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A.D.A. Hansen and T. Novakov

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REAL-TIME MEASUREMENTS OF THE SIZE FRACTIONATION OF AMBIENT BLACK CARBON AEROSOLS AT ELEVATED HUMIDITIES*

A.D.A. Hansen and T. Novakov

Applied Science Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Abstract

The aethalometer is an instrument that responds to the concentration of aerosol black carbon in real time. Recent versions constructed at Lawrence Berkeley Laboratory (LBL) contain two or three channels that may be operated simultaneously. When preceded by size-segregating inlets of differing cut points, this configuration allows for a real-time determination of the size fractionation of the black carbon component of the aerosol. In field measurements at LBL, we studied the incorporation of black carbon into marine fog droplets by comparing the total concentration with the "interstitial aerosol" concentration measured downstream of an interception mesh of 1-μm cutpoint. The data show that up to 80% of the carbon may be occluded by droplets. In separate experiments during the SCAQS program in southern California, a three-channel instrument, equipped with impactors, measured total, < 1 μm, and < 0.3 μm concentrations, and showed diurnal variations of size fractionation of the ambient carbonaceous aerosol. These results imply that a significant fraction of the aerosol black carbon particles may exhibit hygroscopic behavior.

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Introduction

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). In this work, we used the aethalometer to study the response of a specific ambient aerosol component, namely "black" (or "elemental") carbon, to changes in humidity and the presence of fog.

Experimental Details

The aethalometer is an instrument developed at Lawrence Berkeley Laboratory (Hansen et al., 1984) that collects the aerosol on a quartz fiber filter and uses a continuous optical transmission method to determine the concentration of aerosol black carbon in real time. Recent versions contain two or three channels that operate simultaneously. If these channels sample different size fractions of the aerosol, for example, it is possible to determine the relationships between the black carbon contents of these fractions in real time.

We conducted one series of experiments at Lawrence Berkeley Laboratory to study the incorporation of aerosol black carbon into advection fogs, using a two-channel system. One

channel collected the total aerosol through an open probe. The probe was heated in order to evaporate the water from fog droplets so that this aethalometer channel measured the black carbon both in fog droplet cores and in the interstitial aerosol. The other channel sampled the aerosol downstream of a fog droplet impactor, consisting of five layers of polypropylene demister mesh through which the air was drawn at a velocity of 3 m sec^{-1}. The mesh effectively intercepts all particles of diameter greater than a few micrometers but allows smaller aerosols to pass through. From data published by the manufacturers, Kimre Inc., we calculate an interception efficiency of 82% for 5 μ diameter particles and 4% for 1 μ diameter particles under these conditions. This second aethalometer channel therefore measured the concentration of black carbon in the interstitial aerosol. The black carbon incorporated into fog droplets is obtained by subtracting the two channels' measurements. The percentage incorporation of aerosol black carbon into the fog is then this difference divided by the total channel measurement. The equipment was installed on the roof of a building at Lawrence Berkeley Laboratory at a location frequently impacted by summertime marine advection fogs. The fog density was measured semi-quantitatively by an infrared transmissometer operating at approximately 800 nm wavelength over a path length of 20 m.

In separate experiments, we studied the behavior of carbonaceous aerosols under conditions of variable ambient humidity with a three-channel system during the summer and fall periods of the 1987 California South Coast Air Quality Study (SCAQS). In this study 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 first channel was open to the atmosphere and collected the total aerosol; the second channel was preceded by an impactor of cutpoint 1 μm, and the third channel was preceded by an impactor of cutpoint 0.3 μm. By comparing the concentrations of aerosol black carbon measured by the second and third channels at increasing humidities, we can detect the

change in the accumulation mode fraction of the size distribution. During the summer portion of the SCAQS program, the equipment was located at the Claremont College site, an inland receptor location. At this site, stagnation and falling temperatures resulted in elevated humidities and occasional fog or mist in the early morning hours.

Results and Discussion

Incorporation of aerosol black carbon into advection fogs. In Fig. 1 we show data from one episode (1 and 2 September 1987) in which marine fog impacted the sampling site at Lawrence Berkeley Laboratory. The solid line in the figure shows the half-hour average fraction of the black carbon aerosol that was incorporated into the fog droplets, which reached a maximum of approximately 16% during this episode. The broken line shows the fog optical depth measured by the transmissometer over a 20-m path length. With the onset of fog, the incorporation of black carbon into fog droplets is clearly detectable. Total concentrations of aerosol black carbon during this episode ranged from 500 to 700 ng m^{-3}. Figure 2 shows a plot of the incorporated fraction vs. total aerosol black carbon concentration for both foggy and clear periods during 7 days in August/September 1987. Each point in this figure represents a 20-min average of the 1-min data. Two features can be seen. First, the greatest incorporation fractions were observed at the lowest total black carbon concentrations, with the highest point corresponding to 80% incorporation. The second feature is that at any given total concentration, this incorporation fraction can have a range of values between the appropriate maximum and zero. The fog optical depths are not shown on this figure, but the highest incorporation fractions were measured in the densest fogs and intermediate values in lighter fogs. The fraction of aerosol black carbon incorporated into the fog droplets is thus a function of both carbon concentration and fog density.

The data shown in Figs. 1 and 2 clearly indicate that ambient black carbon aerosols can be incorporated into fog droplets to a considerable degree. The data presented in Fig. 2 show an

inverse dependence of incorporation on concentration. This suggests that at low particle concentrations and a large amount of available water vapor per particle, essentially all the ambient carbonaceous aerosol can be activated and incorporated into droplets. As the concentration of particles increases, or as the fog density decreases, the incorporation diminishes. Our explanation of this observation is that a variable fraction of the carbonaceous aerosol may act as fog condensation nuclei, with that fraction increasing as the available water per particle increases. In other words, the carbonaceous aerosol may exhibit a distribution in nucleation properties ranging from hygroscopic to hydrophobic, requiring increasing supersaturations to activate.

Meteorological conditions during this advection fog sampling experiment were generally well ventilated, with westerly winds. The air trajectories passed over the San Francisco urban source area before reaching the sampling site. Fog reached the sampling site generally between 10 pm and 8 am. Thus, during fog episodes, the aerosol sampled was mostly fresh, source-derived material.

Diurnal changes of aerosol black carbon size distribution. Figure 3 shows results from the summer 1987 SCAQS program in suburban Los Angeles. The ratio of aerosol black carbon concentration measured by the aethalometer channel preceded by a 0.3-μm cutpoint impactor to the total aerosol black carbon concentration measured by the total channel is plotted vs. local clock time. The data are averaged by hour for 27 days in June and July and are shown as a median value and standard deviation for that hour. In the late afternoon and evening, the data show that 90 to 95% of the aerosol black carbon was found in the size range smaller than 0.3 μm. After midnight, this fraction diminished, reaching a lowest value of 82% for the average for the hour 5-6 am. Between 7 and 8 am, this fraction dropped sharply and did so again later in the morning. This may reflect the influence of local activities in the immediate vicinity. However, we believe that the data from 5 pm to 6 am were valid and that the drop of 12-15% in the value of this smallest size fraction ratio indeed reflects a change in the aerosol size distribution during this

13-hr period.

Although high levels of ozone were not frequently recorded at this site during this study period, we believe that the nighttime aerosol typically consisted of a mixture of local, fresh source material (mostly traffic), and well-aged, photochemical smog aerosols from the previous day. In the early morning hours, air temperatures were often 20 °C lower than afternoon high temperatures. This temperature drop resulted in visible watery haze and high relative humidity in the morning. The liquid water content of such a haze is much lower than that of marine fog; in addition, the total aerosol black carbon concentrations were typically from 1 to 10 $\mu g\ m^{-3}$, compared with 0.1 to 1 $\mu g\ m^{-3}$ measured during the advection fog study in Berkeley discussed in the previous paragraphs. From Fig. 2 we would therefore not expect the SCAQS data to show a significant growth into the size fraction greater than 1 μm. This result was observed: the data for the total aerosol channel are essentially identical to those for the channel preceded by an impactor of 1 μm cutpoint. 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 μm cutpoint impactor. Thus, a certain fraction of the sub-0.3 μm aerosol grew in size but did not grow larger than 1 μm. This growth may have been humidity related and caused by the accretion of water by a fraction of the carbonaceous particles' population, rather than humidity-independent aerosol coagulation.

Conclusions

The results show that ambient black carbon aerosol particles can have hygroscopic properties. Up to 80% of fresh urban ambient carbonaceous aerosol was found incorporated into marine fog. Lower percentage incorporations were measured at higher total black carbon concentrations, suggesting that the activation process is limited by the availability of liquid water and the range of hygroscopicities displayed by the particles. The size distribution of aged urban aerosol black carbon particles was found to change in the early morning hours and may be associated

with changes in ambient humidity.

Acknowledgments

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Figure Captions

Figure 1 Fraction of ambient black carbon aerosol incorporated into fog droplets measured during a marine advection fog episode. The solid line shows the incorporation fraction derived from continuous measurements gathered into 30-min averages. The broken line shows the fog optical depth measured over a 20-m path length by an infrared (800 nm) transmissometer.

Figure 2 Fraction of ambient black carbon aerosol incorporated into fog droplets during marine advection fog episodes, plotted vs. total black carbon concentration. Each point represents a 20-min average of the continuous data for sampling times during a 7-day interval. Data for both foggy and clear periods are shown.

Figure 3 Fraction of ambient black carbon aerosol of size smaller than 0.3 μm, relative to total concentration. Data averaged by hour (local time) for 27 days in June and July at Claremont College, California (1987 summer SCAQS program).

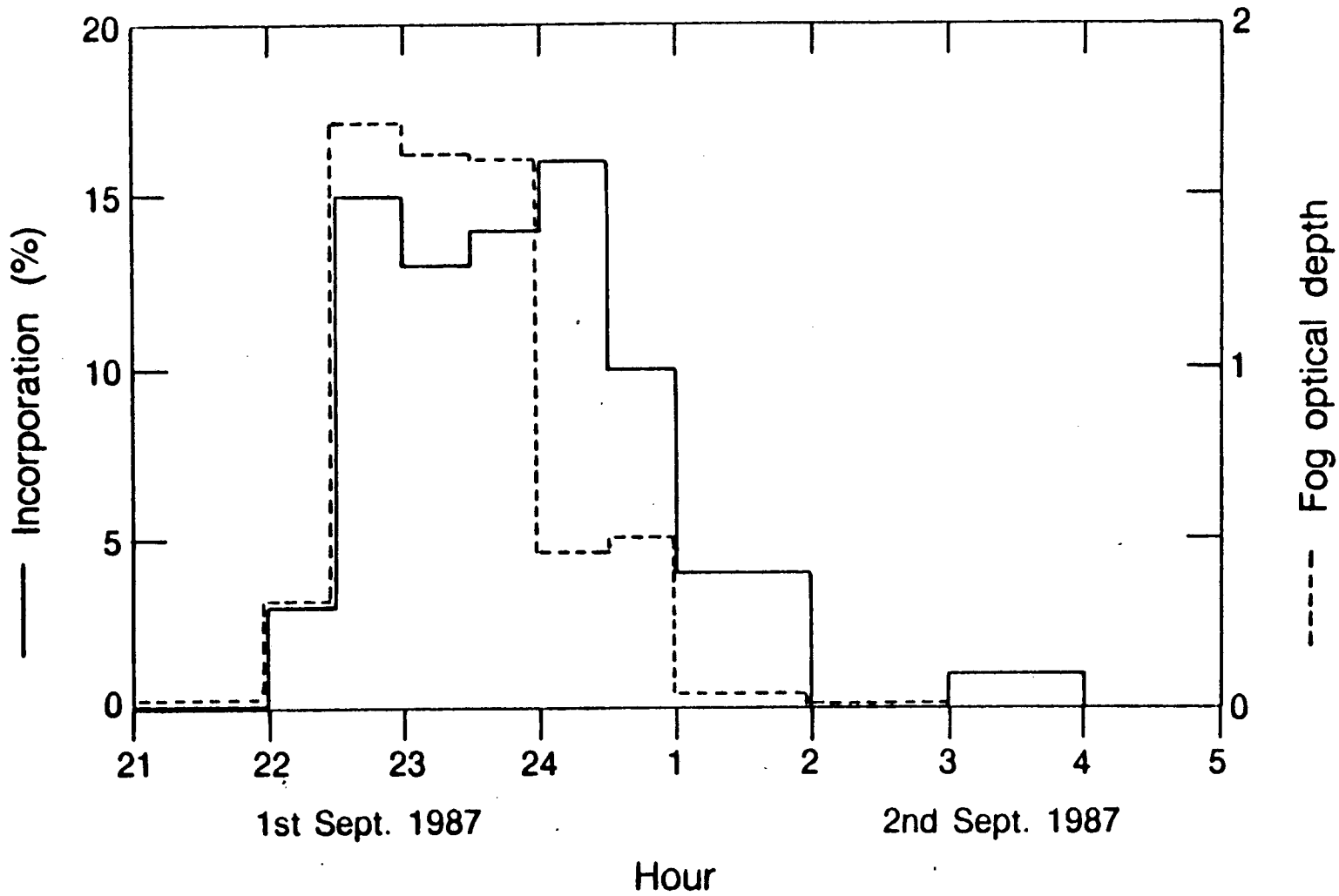

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Figure 1

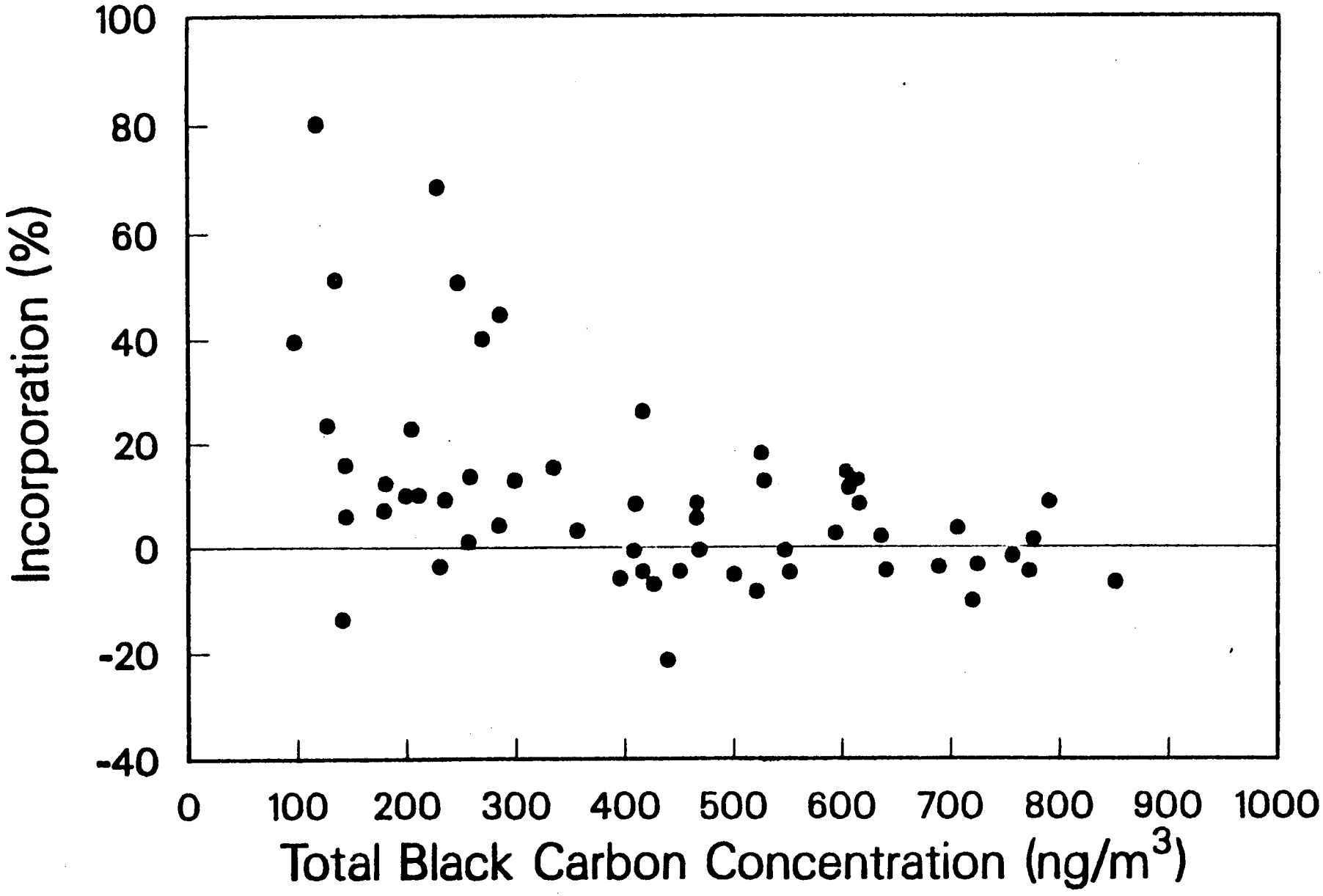

Figure 2

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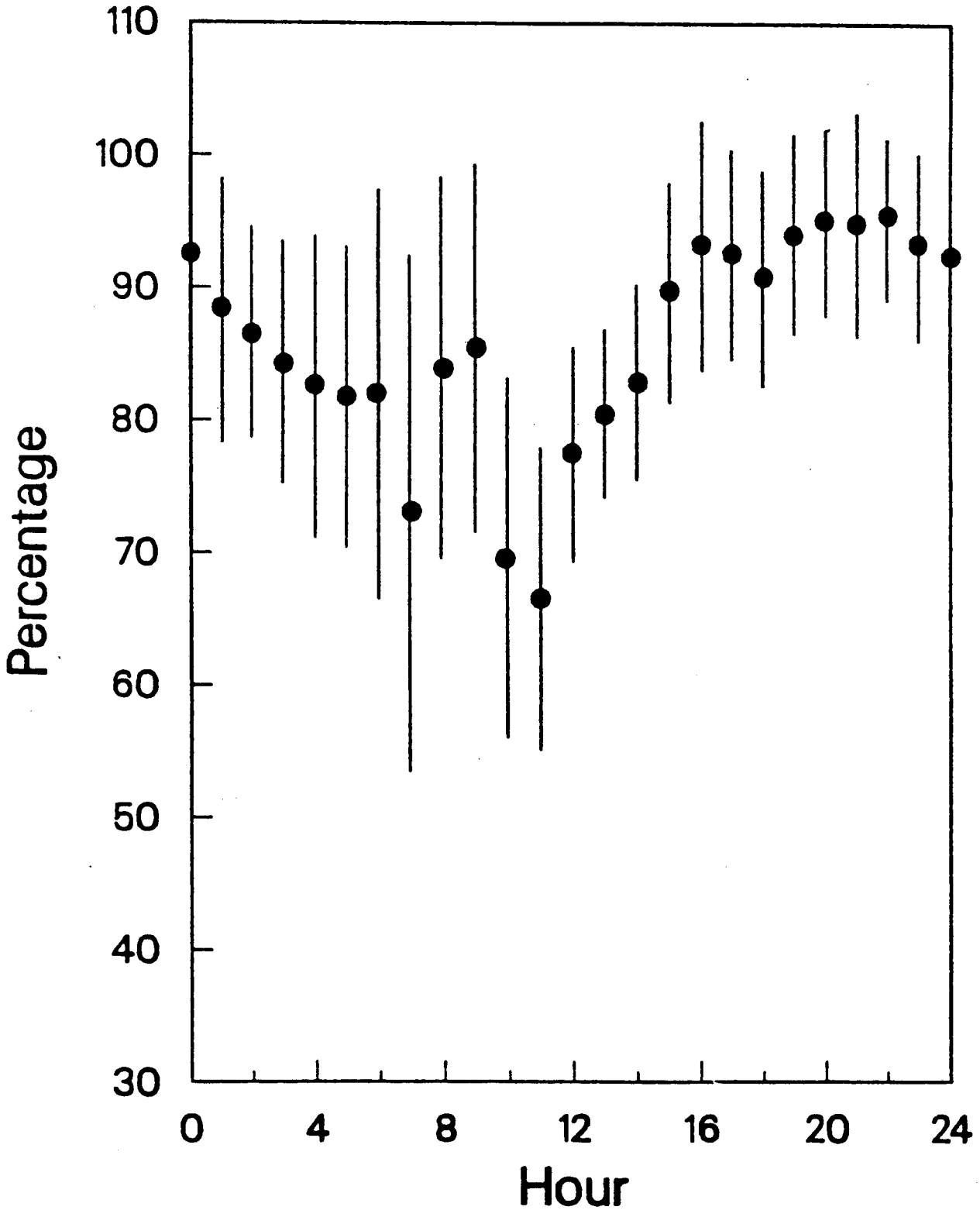

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Figure 3

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