Title

REAL-TIME MEASUREMENT OF THE SIZE FRACTIONATION OF AEROSOL BLACK CARBON DURING THE SOUTHERN CALIFORNIA AIR QUALITY STUDY, JUNE 13-SEPTEMBER 4, 1987, CLAREMONT COLLEGE, CALIFORNIA

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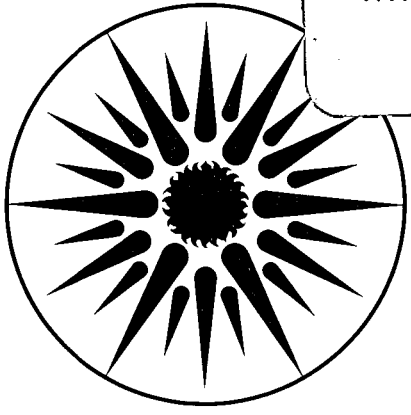
Real-Time Measurement of the Size Fractionation of Aerosol Black Carbon during the Southern California Air Quality Study, June 13–September 4, 1987, Claremont College, California

A.D.A. Hansen and T. Novakov

March 1989



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DISCLAIMER

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Abstract

During the periods June 13 to July 28 and August 17 to September 4, 1987, the Atmospheric Aerosol Group of Lawrence Berkeley Laboratory participated in the South Coast Air Quality Study conducted at Claremont College, Claremont, California. We used a multi-channel aethalometer preceded by size-selective inlets to determine the concentration of aerosol black carbon in two size ranges in real time. We present our results from this study in the form of one-hour averages of carbon concentrations for the aerosol in size range fractions having aerodynamic diameters smaller than approximately 1.0 um and 0.3 um. The concentration results show daily mean values generally ranging from 1 to 4 ug/m^3, with a diurnal cycle showing little variation during nighttime hours and a pronounced peak between the hours of 8 and 10 am. The results for the size fractionation show that the great majority of the aerosol black carbon was found in the size range smaller than 0.3 um: however, this fraction showed a systematic diurnal variation with a decline in the morning and the mid-day periods.

Introduction

One of the components of combustion-derived aerosols is carbon with a microcrystalline graphitic structure (Wolff, 1981). Due to its large optical absorption cross section, this material is termed black carbon. It is produced only during incomplete high-temperature combustion; it cannot be formed or significantly transformed by secondary atmospheric processes. It is therefore a direct tracer for combustion emissions. Due to its long atmospheric lifetime, aerosol black carbon may be transported considerable distances from its source, leading to medium- and long-range impacts on both atmospheric physics (e.g., visibility degradation in distant regions downwind) and atmospheric chemistry (e.g., heterogeneous reactions leading to the oxidation of SO_2).

Both chemical and optical methods for determining the black carbon content of aerosol samples collected on filters have been developed and are in common use at many laboratories. However, these measurements require that a moderate loading of the aerosol be collected on the filter, and it is therefore not generally possible to obtain time resolutions of better than 1-2 hours in most urban locations. The aethalometer uses a continuous optical technique to measure aerosol black carbon in real time.

A single-channel aethalometer was used during the Carbonaceous Species Methods Comparison Study, conducted at Citrus College, Glendora, California from August 12-21, 1986 (Hansen and Novakov, 1987). In that study, data was recorded with one-minute time resolution, resulting in 12252 data points for the nine-day period. The results showed that vehicular sources in the immediate vicinity could have pronounced influence on the concentration of aerosol black carbon on a short time scale. Plumes of duration 3-8 minutes were detected during which the instantaneous concentration of aerosol black carbon increased by a factor of two or three relative to its value when the particular vehicle departed. However, this 1986 study did not give an indication as to the size distribution of the carbonaceous aerosol. One of the objectives of the 1987 SCAQS experiment was to study the size distribution of optically active aerosol species, with a view to investigating sources, size distribution transformations and the influence of humidity on the size distribution.

Ambient atmospheric aerosol particles may contain both hygrophilic and hydrophobic materials. The proportions and the degree of mixing of these constituents will determine the response of the aerosol to humidity. The water associated with aerosols has a substantial influence on aerosol physical and chemical properties. The water layer will influence the optical properties of the aerosol: by both increasing the size and changing the refractive index of the aerosol (Sverdrup and Whitby, 1980; Covert et al., 1980), the adsorption of water will increase the scattering and absorption of light by the aerosol. The nucleation characteristics of the aerosol will determine its growth under high-humidity or condensing conditions and will therefore strongly affect its rate of removal from the atmosphere by "wet" processes (Pueschel et al., 1981; Penner and Edwards, 1986). The presence of liquid water will allow aqueous-phase chemical reactions to occur. Very few species- and element-specific studies of aerosol response to changing humidity have been reported, and those reports deal principally with sulfate and nitrate (Pruppacher et al., 1983). Consequently, we constructed a multi-channel aethalometer: three channels were operated, one channel collecting the total aerosol, the next channel preceded by an impactor whose cut-off removed all particles of aerodynamic diameter greater than 1 um, and the third channel preceded by an impactor of cut-off 0.3 um. The first of these cut points was chosen to exclude "large" particles, i.e. wind-blown dust, soil-derived material, etc. The second of these cut points was chosen to be a value at which the aerosol size distribution has a substantial component in the accumulation mode. Any changes in the aerosol size distribution, due to humidification growth, will then be detected as a shift in the size distribution relative to this cut point value. By comparing the results of these simultaneous measurements it is possible to determine both the aerosol black carbon concentration and attributes of its size distribution.

Experimental Details

The aethalometer operates by measuring the light transmission through a quartz fiber filter while air is being drawn through the filter (Hansen et al., 1982; Hansen et al., 1984). The absorption of light in the visible spectrum by ambient aerosols is primarily due to the presence of microcrystalline graphitic carbon. When suspended as a submicron aerosol and not surrounded by a droplet of water or other adsorbed optically-scattering material, the optical absorption cross-section of this material is approximately 8 m^2/g in the wavelength range 500 - 600 nm (Roessler and Faxvog, 1979). When collected on a fibrous filter, it is postulated that multiple internal reflections enhance the optical absorption approximately threefold and nullify the effects of scattering from the particles (Rosen and Novakov, 1983). Under these circumstances, the attenuation of light transmitted through the filter is due to the absorbing "elemental" or "black" carbon component of the aerosol and is not affected by light-scattering components such as organics, adsorbed water films, or sulfate and nitrate compounds. Solvent extraction followed by thermal analysis of the deposit on the quartz fiber filter can yield a quantitative chemical analysis of the amount of black carbon present (Gundel et al., 1984). Extensive work at LBL and elsewhere (see, for example, Proceedings of the Second International Conference on Carbonaceous Particles in the Atmosphere, Linz, Austria, September 1983: Sci. Tot. Environ., vol. 36, 1984) has shown that the optical transmission attenuation measurement on a sample collected on a quartz fiber filter can be calibrated to provide a quantitation of aerosol black carbon.

The reduction of transmitted light intensity I is proportional to the surface loading S of black carbon on the filter, with the relationship $-\Delta \ln I = \sigma * \Delta S$ where the coefficient σ is the optical attenuation cross section. For quartz fiber filters, this has the value of 25.4 +/- 1.7 $m^2/gram$, measured at a wavelength of 632 nm. (Gundel et al., 1984). The aethalometer draws the ambient air with black carbon concentration C g/m^3 through the filter at velocity V m/s. The increment of black carbon collected in time T results in a decrease in the light transmission of $-\Delta \ln I = \sigma * C * V * T$.

A block diagram of the aethalometer measurement head is shown in Figure 1. The aerosol is collected only on a portion of the filter covering the detectors ("Channel 1", etc.). Another detector placed under a non-collecting portion of the filter gives a reference for the beam intensity. The transparent inlet head is diffusely illuminated; when pumping is applied to the filtering channels, the gradual accumulation of black carbon causes the "signal" intensities to slowly diminish relative to the "reference" intensity. The electronics and microcomputer convert the detectors' outputs into attenuation accumulation rates from which the aerosol black carbon concentration in that channel's airstream can be calculated. The spectral convolution of the output of the incandescent lamp and the response of the detectors gives an effective measurement spectrum peaking in intensity between 500 nm and 700 nm. Previous work has shown that the absorption spectrum of ambient aerosols is essentially uniform and shows very little structure in the visible range. (Rosen et al., 1978).

The collecting spot areas of the filter were 0.71 cm^2, and the air flow rates were 4.5 liters per minute, controlled by critical orifices. Size separation of the aerosol was achieved by preceding two of the aethalometer channels by multi-orifice impactors (manufactured by Pollution Control Systems Corp.) operating at flowrates of 12 standard liters per minute. The remaining flow of 7.5 liters per minute was bypassed. Air flow rates were measured periodically with a standard gas test meter, but were not found to change significantly. The filter was changed usually every 12 hours, resulting in a flow through the active filter area of approximately 4.5 m^3/cm^2. These filters were subsequently analyzed in the laboratory for total black carbon content, using the laser transmissometer whose measurements have been calibrated by the solvent extraction / quantitative thermal analysis method. (Gundel et al., 1984). The results were compared to the integral of the real-time output over the appropriate period to check the calibration. Small discrepancies may be due to changes in the air flow rate, and were corrected by applying an appropriate factor to the aethalometer data form the period in question. The aethalometer was set up at the east end of the SCAQS platform, with its inlet at 5 feet above ground level.

Results

The results are available on disk in several forms as follows. Data for formats (1) and (2) are divided for tabulation convenience into blocks representing sampling from between five to ten days:

(1) results from analyses of the filters, giving average black carbon concentrations for the total aerosol and for the sub - 0.3 um aerosol channel for periods of usually 12 hours;
(2) grouped mean hourly concentrations averaged over all the reporting hours in the data block, for both size ranges;
(3) tabulation of hourly concentration data in the aerodynamic size range < 0.3 um, for each of the study period days; and
(4) tabulation of hourly concentration data in the aerodynamic size range < 1.0 um, for each of the study period days.

(1) Filter analyses

One hundred and twenty three filters were collected by the aethalometer, mostly covering 12-hour periods with changes in the morning and the evening. The total optical attenuation of the filter deposit was calculated both from the aethalometer data and from laboratory re-analysis of the filters. For this latter technique we employed the LBL laser transmissometer operating at a wavelength of 632 nm., and calculated the attenuation of the beam intensity due to the aerosol deposit relative to transmission through a blank portion of the filter. Using the optical attenuation cross-section of 25.4 m^2/g for aerosol black carbon, we determined the surface loading of aerosol black carbon in ug/cm^2 for the filter deposit. Factoring in the total air volume sampled, we derive the mean ambient black carbon aerosol concentration sampled by that aethalometer channel during the sampling period. These concentrations ranged generally from 1 to 4 ug/m^3.

An example of these results is presented graphically in Figure 2, showing the mean concentration of aerosol black carbon measured by the total aerosol channel of the aethalometer for about three weeks of sampling. The horizontal axis tick marks indicate 3-day intervals. The data show lower concentrations that one might at first expect for this location: however, the meteorological conditions during the entire SCAQS timeframe were anomalous, with unusually high ventilations, occasional midsummer rain, weak or non-existent temperature inversions, and conditions generally quite unconducive to the typical summer stagnation smog expected at this inland receptor location.

(2) Grouped hourly averages

Within each data block, the measurements for each hour have been averaged together to form a mean diurnal cycle for the dates covered. Figure 3 shows an example of this data in graphical form. Concentrations were generally stable from the mid-evening to the early morning hours, but show an increase in the morning and afternoon traffic hours. This behaviour is shown more directly by Figure 4 in which the hourly data are shown side by side for several blocks. We see a remarkable nighttime constancy of total aerosol black carbon concentration measurements over these multi-week periods from approximately 6 pm to 6 am, but considerable variability in the morning and daytime traffic-impacted hours.

Figures 5 and 6 show examples of the average diurnal cycles of the fraction of the black carbon aerosol measured in the sub - 0.3 um size range, expressed as percentages. Due to instrumental scaling, these results occasionally appear to exceed 100%, which should be properly interpreted as equalling 100% within the resolution of the system. Generally, the results show that this fraction was steady and close to 100% for most of the evening and the night. Particularly in the earlier portions of the study, this fraction gradually declined during the early morning hours. In all cases, a reduction was seen in the middle of the day. This could be due either to growth of the previously-small aerosol, or dilution of it by the addition of larger-particle carbonaceous aerosols, possibly from the same local sources that were responsible for the daytime increase in total aerosol black carbon concentration. Figure 7 compares this data side by side for the block groupings in the first SCAQS session. Again, results are consistent for the nighttime hours, but show more variability during the day. The gradual decline of the sub-0.3 um fraction percentage of the total is quite evident for the hours midnight to 7 am. This drop of 12-15% reflects a change in the aerosol size distribution during this time period.

It is likely that the nighttime aerosol typically consisted of a mixture of local, fresh source material (mostly traffic), and well-aged aerosols from the previous day. In the early morning hours, air temperatures were often 20°C lower than afternoon high temperatures. This temperature drop coupled with the extensive use of landscape misters and sprinklers in the small hours resulted in visible watery haze and high relative humidity in the morning. The liquid water content of such a haze is low and we would therefore not expect the

data to show a significant growth of the aerosol into the size fraction greater than 1 um. This result was observed: the data for the channel preceded by the impactor of 1 um cutpoint are essentially identical to those for the total aerosol channel. However, we did observe a relative decrease of 10-15% for the concentration of aerosol black carbon measured by the channel preceded by the 0.3 um cutpoint impactor. Thus, a certain fraction of the sub-0.3 um aerosol grew in size but did not grow larger than 1 um. This growth may have been humidity related and caused by the accretion of water by a fraction of the carbonaceous particles' population.

Conclusions

During the summer session of the 1987 South Coast Air Quality Study conducted in the inland region of the California South Coast Air Basin, we performed measurements of black carbon in real time for both the total aerosol and the aerosol component of aerodynamic diameter smaller than 0.3 um. The results from the analysis of 12 -hour filters show average concentrations generally ranging from 1 to 4 ug/m^3. Collecting the real-time data into hourly averages shows concentrations typically stable overnight, but showing peaks between 8 and 10 am every morning. The percentage fraction of the black carbon aerosol in the size range smaller than 0.3 um was generally very close to 100% overnight, gradually decreasing in the early morning hours, and showing a minimum of around 70% during midmorning hours. This species is a tracer for the impact of combustion emissions at a site on any time scale. Over periods of hours, the measurements reflect fuel use patterns, local meteorology, and local to regional transport. On a shorter time base, these scales are correspondingly reduced to those of individual source (e.g., vehicle) activity in the immediate neighborhood. The temporal resolution of the aethalometer therefore makes a valuable contribution to the study of primary combustion emissions. When coupled with size selection, we may obtain insights into the capacity of these aerosols for growth either by coagulation or by the nucleation and accretion of water.

Acknowledgments

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Figure Captions

Figure 1 : Schematic cross-section of aethalometer measurement head, showing two sampling channels and the reference detector. The upper body is machined from translucent material: the lower body from metal. Thus, the light transmitted from the lamp to the photodetectors passes through the quartz fiber filter. Aerosols drawn through the sampling channels are collected by the filter, and the rate at which the transmission of light is progressively attenuated (relative to the reference beam) is proportional to the rate at which aerosol black carbon is collected on the filter.

Figure 2 : Total aerosol black carbon concentration calculated as averages for the periods of operation of filters from 13th June to 3rd July 1987. Each filter period was approximately 12 hours. The tick marks on the horizontal axis indicate 3 - day intervals.

Figure 3 : Mean diurnal cycle of total aerosol black carbon concentrations for 26th June to 3rd July 1987, averaged for each starting hour.

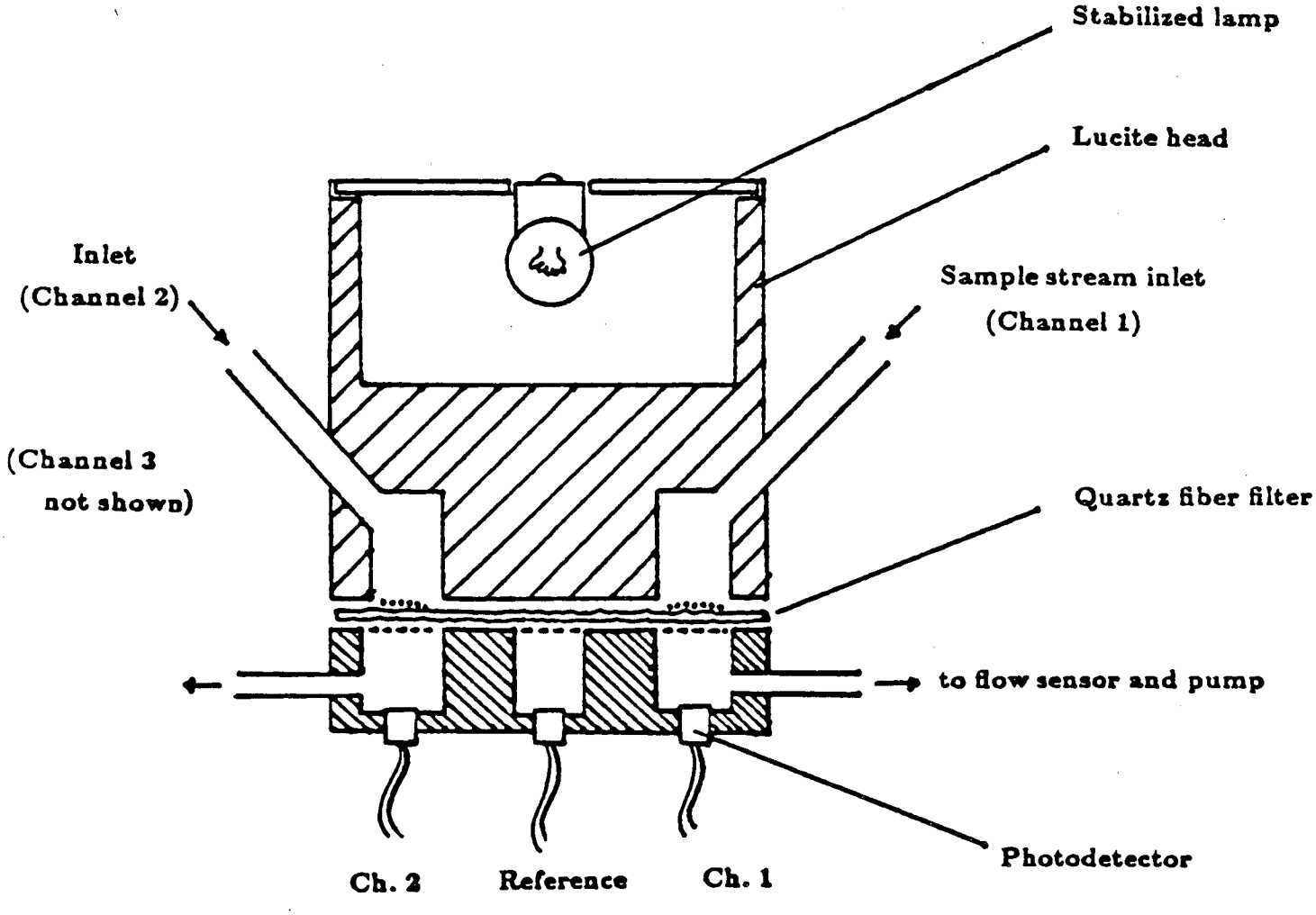
Figure 4 : Comparison of mean diurnal cycles of total aerosol black carbon concentration for blocks 1 - 6 of data, covering the summer 1987 SCAQS session from 13th June to 28th July 1987. Data for each block are represented by columns of different shading.

Figure 5 : Mean diurnal cycle of percentage fraction of aerosol black carbon collected by channel preceded by impactor of cutpoint 0.3 um aerodynamic diameter, relative to total aerosol channel. Data averaged for each starting hour from 18th June to 26th June 1987.

Figure 6 : Mean diurnal cycle of percentage fraction of aerosol black carbon collected by channel preceded by impactor of cutpoint 0.3 um aerodynamic diameter, relative to total aerosol channel. Data averaged for each starting hour from 3rd July to 11th July 1987.

Figure 7 : Comparison of mean diurnal cycles of percentage fraction of aerosol black carbon in sub - 0.3 um aerodynamic diameter size range for blocks 1-6 of data, covering the first session of the summer 1987 SCAQS experiment from 13th June to 28th July 1987. Data for each block are represented by columns of different shading.

Aethalometer measurement head



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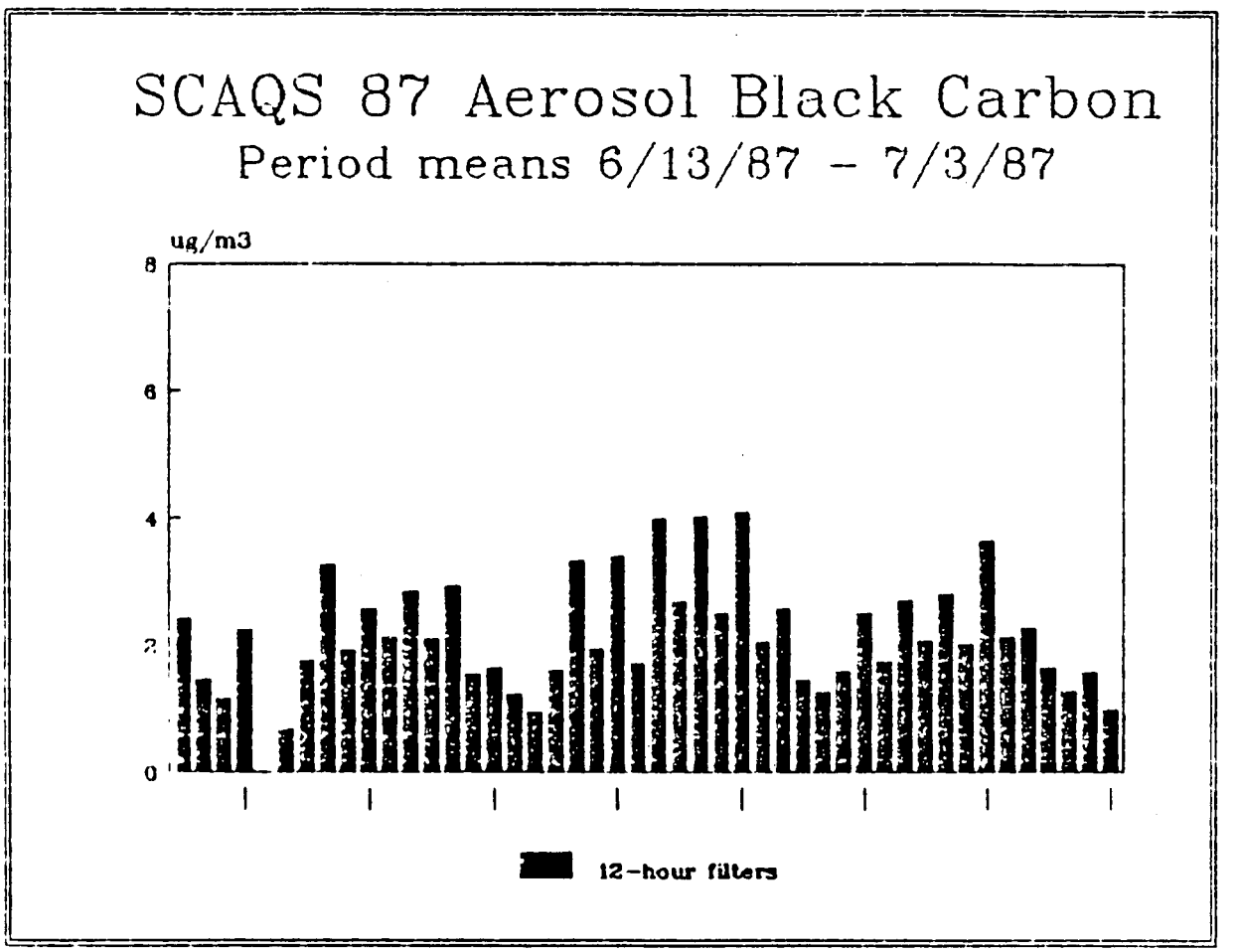

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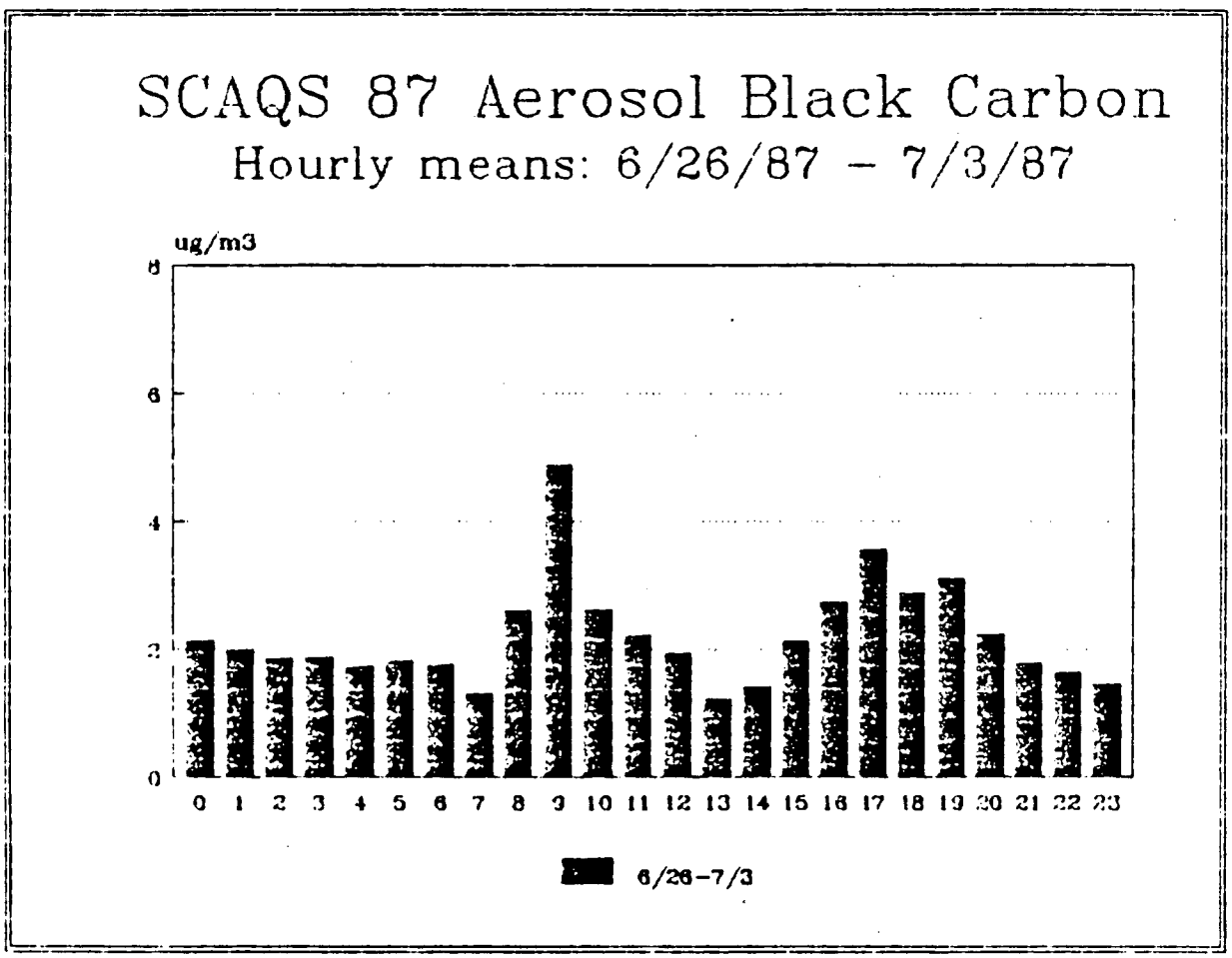


Figure 3 : Mean diurnal cycle of total aerosol black carbon concentrations for 26th June to 3rd July 1987, averaged for each starting hour.

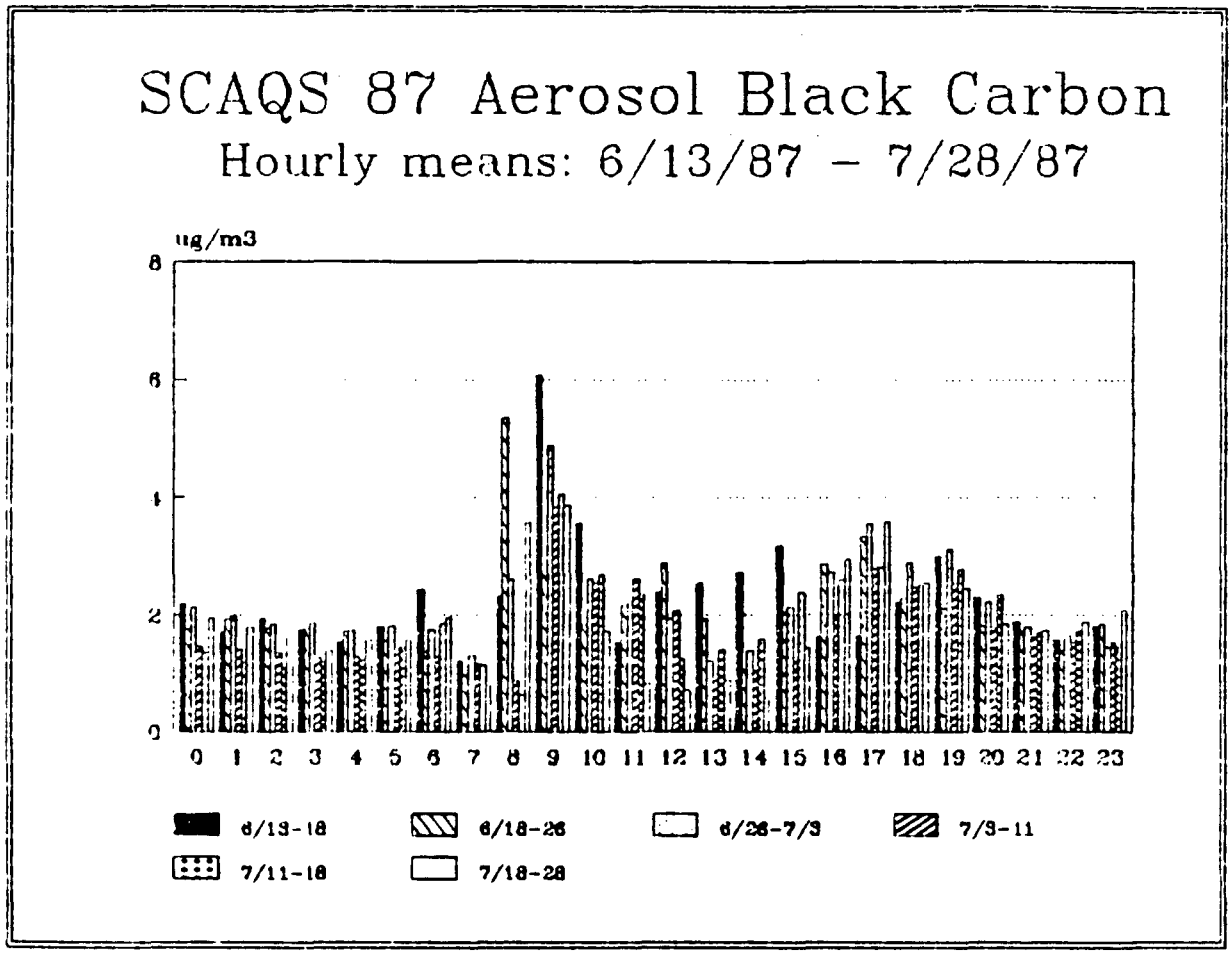


Figure 4 : Comparison of mean diurnal cycles of total aerosol black carbon concentration for blocks 1 - 6 of data, covering the summer 1987 SCAQS session from 13th June to 28th July 1987. Data for each block are represented by columns of different shading.

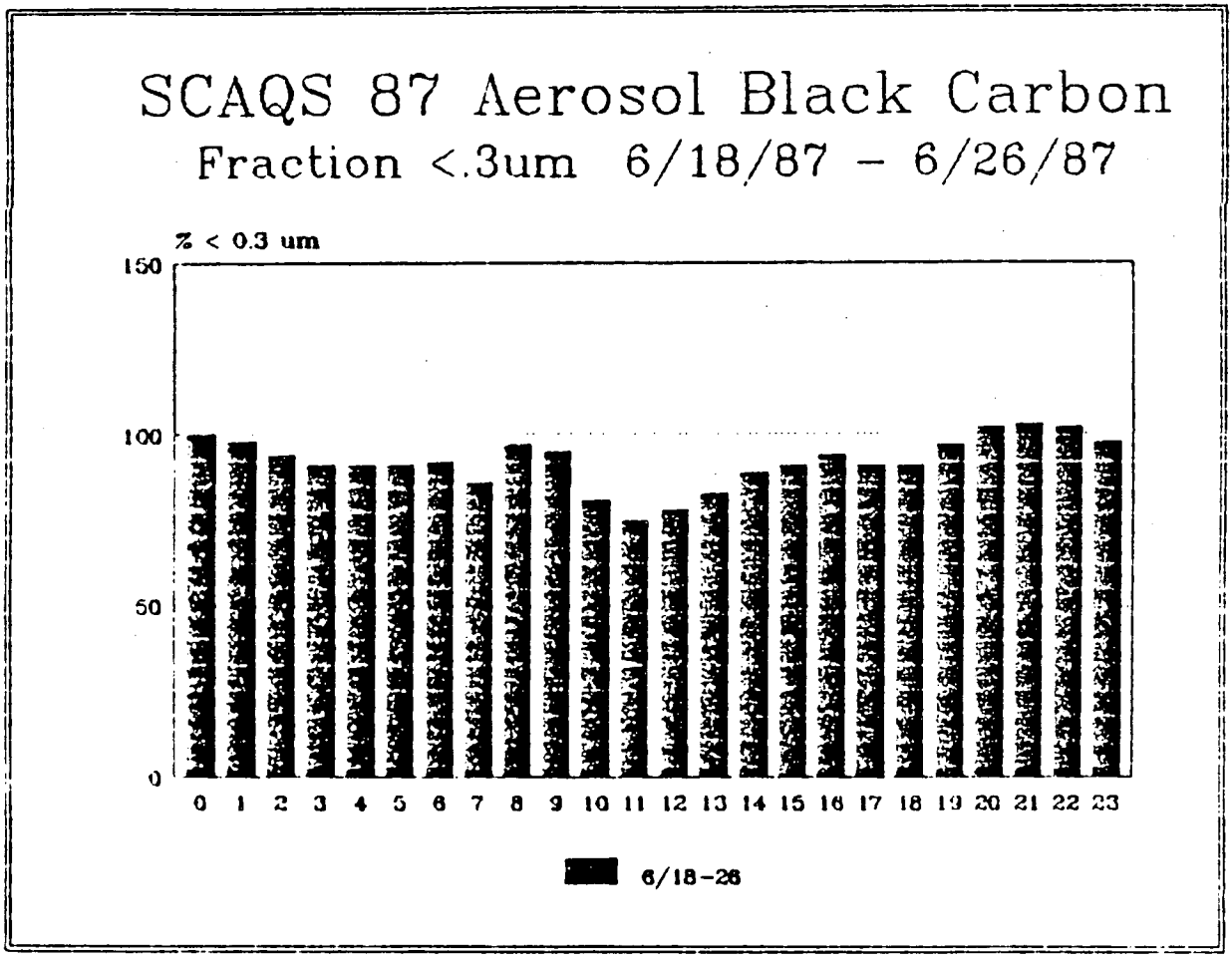
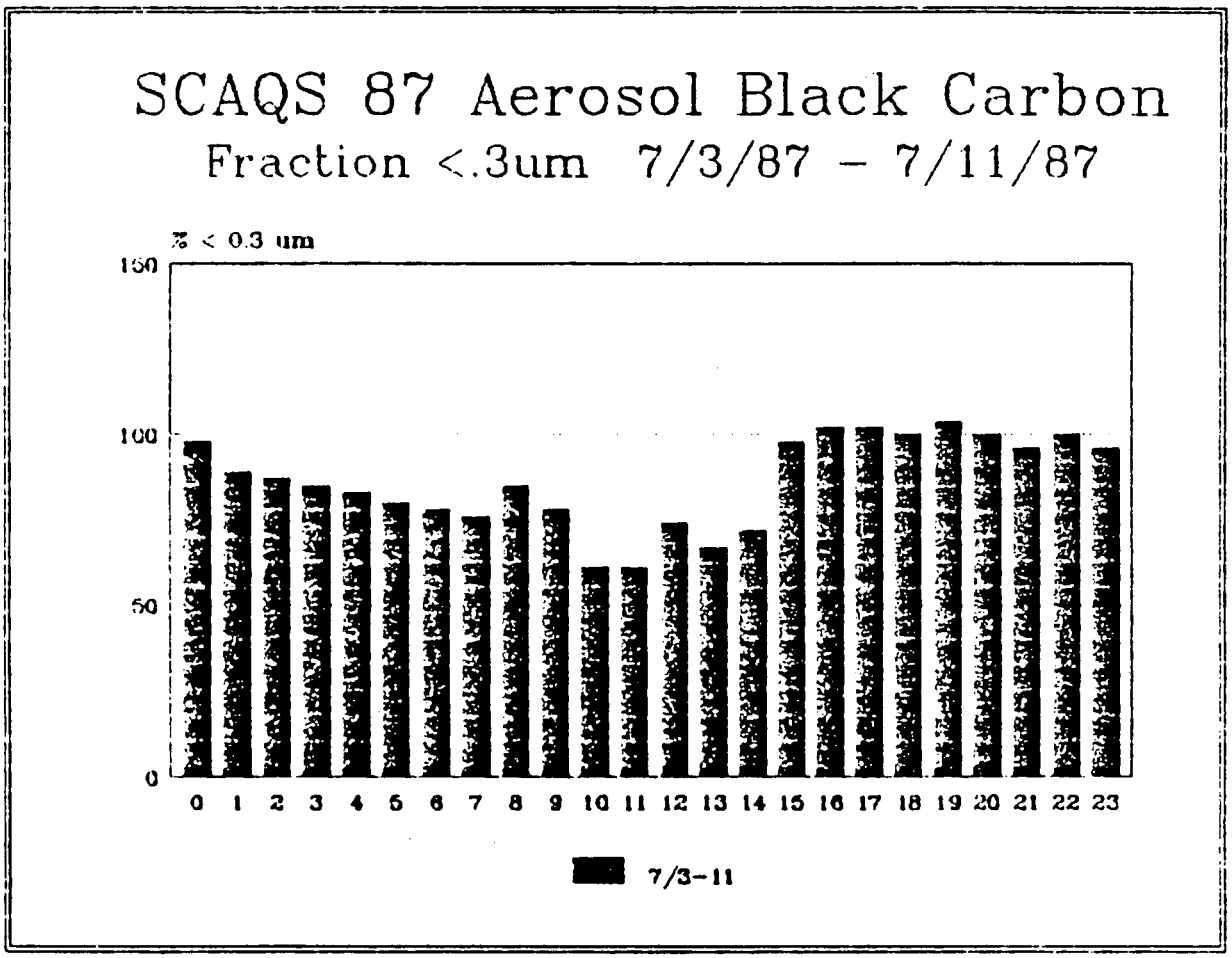


Figure 5 : Mean diurnal cycle of percentage fraction of aerosol black carbon collected by channel preceded by impactor of cutpoint 0.3 um aerodynamic diameter, relative to total aerosol channel. Data averaged for each starting hour from 18th June to 26th June 1987.



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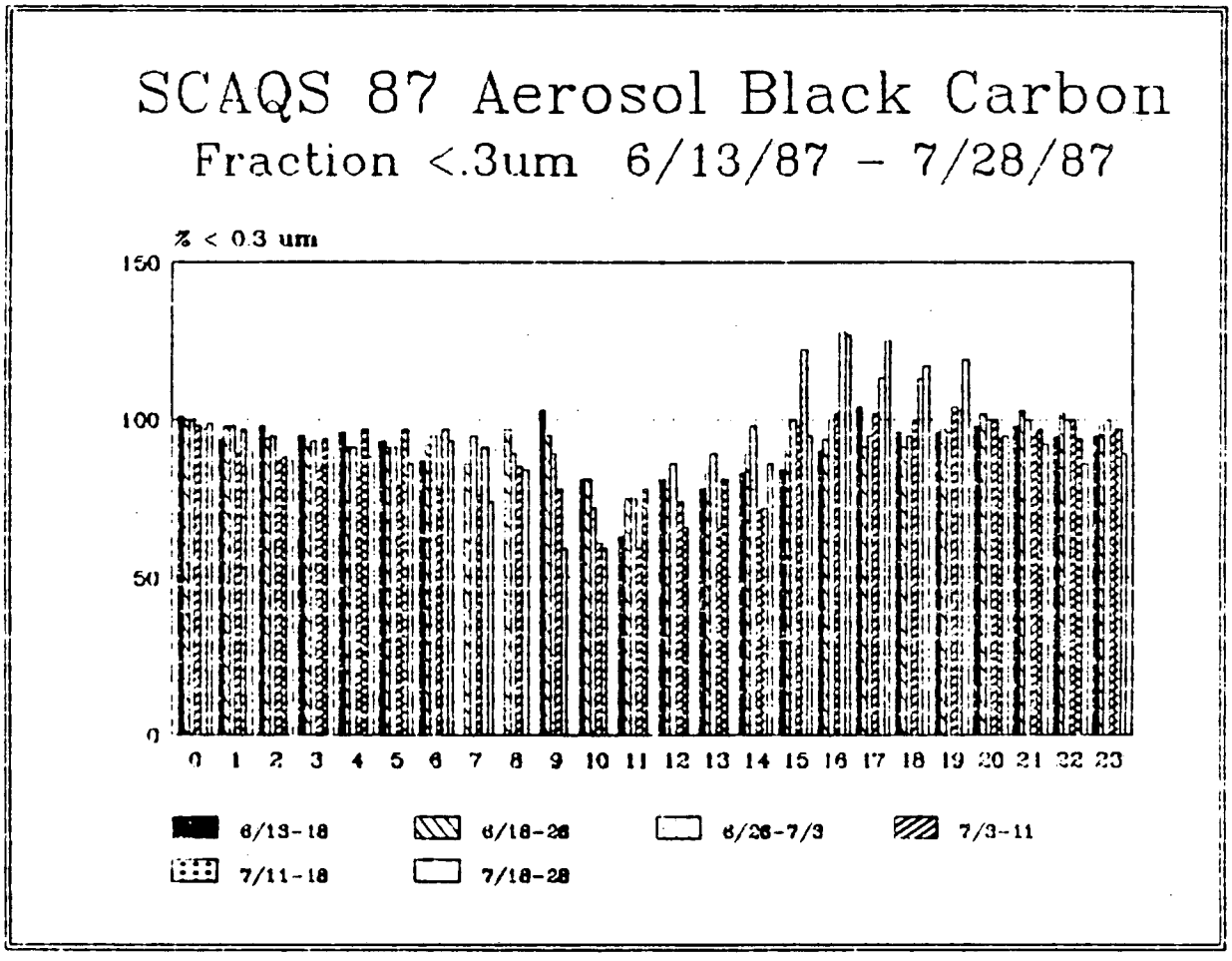

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