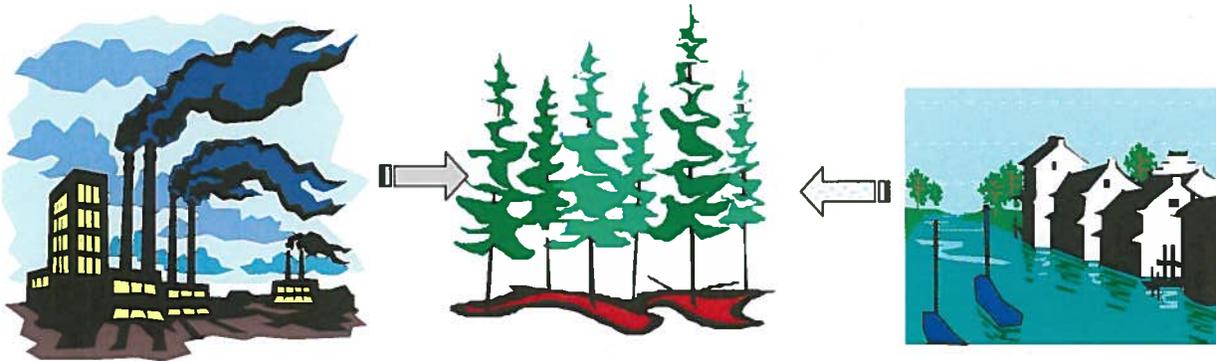
Air pollution is becoming an increasingly difficult management issue on public lands. While urban sources have been singled out for many years, agricultural sources of ammonium, pesticides and fugitive dust are coming under greater scrutiny as farming systems become more intensive. On top of these sources, pollutants generated from wildland fires and controlled prescribed fires have come under regulatory purview. Traditionally, monitoring methods have focused on urban sources and for the most part on urban response issues; therefore regulatory agencies could afford to invest in a few well-equipped monitoring stations with expensive real time monitoring instruments. As the issue of air quality and visibility in natural settings becomes more prominent, the need for more widespread monitoring becomes critical. But with such dispersed landscapes, and the tendency for rural and fire-related pollution to be episodic and unpredictable, investment in sophisticated instrumentation is neither practical nor feasible.

Passive sampling techniques offer a cost effective alternative. Unlike "active" monitors, they can be deployed in remote wilderness areas where access is difficult and line power unavailable. And because they are small and inexpensive, they can be used in large network designs to evaluate regional and temporal pollutant patterns in complex terrain where meteorologic models have difficulty predicting air mass movement. The science of passive sampling is young, however. Like the status of active monitors, some pollutants, most notably ozone, have very good passive methods available, but fewer methods have been developed for ecologically significant pollutants like NH<sub>3</sub> and H/NO<sub>x</sub>.

A wide array of active monitors for particulates are available. The regulatory standard approved by EPA is a gravimetric method, but the equipment is expensive, stationary and relatively labor intensive. Many other, non-regulatory instruments are available. These fall into two general categories, those that use gravimetric determinations of mass, and those that use measurements of light scattering or absorption characteristics to determine concentration, both types depend heavily on particle size distribution. Manufacturers have reduced the size and weight of many units so that they are portable and several are capable of running off of batteries or solar power. However, virtually no passive systems exist for particulate monitoring. This is in part because, unlike the gases, particulate pollutants and the regulatory issues surrounding them are highly varied. Particulate size, (PM 10, PM 2.5 and PM sub1) have human health ramifications, but chemical composition of particulates also has health effects and more significantly ecological importance. Furthermore, in terms of statutory regulation for natural areas, it is the effect of particulates on visibility that is the issue, regardless of source or composition. So the question becomes: What do you want the particulate monitor to measure? For example, if pollutants generated by wild fires are of interest, smoke can be monitored for "soot" (mostly black carbon), or unburnt particles. Fire also generates a tremendous amount of CO<sub>2</sub>, nitrogenous gases and volatile organic carbon compounds, all of which participate in secondary reactions creating ozone, nitric acid and aerosols among others.

## Experimental objective

Our goal was to develop a method that could be used to measure several different components of particulate pollutants either simultaneously or independently. We were interested in not only monitoring air-borne particulates, but also exploring means of determining deposition or accumulation of these pollutants to terrestrial ecosystems.



**Figure 1.** Wind direction and wind speed determine the effects of air pollutants on ecosystems.

## Design theory

The main difference between a typical active air pollution monitor and corresponding passive monitor is delivery of the air stream to the collection surface or detector. For example a Dasibi ozone monitor draws the ambient air at a constant rate into the detector and by calibration and modeling calculates an ambient concentration. An Ogawa passive ozone monitor, on the other hand, employs diffusion of ambient air by preventing turbulent flow with physical barriers. Ambient concentrations are collected on a reaction surface and again by calibration and modeling, an average ambient concentration over the exposure period is calculated.

It would seem, however, that in terms of relevant ecological responses,  $1 \mu\text{g per m}^3$  of  $\text{HNO}_3$  in still air would have a very different effect from the same concentration being delivered at  $2 \text{ m sec}^{-1}$ . Recognizing that delivery and subsequent deposition of air pollutants is dependent on laminar and turbulent flow (wind speed, direction and patterns) our theoretical approach was to design a passive monitoring system that was sensitive to wind speed and direction. The premise being that such a system would model the interactions between air pollution transport and a tree, a forest stand or location, so that not only ambient concentrations are determined, but the amount of pollutant actually contacting the site of interest could be calculated.

A second requirement was for a collection media that would trap pollutants both chemically and physically. The chemical trap needed to be non-specific enough to absorb several pollutants, and the physical trap needed to be effective enough to quantitatively hold pollutants, but also permit extraction and release of those pollutants for determination of concentration. And finally, if the device was to use wind velocity as delivery mechanism we needed to be able to monitor wind speed and direction.

## Materials – testing and selection

Collecting media:

Several materials were evaluated for suitability:

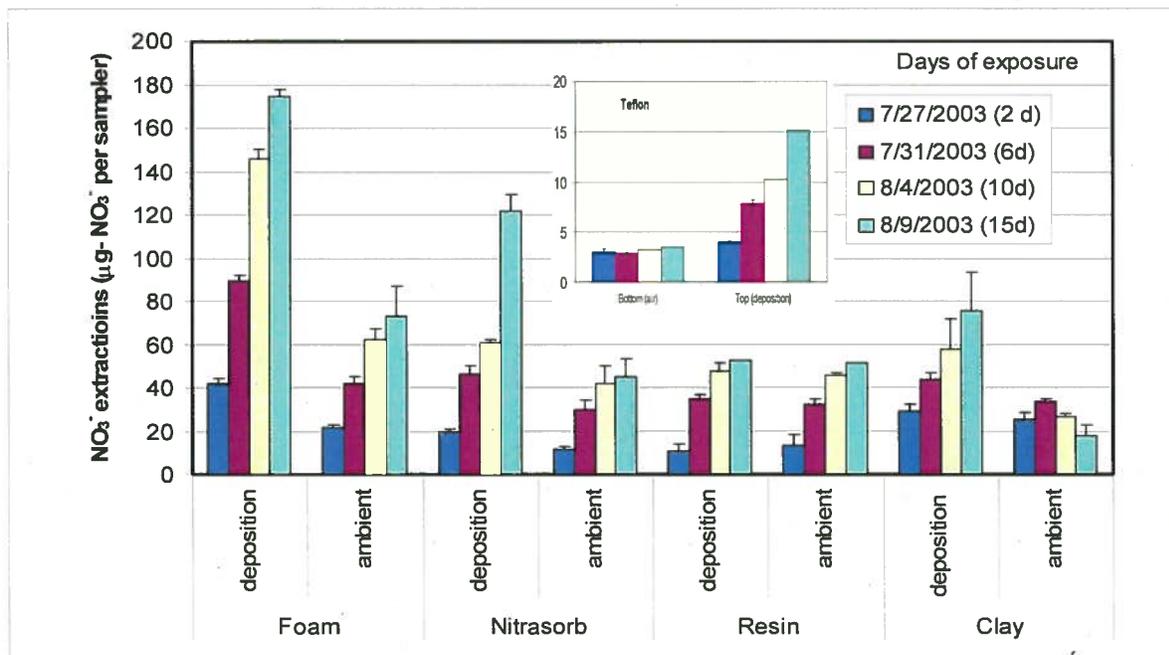
- Dowex anion exchange resin, a laboratory grade ion exchange resin
- NitraSorb, a mixed bed resin used in aquariums
- Ceramic blocks, baked kaolinite pottery clay
- PolyFilter, an ion exchange foam used in aquariums

Ion exchange resins are used occasionally for ambient air monitoring. Typically the beads are loosely held in a “tea-bag” arrangement. The problem with this technique has been in determining the surface area component important for calculations of deposition rates. Rather than a “tea-bag”, we affixed a single layer of resin to 5 cm plastic petri dishes. Although the total surface area was not known (it could be estimated), the exposure area was. NitraSorb is one of several mixed bed resins available for a number of applications. This particular proprietary mix was design for purification of aquarium water. Although it might seem odd to use materials designed for aqueous applications, there are in fact many similarities between solid-aqueous and solid-gaseous physical chemistry. (As an aside most of the laws of physical chemistry are derived from gaseous behavior, but most of the practical applications are aqueous) Ceramic blocks were chosen for a number of reasons, most importantly fumigation studies had shown that deposition to clay-sized particle in soils was linear with respect to dose and required very long exposures before they began to saturate. Ceramics are basically clays that have baked and fused. They are available in a wide variety of mineral content, which control the surface chemistry, and depending on the intended use can be quite pure. We used a kaolinite clay purchased from a pottery company. Uniform blocks of clay were made and baked at low temperature so that they remained very porous. In general the higher the temperature, the more fused the clays become and the less porous. (Think of a fine china plate vs. a clay flowerpot. They may be of the same mineralogy, but difference in oven temperatures and duration changes the surface characteristics.) The last material, PolyFilter, is also a proprietary material designed for aquarium filtration. It is also being developed for drinking water purification systems. The manufacture claims that it takes the place of ion exchange resins and activated charcoal for removal of undesirable solutes, and glass wool for removal of particulates in aquarium filtration systems.



**Figure 2.** First test to evaluate the materials ability separate ambient concentrations from atmospheric deposition. (a) Teflon filter mounted for open exposure (b) Teflon filter mounted for ambient monitoring using a turbulent flow inhibitor.

The ability of each material to adsorb nitrogenous pollutants was assessed. We chose to focus on nitrogen-containing gases and particulates because they are found in both anionic ( $\text{NO}_3^-$ ) and cationic ( $\text{NH}_4^+$ ) forms and in particulates of a wide range of sizes. These were compared to Teflon filters (a negative control). Ambient adsorption due to diffusion fluxes was compared to adsorption due to “deposition”. Each material was mounted beneath a protective cup to reduce turbulent flow, and on top of the protective cup to allow full exposure to wind delivery. The purpose was to ensure that the collecting material could differentiate between free air ambient concentrations and pollutants delivered by turbulent flow. The test was run for a total 15 days with a subset collected on day 2,6, and 10



**Figure 3.** Extractable  $\text{NO}_3^-$  concentrations from the 4 candidate materials and Teflon filters (inset). A comparison of ambient concentrations to concentrations collected by depositional processes. (Error bars = 1SE n=3)

All materials collected significantly more  $\text{NO}_3^-$  than did Teflon (Figure 2). The ion exchange resins demonstrated no ability to differentiate ambient concentrations delivered by diffusion from turbulent flow delivery and the clay samplers were adequate deposition collectors, but poor ambient monitors. Both the foam and the mixed bed resins preformed well, but the foam was both more responsive and easier to handle

## PolyFilter

### *Chemical response*

PolyFilter is a dense fiber mesh approximately ½ inch thick. In appearance it is similar to mesh-type filters used in heating inlets. Although we referred to as foam it is not an expanded plastic product such as Styrofoam. It is made by a single manufacture, Poly-Bio-Marine Inc. An Australian group has developed a similar material, but for lack of funding and interest it has been shelved for the time being (e-mail communication 7/5/2002). The manufacturer makes several claims on the website (<http://www.poly-bio-marine.com/>) regarding its use and application, some of which seemed a little outlandish by our chemistry collaborators who conducted the preliminary chemical evaluations. (Drs. Chris Amhrien and Dave Parker Dept. of Environmental Sciences, UCR). Several tests were conducted to evaluate retention of key solutes and desorption of retained solutes. For our application, the foam needed to quantitatively retain solutes and those solutes must elute quantitatively. The retention tests indicated that 90% of the  $\text{NO}_3^-$  was retained from 20ml of a 1mm  $\text{HNO}_3$  solution, which is roughly equivalent to 3 months of very high atmospheric concentrations. Interestingly, it retained only 74% of the  $\text{NO}_3^-$  from 20 ml of a 1mm  $\text{NaNO}_3$  solution. Analysis of the eluted solution suggests the 75% or the retention is due to exchange with  $\text{Cl}^-$ , (no other commonly used exchangeable ion was detected), suggesting some mechanism other than ion exchange was at work with the acid form of the anion. Although the chemistry is unclear, it appears that the foam has retention characteristics other than a straightforward ion exchange. Retention of  $\text{NH}_4^+$  was pH dependent which is consistent with the  $\text{NO}_3^-$  data. At the lower pH 6, 50% of the  $\text{NH}_4^+$  was retained from a 1mm  $\text{NH}_4\text{Cl}$  solution, while less than 1% was retained from a pH 8.5 solution.

Elution and recovery of solutes was complicated by the multiple mechanisms employed by the foam. 50% to 70% of the  $\text{NO}_3^-$  loaded on the foam samples was recovered by standard ion exchange techniques. However, more significantly, the recovery was reproducible and replicates were within 10% of one another. The optimum elution method is still in development.

The efficacy of gaseous trapping was determined in continuously stirred tank reactors (CSTR, Figure 4) designed to synthesize and monitor  $\text{HNO}_3$  vapor. The foam was enclosed in a PVC pipe placed in an air stream containing 40 to 70 ppb  $\text{HNO}_3$ . At the opposite end of the pipe a Nylasorb filter was mounted to catch any  $\text{HNO}_3$  that escaped through the foam. Analysis showed no  $\text{NO}_3^-$  on the filters, indicating that the foam was an effective trap for  $\text{HNO}_3$ .

### *Porosity and density of the medium*

The material is highly porous, but dense. The thickness and the density are inconsistent across the 12" by 12" sheet; it is unclear why, but presumably it has something to do with the manufacturing process. For our purposes, the lack of uniformity may prove to be a problem for landscape scale assessments - that has yet to be determined. The design requires air streams to be able to pass through the foam with greater than 50% efficiency. Initial tests on ½ diameter plugs mounted in PVC as described above indicated that wind speeds had to reach 6 m sec<sup>-1</sup> (pretty much gale-force) before air movement could be detected at the opposite end. We have since increased the plug diameter and manipulated the fibers to increase wind passage, but additional tests are needed.



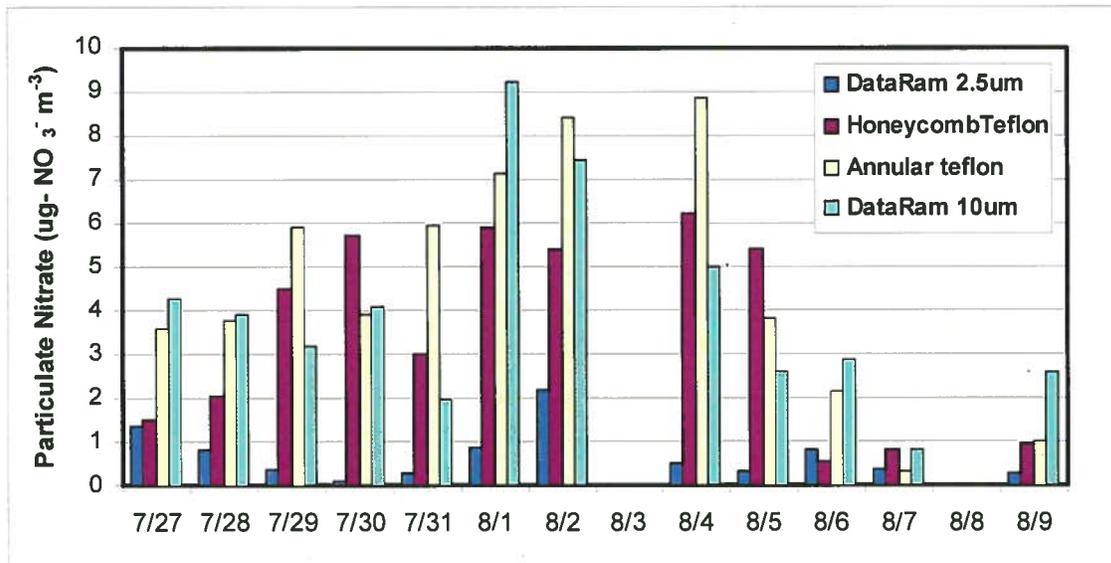
**Figure 4.** Evaluating gaseous trapping in CSTR. Foam plugs were inserted into one end of a ½ inch PVC pipe. Nylasorb filters were mounted at the other end (blue colored sheets). The foam end was inserted into the HNO<sub>3</sub> air stream.

### **Establishing appropriate monitoring comparisons.**

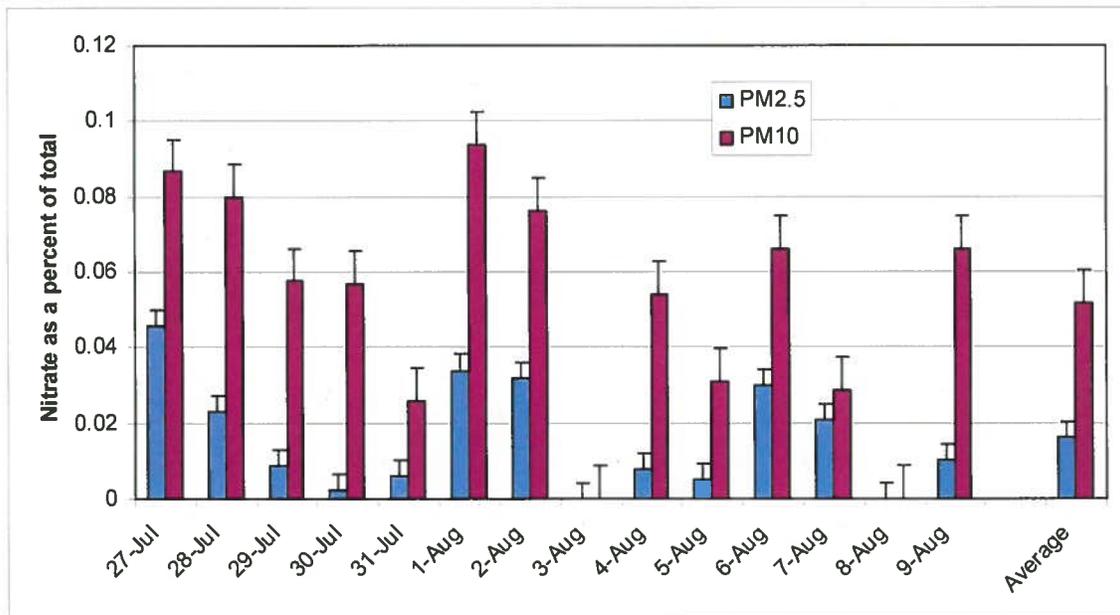
Two MEI (now a part of Thermo-Anderson) DataRam 4000 (DR4000) particulate monitors were purchased for this project. The DR4000s use light scattering to measure particulate density and, within certain parameters, particulate size. The standard inlet has a cyclone cut off that eliminates particulates greater than 10µm. Cut point inlets for 2.5µm and 1.0µm can be installed on the inlets to further reduce particle sizes. We used both 10µm and 2.5µm cut sizes for the tests. Unlike most particulate samplers the DR4000 has a filter-trapping feature that enables particulates to be collected for chemical analysis. Our intent is to use this feature to compare the efficacy of the passive systems to the active monitors.

Since we began using nitrogenous pollutants as our test pollutant species, we evaluated the DR4000 collection surface against the more established denuder systems for monitoring nitrogenous pollutants. We compared the nitrate containing particulates collected by honeycomb denuders, and annular denuders to the DR4000 using the 2.5µm cut point inlet and the, factory calibrated 10µm cyclone. Each system used Teflon filters to catch particulates, which were eluted and analyzed by standard method. Filters were exchanged on each instrument every 24 hours at the same time. Theoretically, both denuder systems were using a 2.5 cut size, although nitrate concentrations were clearly closer to the DR4000 PM10 range. Since each day was different and there was no replication of the DR4000 and only duplicates for the denuders, the error of the sampling cannot be established. However the DR4000 2.5 sampler appears to be in a separate class, whereas the other 3 systems produced similar results (Figure 5). When the percent of the total particulate load was compared to the nitrate-containing load, the nitrate-containing pollutants were more likely to be found in the larger particles (error bars = 1 SE for the entire data set, not

replicated samples for each day). The nitrate containing particles were a small fraction of the total, at less than 1% (Figure 6).

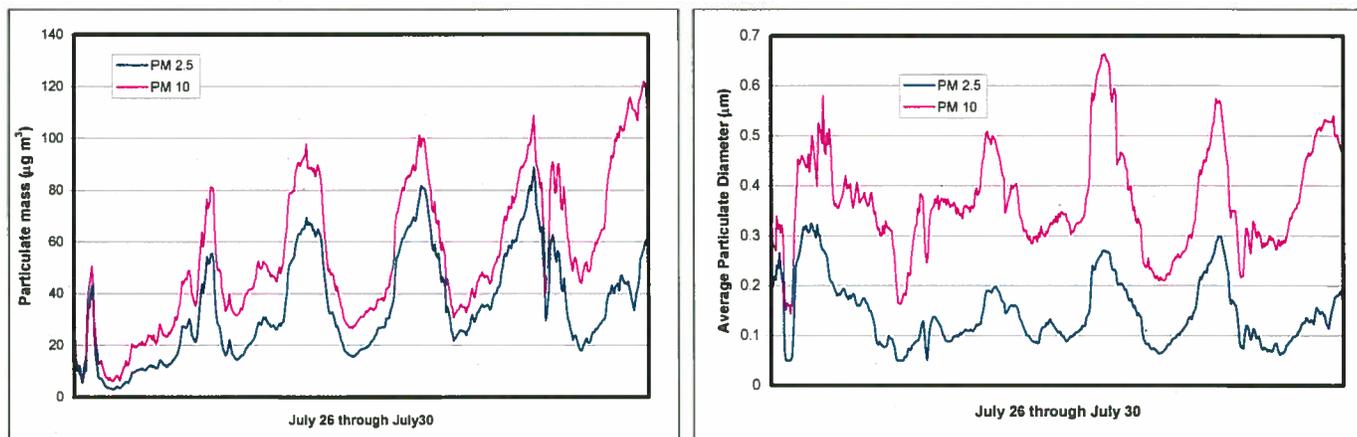


**Figure 5.** Nitrate concentration from particulates collected by denuders and DR4000. The data are the average of 2 systems for honeycomb denuders and annular denuders, and single instruments for 10 $\mu\text{m}$  and 2.5 $\mu\text{m}$  DataRams.



**Figure 6.** Nitrate mass as a percentage of the total particulate mass.

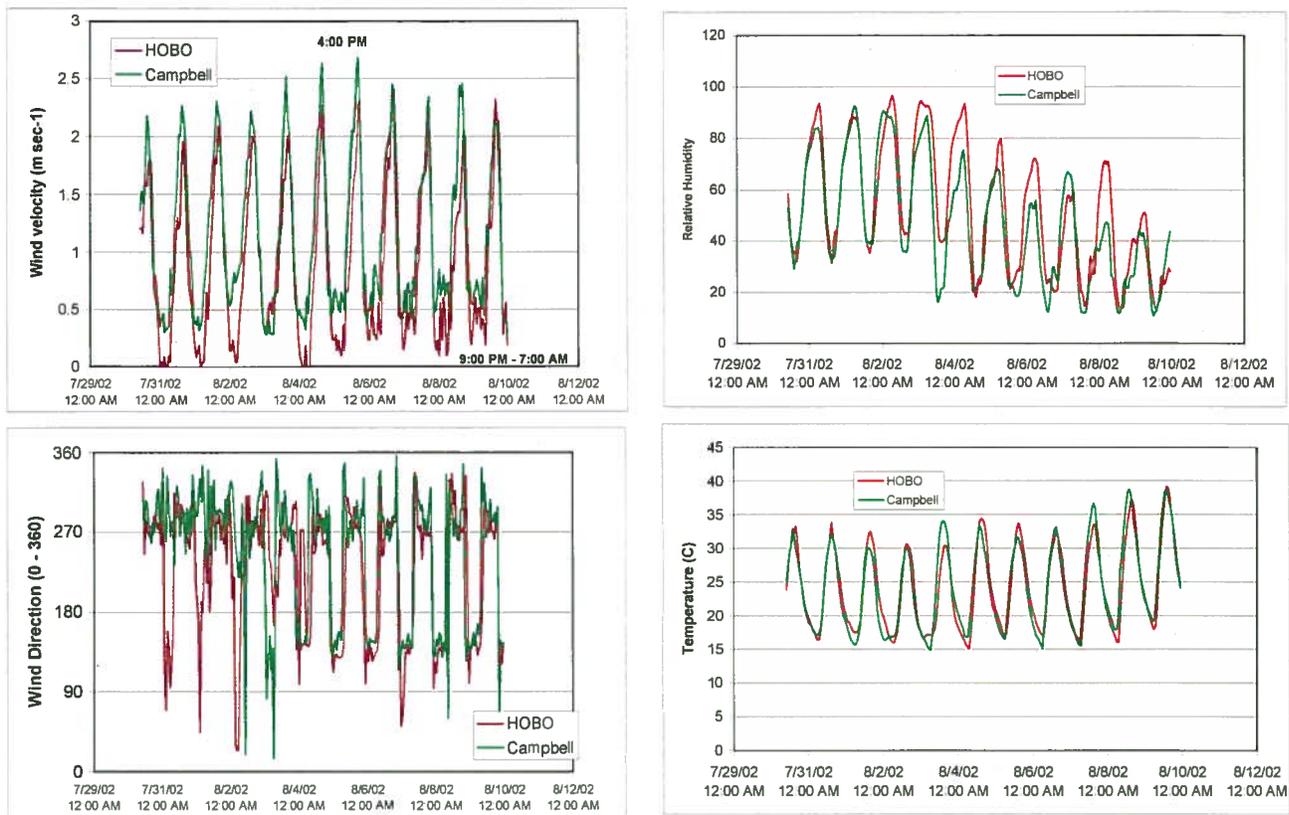
One of the more surprising pieces of information to emerge from the DR4000 evaluations was the diurnal pattern of particle size (Figure 7). The increasing availability of real time monitors for particulate size has revealed that, not only are atmospheric loads subject to daily fluctuations due to physicochemical aerosol formation and wind patterns, but the size of the particles also changes during the day.



**Figure 7.** Typical diurnal patterns of atmospheric load and average particle size. The figures display a 5-day interval of data collected from 2 different DR4000, one maintaining the calibrated PM10 range and the second operating with the PM2.5 inlet.

## Weather monitoring

Onset Computers (who produces the “HOBO” series of dataloggers) in recent years have developed highly efficient, low cost, weather stations. These systems are easily deployed in remote locations being powered by common D cell batteries, which last for several months depending the number of sensors. At the time this project was begun, Onset had just released a combination wind speed and wind direction unit. As part of the project, we purchased 2 systems and compared their output to the most commonly used scientific weather instruments produced by Campbell Scientific Instruments. Temperature and relative humidity (RH) were generally within 10% on one another (Figure 8). The correlation factor was a little better for temperature ( $r=0.88$ ) than for RH ( $r= 0.8$ ). Some of the differences may have been in the original calibration of the sensors and possibly in the datalogging. The output on the Campbell system uses a 5-minute average of 5 readings, while the Onset system records a single reading every 5 minutes.



**Figure 8.** Comparison of readout data from a Campbell Met station and the Onset Computer Met station.

More importantly, the wind data were also comparable, although the Campbell system seemed to have a calibration error as wind speeds below  $0.4 \text{ m sec}^{-1}$  were rarely recorded (Figure 8). The data comparisons of wind direction were more variable, particularly at low wind speeds, however. The Onset instrument recorded more significant winds out of the west ( $90^\circ$ ) than were detected by Campbell instrument. If the wind speed detector was out of calibration or not operating smoothly, it is likely that the director detector was as well. It is also possible that the difference in datalogging method describe about may have affected the recorded data.

During the summer of 2003, the Onset weather stations were deployed at 3 remote locations, 1 in the Eastern Sierra and 2 in the San Bernardino Mountains for 2 months. One system developed a short in a sensor wire, which resulted in rapid loss of battery power. The source of the problem turned out to be wildlife interference; something, most likely rodents, chewed on one of the cables, creating an electrical problem. Other than that, all 3 systems worked flawlessly. We concluded that the Onset HOBO weather stations were comparable to the Campbell systems, and given the cost and ease of installation they were incorporated into our prototype.

## Prototype design



**Figure 7.** Prototype for particle sampling.

The sampling device is mounted on top of the wind speed/direction sensor, which is plugged into the data logger. The original concept was to have one collector facing into the wind and a second out of the wind. The collector out of the wind that would collect ambient concentrations similar to those described for passive analysis of gaseous pollutants. For aerodynamic reasons, there is good reason to believe that this approach will not work, although monitoring of the still air concentrations is still desirable. As the wind shifts direction, the sampler is always collecting what is delivered to that location; meanwhile the data logger records wind direction and speed. In many areas there are seasonally dominant wind directions. Shifts in direction often signal storms or changing weather patterns such as the Santa Ana winds of Southern California. During these events pollutant loads can shift dramatically. This monitoring system could be made sensitive enough to detect such changes. It could be used to monitor emissions if a source is known, or to help locate a source if it is not.

The wind vanes need not be plugged into a data logger. Several applications where 1 central wind sensor with several satellite collectors can be envisioned. As shown here, several collectors could also be stacked if different collection media are required.

### *Estimated cost:*

Onset weather station kits include datalogger, wind/direction sensor, temperature/RH sensor with shelter, 3m tripod and stand, required software: \$1200 (discounts for multiples)

Datalogger separately: \$200

Wind speed/direction sensor: \$450

Particulate collector: Expendable PolyFilter \$60 per 12" X 12" sheet  
Housing \$15 (prototype, less once the design is established)

## **Next stages of experiments**

This activity was launched late in the Joint Fire Sciences project funding cycle. It was not necessary part of the original proposal, but brainstorming among the group indicated that development of passive particulate sampling methods would be extremely beneficial to the goals of the project. Further investigation suggested that it was also feasible. We have several studies that need to be completed before we can confidently recommend this approach to determining particulate loads in remote locations.

Several more physical and chemical tests of the PolyFilter will be undertaken.

Among them are:

- Addressing the air flow-through properties of the foam
- Evaluation of elution techniques for retained solutes
- Controlled exposures to non-nitrogenous particulates
- Detection methods for non-nitrogenous particulates need to be developed:
  - Gravimetric
  - Elemental carbon
  - Silica
  - Other?

Field-testing both at the Riverside Fire Lab (RFL), where we have extensive monitoring equipment, and at remote sites needs to be conducted. Riverside is well known for its high pollution loads during the summer and the ambient pollution in Riverside is often used as “experimental treatments”. The proximity to personnel and the analytical laboratory enables detailed evaluation of sampler performance and adjustment to prototypes as the data accumulates. Riverside is also adjacent to the San Bernardino National Forest, perhaps the best characterized natural ecosystem with regard to pollution impacts in the US. Gradients in atmospheric contamination have been long established in the San Bernardino’s. We expect to use the gradients to further evaluate sampler performance. Additionally, as part of a unique study to determine distribution, transport, and effect of limestone mining on carbonate plant species in the San Bernardino’s, we will deploy the prototypes to monitor calcium carbonate particulates side-by-side with the DR4000. We have developed sound methods for measuring limestone deposition that will be serviceable for extraction of the PolyFilter.

## **Expected products**

Detection and measurement of airborne particulates is currently expensive and labor intensive. This project was initiated to develop a method that could be used in remote locations and was inexpensive enough enable monitoring of many sites simultaneously. We expect to produce a reliable, flexible device in the next few years.

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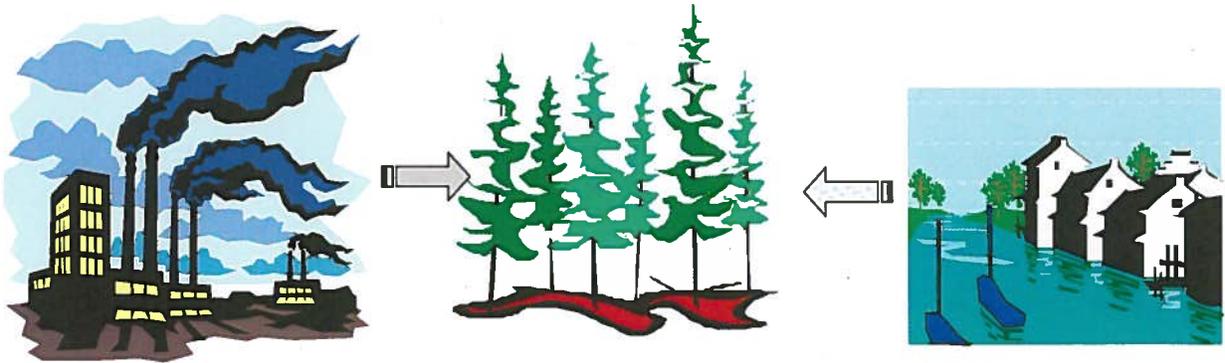
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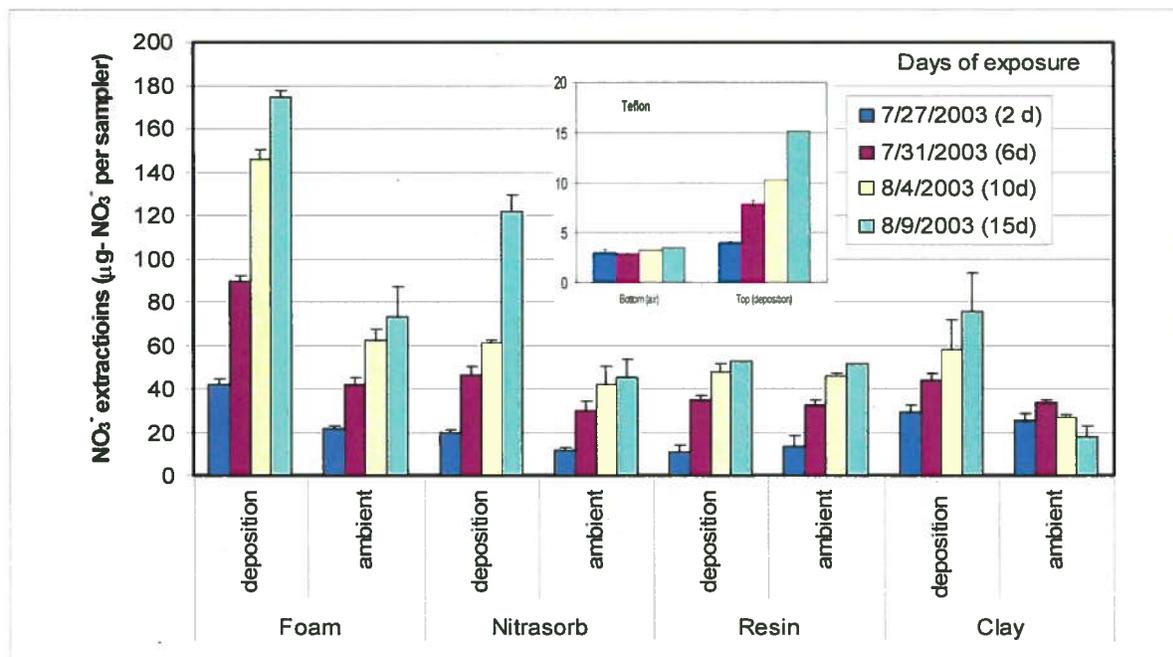
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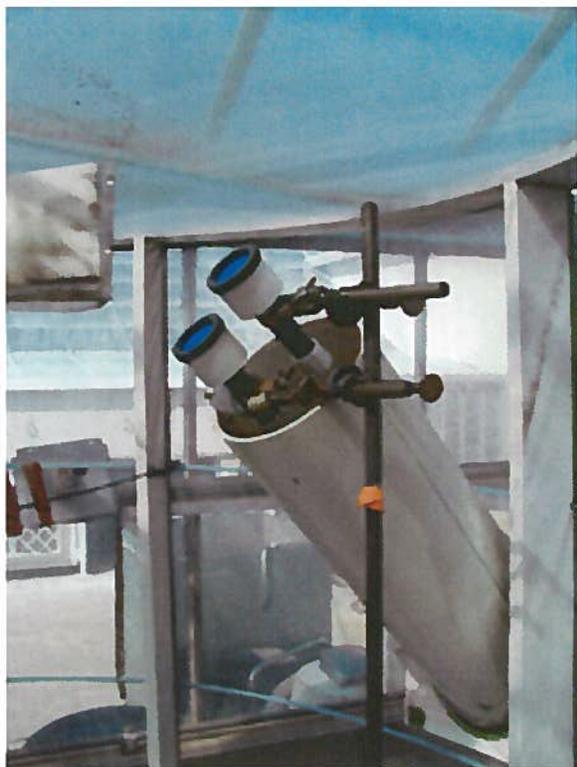
PolyFilter is a dense fiber mesh approximately ½ inch thick. In appearance it is similar to mesh-type filters used in heating inlets. Although we referred to as foam it is not an expanded plastic product such as Styrofoam. It is made by a single manufacture, Poly-Bio-Marine Inc. An Australian group has developed a similar material, but for lack of funding and interest it has been shelved for the time being (e-mail communication 7/5/2002). The manufacturer makes several claims on the website (<http://www.poly-bio-marine.com/>) regarding its use and application, some of which seemed a little outlandish by our chemistry collaborators who conducted the preliminary chemical evaluations. (Drs. Chris Amhrien and Dave Parker Dept. of Environmental Sciences, UCR). Several tests were conducted to evaluate retention of key solutes and desorption of retained solutes. For our application, the foam needed to quantitatively retain solutes and those solutes must elute quantitatively. The retention tests indicated that 90% of the  $\text{NO}_3^-$  was retained from 20ml of a 1mm  $\text{HNO}_3$  solution, which is roughly equivalent to 3 months of very high atmospheric concentrations. Interestingly, it retained only 74% of the  $\text{NO}_3^-$  from 20 ml of a 1mm  $\text{NaNO}_3$  solution. Analysis of the eluted solution suggests the 75% or the retention is due to exchange with  $\text{Cl}^-$ , (no other commonly used exchangeable ion was detected), suggesting some mechanism other than ion exchange was at work with the acid form of the anion. Although the chemistry is unclear, it appears that the foam has retention characteristics other than a straightforward ion exchange. Retention of  $\text{NH}_4^+$  was pH dependent which is consistent with the  $\text{NO}_3^-$  data. At the lower pH 6, 50% of the  $\text{NH}_4^+$  was retained from a 1mm  $\text{NH}_4\text{Cl}$  solution, while less than 1% was retained from a pH 8.5 solution.

Elution and recovery of solutes was complicated by the multiple mechanisms employed by the foam. 50% to 70% of the  $\text{NO}_3^-$  loaded on the foam samples was recovered by standard ion exchange techniques. However, more significantly, the recovery was reproducible and replicates were within 10% of one another. The optimum elution method is still in development.

The efficacy of gaseous trapping was determined in continuously stirred tank reactors (CSTR, Figure 4) designed to synthesize and monitor  $\text{HNO}_3$  vapor. The foam was enclosed in a PVC pipe placed in an air stream containing 40 to 70 ppb  $\text{HNO}_3$ . At the opposite end of the pipe a Nylasorb filter was mounted to catch any  $\text{HNO}_3$  that escaped through the foam. Analysis showed no  $\text{NO}_3^-$  on the filters, indicating that the foam was an effective trap for  $\text{HNO}_3$ .

### *Porosity and density of the medium*

The material is highly porous, but dense. The thickness and the density are inconsistent across the 12" by 12" sheet; it is unclear why, but presumably it has something to do with the manufacturing process. For our purposes, the lack of uniformity may prove to be a problem for landscape scale assessments - that has yet to be determined. The design requires air streams to be able to pass through the foam with greater than 50% efficiency. Initial tests on ½ diameter plugs mounted in PVC as described above indicated that wind speeds had to reach 6 m sec<sup>-1</sup> (pretty much gale-force) before air movement could be detected at the opposite end. We have since increased the plug diameter and manipulated the fibers to increase wind passage, but additional tests are needed.



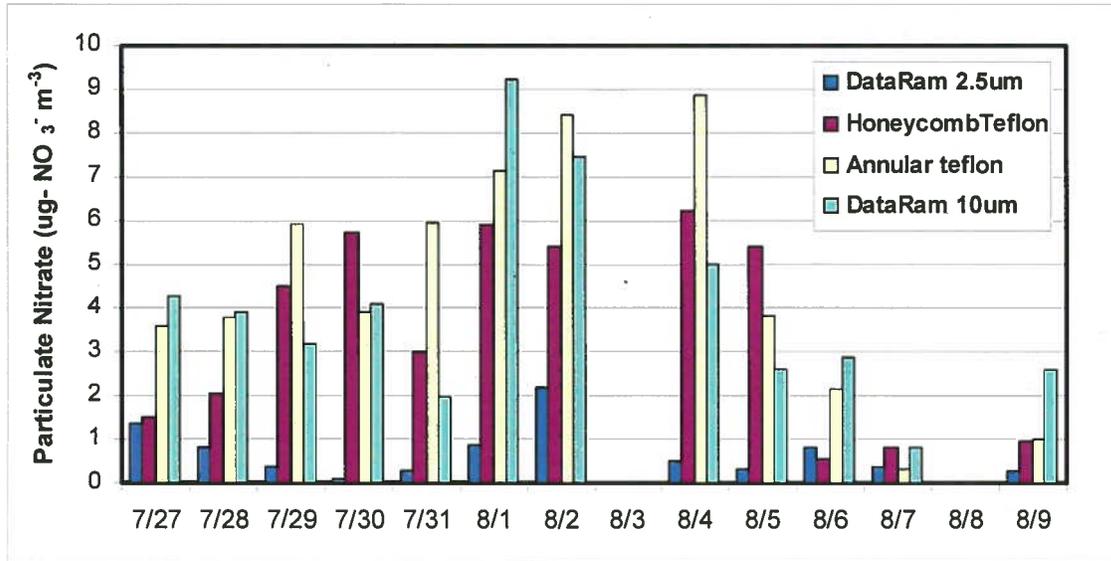
**Figure 4.** Evaluating gaseous trapping in CSTR. Foam plugs were inserted into one end of a ½ inch PVC pipe. Nylasorb filters were mounted at the other end (blue colored sheets). The foam end was inserted into the HNO<sub>3</sub> air stream.

### **Establishing appropriate monitoring comparisons.**

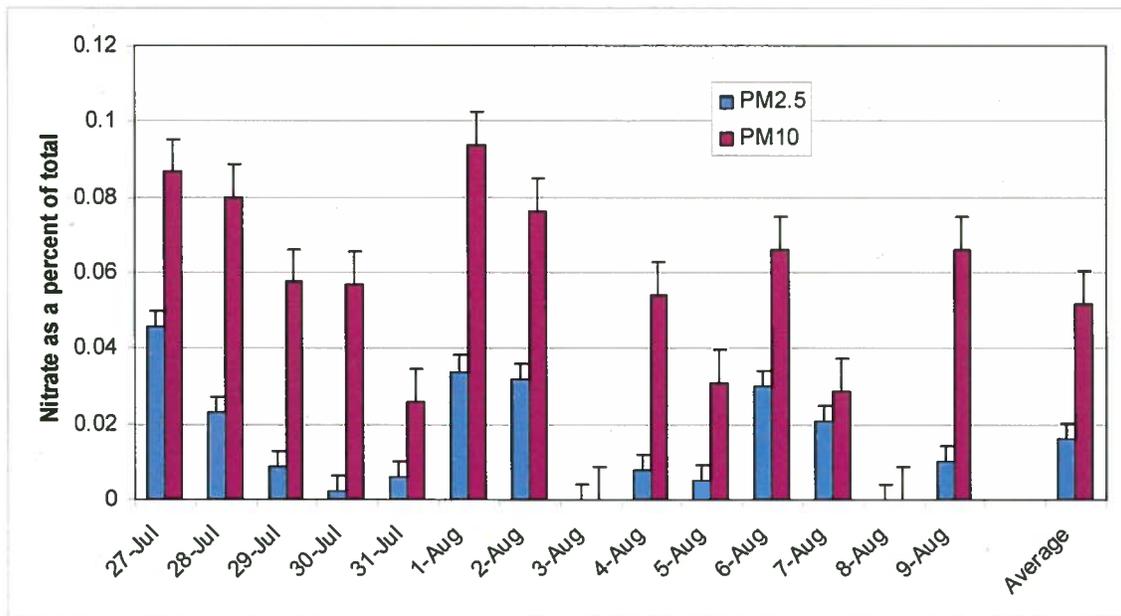
Two MEI (now a part of Thermo-Anderson) DataRam 4000 (DR4000) particulate monitors were purchased for this project. The DR4000s use light scattering to measure particulate density and, within certain parameters, particulate size. The standard inlet has a cyclone cut off that eliminates particulates greater than 10µm. Cut point inlets for 2.5µm and 1.0µm can be installed on the inlets to further reduce particle sizes. We used both 10µm and 2.5µm cut sizes for the tests. Unlike most particulate samplers the DR4000 has a filter-trapping feature that enables particulates to be collected for chemical analysis. Our intent is to use this feature to compare the efficacy of the passive systems to the active monitors.

Since we began using nitrogenous pollutants as our test pollutant species, we evaluated the DR4000 collection surface against the more established denuder systems for monitoring nitrogenous pollutants. We compared the nitrate containing particulates collected by honeycomb denuders, and annular denuders to the DR4000 using the 2.5µm cut point inlet and the, factory calibrated 10µm cyclone. Each system used Teflon filters to catch particulates, which were eluted and analyzed by standard method. Filters were exchanged on each instrument every 24 hours at the same time. Theoretically, both denuder systems were using a 2.5 cut size, although nitrate concentrations were clearly closer to the DR4000 PM10 range. Since each day was different and there was no replication of the DR4000 and only duplicates for the denuders, the error of the sampling cannot be established. However the DR4000 2.5 sampler appears to be in a separate class, whereas the other 3 systems produced similar results (Figure 5). When the percent of the total particulate load was compared to the nitrate-containing load, the nitrate-containing pollutants were more likely to be found in the larger particles (error bars = 1 SE for the entire data set, not

replicated samples for each day). The nitrate containing particles were a small fraction of the total, at less than 1% (Figure 6).

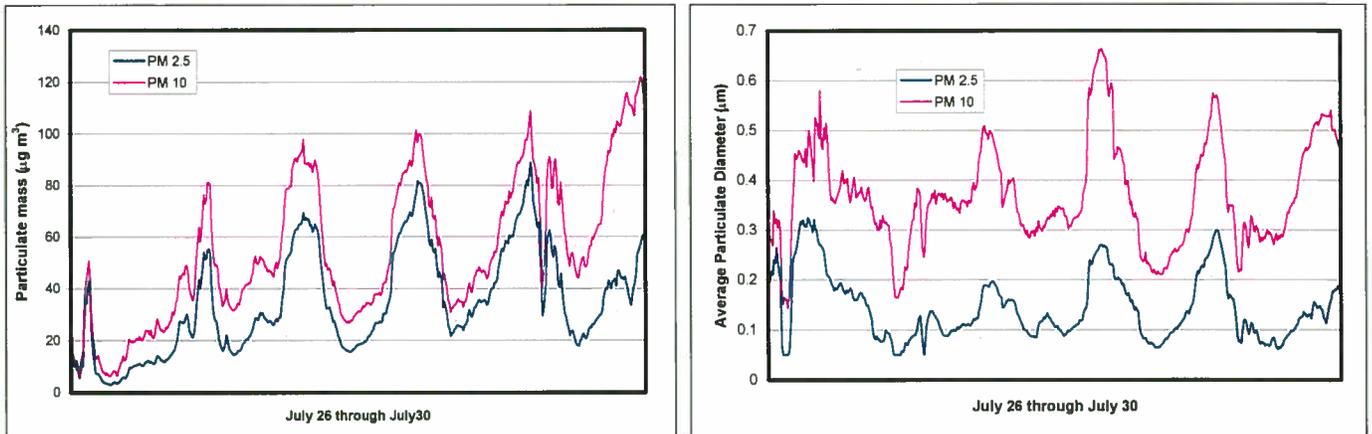


**Figure 5.** Nitrate concentration from particulates collected by denuders and DR4000. The data are the average of 2 systems for honeycomb denuders and annular denuders, and single instruments for 10 $\mu\text{m}$  and 2.5 $\mu\text{m}$  DataRams.



**Figure 6.** Nitrate mass as a percentage of the total particulate mass.

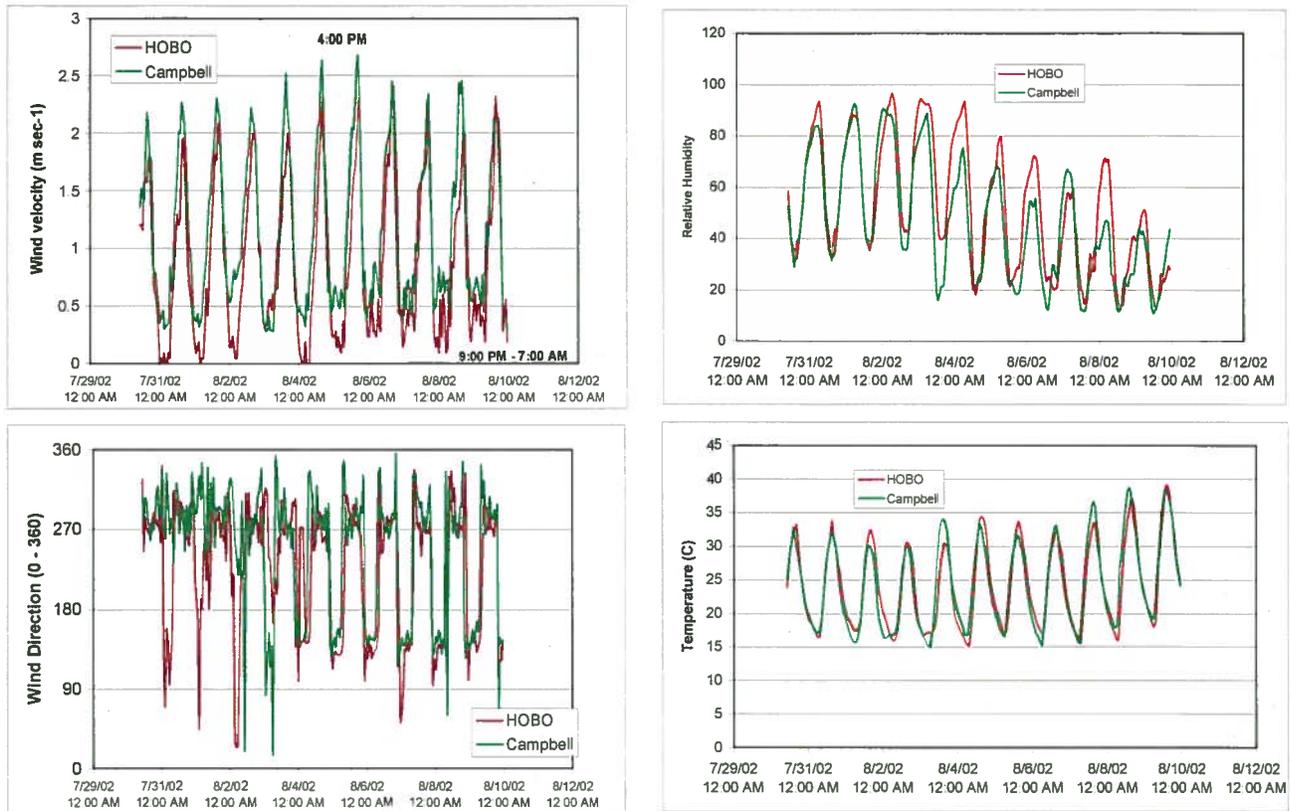
One of the more surprising pieces of information to emerge from the DR4000 evaluations was the diurnal pattern of particle size (Figure 7). The increasing availability of real time monitors for particulate size has revealed that, not only are atmospheric loads subject to daily fluctuations due to physicochemical aerosol formation and wind patterns, but the size of the particles also changes during the day.



**Figure 7.** Typical diurnal patterns of atmospheric load and average particle size. The figures display a 5-day interval of data collected from 2 different DR4000, one maintaining the calibrated PM10 range and the second operating with the PM2.5 inlet.

## Weather monitoring

Onset Computers (who produces the “HOBO” series of dataloggers) in recent years have developed highly efficient, low cost, weather stations. These systems are easily deployed in remote locations being powered by common D cell batteries, which last for several months depending the number of sensors. At the time this project was begun, Onset had just released a combination wind speed and wind direction unit. As part of the project, we purchased 2 systems and compared their output to the most commonly used scientific weather instruments produced by Campbell Scientific Instruments. Temperature and relative humidity (RH) were generally within 10% on one another (Figure 8). The correlation factor was a little better for temperature ( $r=0.88$ ) than for RH ( $r=0.8$ ). Some of the differences may have been in the original calibration of the sensors and possibly in the datalogging. The output on the Campbell system uses a 5-minute average of 5 readings, while the Onset system records a single reading every 5 minutes.



**Figure 8.** Comparison of readout data from a Campbell Met station and the Onset Computer Met station.

More importantly, the wind data were also comparable, although the Campbell system seemed to have a calibration error as wind speeds below  $0.4 \text{ m sec}^{-1}$  were rarely recorded (Figure 8). The data comparisons of wind direction were more variable, particularly at low wind speeds, however. The Onset instrument recorded more significant winds out of the west ( $90^\circ$ ) than were detected by Campbell instrument. If the wind speed detector was out of calibration or not operating smoothly, it is likely that the director detector was as well. It is also possible that the difference in datalogging method describe about may have affected the recorded data.

During the summer of 2003, the Onset weather stations were deployed at 3 remote locations, 1 in the Eastern Sierra and 2 in the San Bernardino Mountains for 2 months. One system developed a short in a sensor wire, which resulted in rapid loss of battery power. The source of the problem turned out to be wildlife interference; something, most likely rodents, chewed on one of the cables, creating an electrical problem. Other than that, all 3 systems worked flawlessly. We concluded that the Onset HOB0 weather stations were comparable to the Campbell systems, and given the cost and ease of installation they were incorporated into our prototype.

## Prototype design



**Figure 7.** Prototype for particle sampling.

The sampling device is mounted on top of the wind speed/direction sensor, which is plugged into the data logger. The original concept was to have one collector facing into the wind and a second out of the wind. The collector out of the wind that would collect ambient concentrations similar to those described for passive analysis of gaseous pollutants. For aerodynamic reasons, there is good reason to believe that this approach will not work, although monitoring of the still air concentrations is still desirable. As the wind shifts direction, the sampler is always collecting what is delivered to that location; meanwhile the data logger records wind direction and speed. In many areas there are seasonally dominant wind directions. Shifts in direction often signal storms or changing weather patterns such as the Santa Ana winds of Southern California. During these events pollutant loads can shift dramatically. This monitoring system could be made sensitive enough to detect such changes. It could be used to monitor emissions if a source is known, or to help locate a source if it is not.

The wind vanes need not be plugged into a data logger. Several applications where 1 central wind sensor with several satellite collectors can be envisioned. As shown here, several collectors could also be stacked if different collection media are required.

### *Estimated cost:*

Onset weather station kits include datalogger, wind/direction sensor, temperature/RH sensor with shelter, 3m tripod and stand, required software: \$1200 (discounts for multiples)

Datalogger separately: \$200

Wind speed/direction sensor: \$450

Particulate collector: Expendable PolyFilter \$60 per 12" X 12" sheet  
Housing \$15 (prototype, less once the design is established)

## **Next stages of experiments**

This activity was launched late in the Joint Fire Sciences project funding cycle. It was not necessary part of the original proposal, but brainstorming among the group indicated that development of passive particulate sampling methods would be extremely beneficial to the goals of the project. Further investigation suggested that it was also feasible. We have several studies that need to be completed before we can confidently recommend this approach to determining particulate loads in remote locations.

Several more physical and chemical tests of the PolyFilter will be undertaken.

Among them are:

- Addressing the air flow-through properties of the foam
- Evaluation of elution techniques for retained solutes
- Controlled exposures to non-nitrogenous particulates
- Detection methods for non-nitrogenous particulates need to be developed:
  - Gravimetric
  - Elemental carbon
  - Silica
  - Other?

Field-testing both at the Riverside Fire Lab (RFL), where we have extensive monitoring equipment, and at remote sites needs to be conducted. Riverside is well known for its high pollution loads during the summer and the ambient pollution in Riverside is often used as “experimental treatments”. The proximity to personnel and the analytical laboratory enables detailed evaluation of sampler performance and adjustment to prototypes as the data accumulates. Riverside is also adjacent to the San Bernardino National Forest, perhaps the best characterized natural ecosystem with regard to pollution impacts in the US. Gradients in atmospheric contamination have been long established in the San Bernardino’s. We expect to use the gradients to further evaluate sampler performance. Additionally, as part of a unique study to determine distribution, transport, and effect of limestone mining on carbonate plant species in the San Bernardino’s, we will deploy the prototypes to monitor calcium carbonate particulates side-by-side with the DR4000. We have developed sound methods for measuring limestone deposition that will be serviceable for extraction of the PolyFilter.

## **Expected products**

Detection and measurement of airborne particulates is currently expensive and labor intensive. This project was initiated to develop a method that could be used in remote locations and was inexpensive enough to enable monitoring of many sites simultaneously. We expect to produce a reliable, flexible device in the next few years.