5. Air Quality Monitoring

Purpose

Air quality monitoring for Project MOHAVE has many applications. The extinction budget analysis requires data for all the major particle components (e.g. sulfate, organic and elemental carbon, crustal, and liquid water as estimated by relative humidity) by particle size to be used in conjunction with optical data (scattering and extinction coefficients). The hybrid and receptor models need particle and gaseous sulfur concentrations and particulate trace elements as endemic tracers (such as arsenic for smelters) in addition to measurements of artificial tracer. Oxidants, especially hydrogen peroxide, should be monitored to assess the potential oxidant limitations of SO_2 to sulfate conversion. The air quality monitoring network will document the regional distribution of particulate and SO_2 and establish boundary conditions for the study area; used along with wind field information, transport of pollutants into the area will be identified. Eigenvector analysis of the pollutant fields will identify common patterns and may identify specific sources with the patterns. These data will also provide for a check of the deterministic modeling results.

IMPROVE Samplers

The IMPROVE sampler consists of four independent filter modules and a common controller, as shown in Figure 9. Each module has its own inlet, PM-2.5 or PM-10 sizing device, flow rate measurement system, flow controller, and pump. In the three PM-2.5 modules, the airstream passes through a cyclone that removes particles larger than 2.5 μm in diameter. The airstream then passes through a filter, which collects all the fine particles. In the PM-10 module, the inlet prevents particles larger than 10 μm from being sampled.

Channel A collects fine particles (<2.5 μm) on a Teflon filter and provides total fine mass, elemental analysis (H and Na-Pb), and absorption. Particle Induced X-Ray Emission (PIXE) analysis gives the concentration of the elements Na-Pb; Hydrogen is obtained by Proton Elastic Scattering Analysis (PESA). Absorption is determined by the Laser Integrating Plate Method (LIPM).

Channel B uses a fine nylon filter behind a nitrate denuder for ion chromatography analysis (Cl^-, NO_2^-, NO_3^- and SO_4^{2-}). Channel C is used to obtain organic and elemental carbon from a fine quartz filter. A thermal/optical carbon analyzer which makes use of the preferential oxidation of organic and elemental carbon compounds at different temperatures is used. Channel D measures PM-10 total mass on a Teflon filter and SO_2 with an impregnated quartz filter. More detailed descriptions of the IMPROVE samplers, analysis methodologies, and protocol appear in Pitchford and Joseph (1990), and Eldred *et al.* (1988). The location of sites and monitoring schedules for IMPROVE samplers is shown in Section 3.

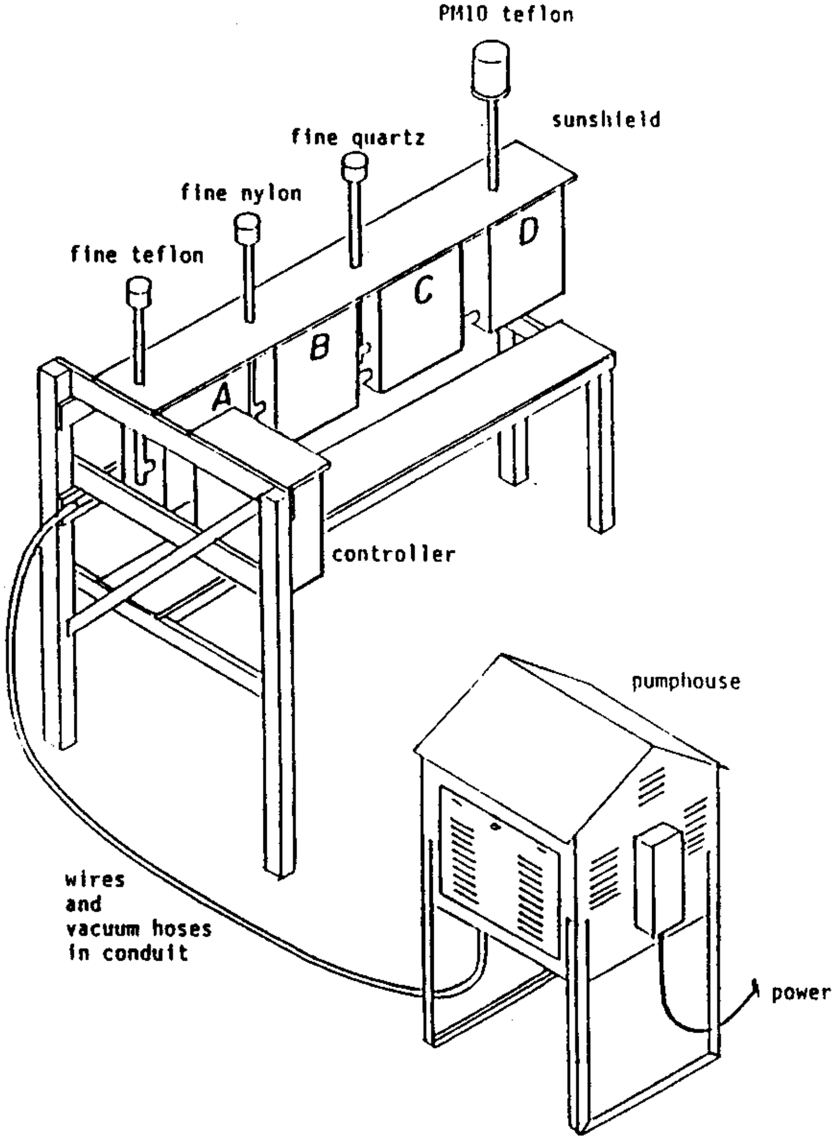

Figure 9. Schematic of IMPROVE sampler.

DRUM Samplers

DRUM (Davis Rotating-drum Universal-size-cut Monitoring) samplers will be used at six locations. The DRUM particulate samplers partition the aerosol into eight size ranges. This provides critical information to relate aerosol to extinction because of the strong relationship between particle size and light scattering. PIXE and PESA analysis is done to determine the concentration of each element (H and Na-Pb) by size range. The size distribution, hence the light scattering efficiencies, for different particulate component species can be inferred, if sufficient material is collected (e.g. see Cahill *et al.*, 1987). The DRUM sampler is described by Raabe *et al.* (1988).

Six DRUM samplers will be deployed. The sampling time will be either four or six hours. The receptor sites will have DRUM sampling for the entire study; the remaining samplers will be placed at other locations of interest yet to be identified. Among the possible sites are Tehachapi Pass, Cajon Pass and Spirit Mountain. Analysis of all samples is beyond the resources of Project MOHAVE. All samples will be archived; analysis of samples will be done for selected periods of interest.

High Volume Dichotomous Samplers

High volume (300 L/minute) dichotomous samplers will be used to improve the trace metal data base for receptor modeling with endemic tracers. Aerosols in the size ranges 0.05-2.5 μm and 2.5-20 μm will be collected on Teflon filters. Instrumental Neutron Activation Analysis (INAA) and X-Ray Florescence (XRF) will be done on the samples. Three samplers will be used. One sampler will be equipped with a trap to collect semi-volatile organics. The locations have not been decided yet; one will characterize background and one will be near the mouth of the Grand Canyon.

Scanning Electron Microscopy (SEM) will be used to characterize individual particle morphology and elemental composition. In addition, Computer-Controlled SEM (CCSEM) analysis can be used to increase the numbers of particles analyzed and eliminate possible human operator microscopy bias. CCSEM data can then be used in data analysis approaches that require quantitative composition as a function of particle size and shape distributions. Mie Theory calculations to determine extinction budgets can use this data. Unlike other data sets, CCSEM data allow for direct analysis of the questions of aerosol mixture (i.e., the extent to which component species are constant in all particles in an individual sample). Receptor models can be based upon an endemic tracer approach using CCSEM data, or it can use the individual particle characterization information to aide in resolving issues raised by other attribution approaches.

Hydrogen Peroxide Measurements

Hydrogen peroxide (H_2O_2) is likely to have a significant role in the formation of sulfate in the study region when clouds are present. Aqueous phase conversion of SO_2 to SO_4^{2-} is critically dependent upon hydrogen peroxide (H_2O_2) and ozone (O_3) (Penkett *et al.*, 1979; Calvert *et al.*, 1985). Hydrogen peroxide is thought to be the leading oxidant of dissolved SO_2 in the eastern United States, where the pH of atmospheric water is generally below 4.5 (Heikes *et al.*, 1987). In the desert southwest, where the pH of atmospheric water is typically higher, ozone may also be important in the aqueous phase oxidation of SO_2. Saxena and Seigneur (1986) also identify O_2 catalyzed by Fe^{3+} and Mn^{2+} as an important aqueous phase oxidant of SO_2. Hydrogen peroxide reaction rates with dissolved SO_2 are typically 50-100% per hour (Lee *et al.*, 1986); thus the presence of clouds with sufficient H_2O_2 present can result in rapid sulfate formation. The amount of hydrogen peroxide available for oxidizing SO_2 may be limited, especially during winter, when photochemical generation of H_2O_2 is low (Calvert *et al.*, 1985; Kleinman, 1986).

The NAS review of WHITEX noted that H_2O_2 measurements were not made; the NAS used values measured in Tennessee (about the same latitude as GCNP) to estimate potential sulfate formation. Members of the Committee on Haze in National Parks and Wilderness Areas suggested that Project MOHAVE make some measurements of hydrogen peroxide. If measurements of hydrogen peroxide show sufficient amounts to convert all the SO_2 to sulfate, we can likely conclude the atmosphere is not oxidant limited. However, showing that molar quantities of hydrogen peroxide less than sulfur dioxide does not necessarily indicate oxidant limiting conditions. Ozone effects may be significant if the pH is adequately high. Heikes *et al.*, found that SO_2 concentrations were a factor of 3-5 greater than H_2O_2 concentrations in the surface layer, but above the surface layer H_2O_2 concentrations were twice the SO_2 concentrations. Even with aircraft vertical profile measurements, Heikes *et al.* concluded that the hydrogen peroxide measurements were ambiguous in determining if the atmosphere was oxidant limited. Their near cloud observations suggested that physical-dynamical processes may be as or more important than a simple molar comparison of SO_2 to H_2O_2 at ground or cloud level.

It is not possible for Project MOHAVE to fully characterize the temporal and spatial distribution of atmospheric hydrogen peroxide necessary to conclusively determine oxidant limitations. However, limited measurements may provide some insight into the potential for hydrogen peroxide oxidation of SO_2. As in the NAS report, sulfate concentrations may be compared to H_2O_2 concentrations to see if sufficient H_2O_2 existed to account for the measured sulfate values. Project MOHAVE will make a limited number of hydrogen peroxide measurements. The SRP NGS study made hydrogen peroxide measurements during the winter of 1990. These measurements may be used to estimate H_2O_2 for the winter intensive.

Methylchloroform Measurements

Methylchloroform has been identified as a tracer of weekday emissions from the Los Angeles Basin (White *et al.*, 1990). Miller *et al.* (1990) found that methylchloroform levels at Spirit Mountain are correlated with particulate light scattering, with the majority of hazy conditions having elevated methylchloroform levels. Methylchloroform measurements, in conjunction with meteorological data and modeling, can aid in identifying periods when air previously in the Los

Angeles Basin is in the study area. However, a limitation of methylchloroform as a Los Angeles Basin tracer is that the emissions are primarily weekday emissions, with weekend emissions being much lower. Thus weekend emissions from the Los Angeles Basin might not be tracked using this tracer and the absence of methylchloroform does not necessarily indicate an absence of air from the Los Angeles Basin.

Desert Research Institute will measure methylchloroform at Spirit Mountain, Meadview, and Long Mesa. These data will be investigated for use in identifying the presence of air previously in the Los Angeles Basin. During the summer intensive the release of perfluorocarbon tracers from the Los Angeles Basin and San Joaquin Valley should provide a check on the utility of methylchloroform as a Los Angeles Basin tracer.