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# IDENTIFICATION OF SOOT IN URBAN ATMOSPHERES BY AN OPTICAL ABSORPTION TECHNIQUE

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ABSTRACT

We have used the high optical absorptivity of urban and source particulates to trace their "graphitic" component. The optical absorptivity and the particulate carbon loading show a strong correlation. Analyses of the data indicate that primary soot emissions compose a major fraction of the carbonaceous aerosol and put a low limit on secondary organics produced in correlation with the ozone concentration.

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Particulate carbon is a major fraction of the respirable particulate burden in urban atmospheres, yet the chemical composition and origin of this component are poorly understood. The major cause of these particles is fossil fuel combustion, which produces both primary particulate carbonaceous emissions (soot) and gaseous hydrocarbons, which can be transformed in the atmosphere by gas-to-particle conversion processes to secondary organic material.[1] For an effective control strategy, it is necessary to establish the relative importance of each of these components. In this paper we describe the application of a new method of analysis which uses the unique optical properties of "graphitic"[2] soot to trace the primary component of the carbonaceous particulates under widely different atmospheric conditions over a wide geographical area. The results of our work are consistent with the earlier work of Novakov et al.[3] and indicate that primary soot emissions compose a major fraction of the urban carbonaceous aerosol.

Soot consists of a "graphitic" component and an organic component. The "graphitic" component can be conveniently monitored because of its large and uniform optical absorptivity, which has recently been shown to be responsible for the grey or black appearance of ambient and source particulate samples collected on various filter media.[4-6] The "graphitic" content of the aerosol can be measured by an optical attenuation method developed in our laboratory.[4] In addition to the attenuation, we have also determined total particulate carbon, which enables us to study the correlation between the "graphitic" and the total carbon content of the aerosol.[7] The correlation or lack of it should depend on the relative amounts of primary and secondary material.

Measurements of the optical attenuation and the total carbon content of over 1000 ambient samples collected in two California air basins and in the Chicago area have been obtained. These samples have been collected daily from 1 June 1977 at Lawrence Berkeley Laboratory, Berkeley, California; from 15 July 1977 at

the Bay Area Air Quality Management District monitoring station, Fremont, California; and from 19 August 1977 at the South Coast Air Quality Management District monitoring station, Anaheim, California. Samples were also taken from 23 March 1978 to 9 April 1978 and then continued from 19 February 1979 at Argonne, Illinois. All these samples were taken in parallel on 47-mm diameter Millipore filter membranes (1.2-μm nominal pore size, type RATF), which were used for the optical attenuation measurements, and prefired quartz fiber filters (Pallflex type 2500 QAO), which were used for the carbon determinations. The monitored flow rates varied between 1.0 and 2.6 $m^3/cm^2$-day (i.e., 0.24 to 0.62 CFM for the total exposed filter area of 9.6 $cm^2$), corresponding to face velocities of 11.6 to 30.1 cm/sec. The samples were not size segregated. A number of representative source particulates have also been sampled and analyzed. These include particles collected 1) in a freeway tunnel, 2) in an underground parking garage, 3) from a small 2-stroke engine, and 4) from a 4-stroke diesel engine. The optical attenuation is defined as

$$ATN = -100 \ln (I/I_0)$$

where $I_0$ is the intensity of the light ($\lambda$ = .63 μ) transmitted through a blank Millipore filter and I is the intensity through a loaded filter. If we assume fixed optical constants, this quantity should be proportional to the "graphitic" content of the aerosol. The carbon loading on the quartz fiber filters was determined by a total combustion/$CO_2$ evaluation method.[8] The quartz filters were prefired overnight at 800°C to remove all combustible carbon before sample collection. Periodic analysis of blanks typically yielded about 0.5 μg C/$cm^2$, compared with loadings after exposure in the range 20-100 μg C/$cm^2$.

Photochemical gas-to-particle conversion reactions should be most pronounced in the summer in the Los Angeles air basin, while in the winter in Argonne or Berkeley, these reactions should play a much smaller role and the primary component

should be much more important. These different photochemical conditions should manifest themselves in the ratio of the "graphitic" soot to total carbon content of the particles. That is, under high photochemical conditions one would expect this ratio to be significantly smaller than under conditions obviously heavily influenced by sources. In view of the above, the graphs of optical attenuation versus carbon loading shown in Figure 1 for samples collected at Berkeley, Fremont, and Anaheim, California, and Argonne, Illinois, as well as various combustion sources, are unexpected. Analyses of the data show that:

1. There is a strong correlation ($r > 0.85$) between optical attenuation and total suspended particulate carbon at every site.

2. The least squares fit of the data shows relatively small regional differences with a trend toward increasing slope (enrichment in primary carbonaceous matter) for samples collected respectively at Berkeley, Fremont, Anaheim, and Argonne.

3. There is a strong correlation between the optical attenuation and the carbon loading for the source samples, and the slope of the least squares fit is comparable to that found in the ambient samples.

Result 1 shows that it is possible to predict the total amount of particulate carbon with an RMS deviation of 30% by means of a simple measurement of optical attenuation. This implies that the fraction of "graphitic" soot to total particulate carbon is approximately constant under the wide range of conditions occurring at a given site. On specific days there can be large variations in the ratio, but no large systematic differences are found as a function of the ozone concentration, which has been viewed as a monitor of the photochemical activity. This is graphically demonstrated in Figure 2, which shows the distribution of the ratios of the optical attenuation to total carbon content for ambient samples from all the California sites taken together, subdivided according to peak hour ozone

concentration. Clearly there is no trend for high-ozone days to be characterized by aerosols which have a significantly reduced "graphitic" fraction. This places a rather low limit on the maximum importance of secondary organic particulates formed in correlation with the ozone concentration.

The least squares fit of the data in Figure 1 shows regional differences which are presumably related to the fraction of the carbonaceous aerosol due to primary emissions. These differences would suggest an increase in the relative importance of the primary component for samples collected respectively at Berkeley, Fremont, Anaheim, and Argonne. From the photochemical viewpoint, the results for Argonne are quite reasonable since many of the samples were collected in the winter. However, the trend of the California sites is surprising, and indeed is opposite to what would be expected if a significant secondary component was produced as a result of photochemical activity, which should be at its highest level in Anaheim and its lowest in Berkeley.

As seen in Figure 1e, a strong correlation is also observed between the optical attenuation and the carbon content of the source samples. The slope of the least squares fit of the source data is somewhat larger than that found for the ambient samples, but there is still considerable overlap between the two data sets. This similarity in the absorbing properties of the ambient and source samples strongly suggests that a large component of the carbonaceous aerosol studied is of primary origin. However, due to the spread in both the ambient and the source data, these results do not exclude the possibility of significant secondary species produced in nonzone-related reactions. Indeed the results of Grosjean,[9] Gundel et al.,[10] and others[11] suggest that the polar component of the carbonaceous aerosol cannot be accounted for directly from primary emissions. The trend of the sources to have higher optical attenuation per unit carbon than that found in urban air may also be indicative of a secondary component. An analysis based on comparing the least squares fit of the source and ambient data at all

sites is consistent with a secondary component, which ranges between 15 and 35% of the carbonaceous mass. The data presented here were taken in two California air basins and in the Chicago area. The generality of these results to other areas across the United States and in some areas of Europe is presently being tested. Preliminary data obtained on samples from New York City, Denver, Seattle, Washington, D.C., and Portland are in agreement with the findings outlined in this paper.

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References and Notes

1. For a review of chemical mechanisms for secondary organic formation, see D. Grosjean, in Proceedings, Conference on Carbonaceous Particles in the Atmosphere (Lawrence Berkeley Laboratory Report LBL-9037, 1979, available from NTIS), p. 107.

2. The use of the term "graphitic" is not meant to imply the three-dimensional structure of graphite, but only to indicate a structure similar to that of carbon black. This structure can be viewed to a first approximation as made up of small layered crystallites which have the hexagonal graphitic structure within aromatic planes but a random orientation of the planes about the C axis of the crystallites.

3. The hypothesis that much of the carbonaceous material in urban environments is soot was first advanced by Novakov, A.B. Harker, and W. Siekhaus, in Proceedings, First Annual NSF Trace Contaminants Conference (Oak Ridge National Laboratory Report CONF-730802, 1974, available from NTIS), pp. 354, 379. Additional results strengthening this hypothesis are in (a) T. Novakov, Proceedings, Second Joint Conference on Sensing of Environmental Pollutants (Pittsburgh, Instrument Society of America, 1973), p. 197; (b) T. Novakov, S.G. Chang, and A.B. Harker, Science 186, 259 (1974); (c) S.G. Chang and T. Novakov, Atmos. Environ. 9, 495 (1975).

4. H. Rosen, A.D.A. Hansen, L. Gundel, and T. Novakov, Applied Optics 17, 3859 (1978).

5. H. Rosen, A.D.A. Hansen, L. Gundel, and T. Novakov, in Proceedings, Conference on Carbonaceous Particles in the Atmosphere (Lawrence Berkeley Laboratory Report LBL-9037, 1979, available from NTIS), p. 49.

6. Z. Yasa, N.M. Amer, H. Rosen, A.D.A. Hansen, and T. Novakov, Applied Optics 18, 2528 (1979).

7. Preliminary evidence for the correlation between optical attenuation and total particulate carbon were presented by H. Rosen, A.D.A. Hansen, R.L. Dod, and

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T. Novakov, in Proceedings, Fourth Joint Conference on Sensing of Environmental Pollutants (Washington, American Chemical Society, 1978), p. 640; and by A.D.A. Hansen, H. Rosen, R.L. Dod, and T. Novakov in Proceedings, Conference on Carbonaceous Particles in the Atmosphere (Lawrence Berkeley Laboratory Report LBL-9037, 1979, available from NTIS), p. 116.

8. A similar system is described by P.K. Mueller, R.W. Mosley, and L.B. Pierce, in Proceedings, Second International Clean Air Congress (New York, Academic Press, 1971), p. 532.

9. D. Grosjean, Anal. Chem. 47, 797 (1975).

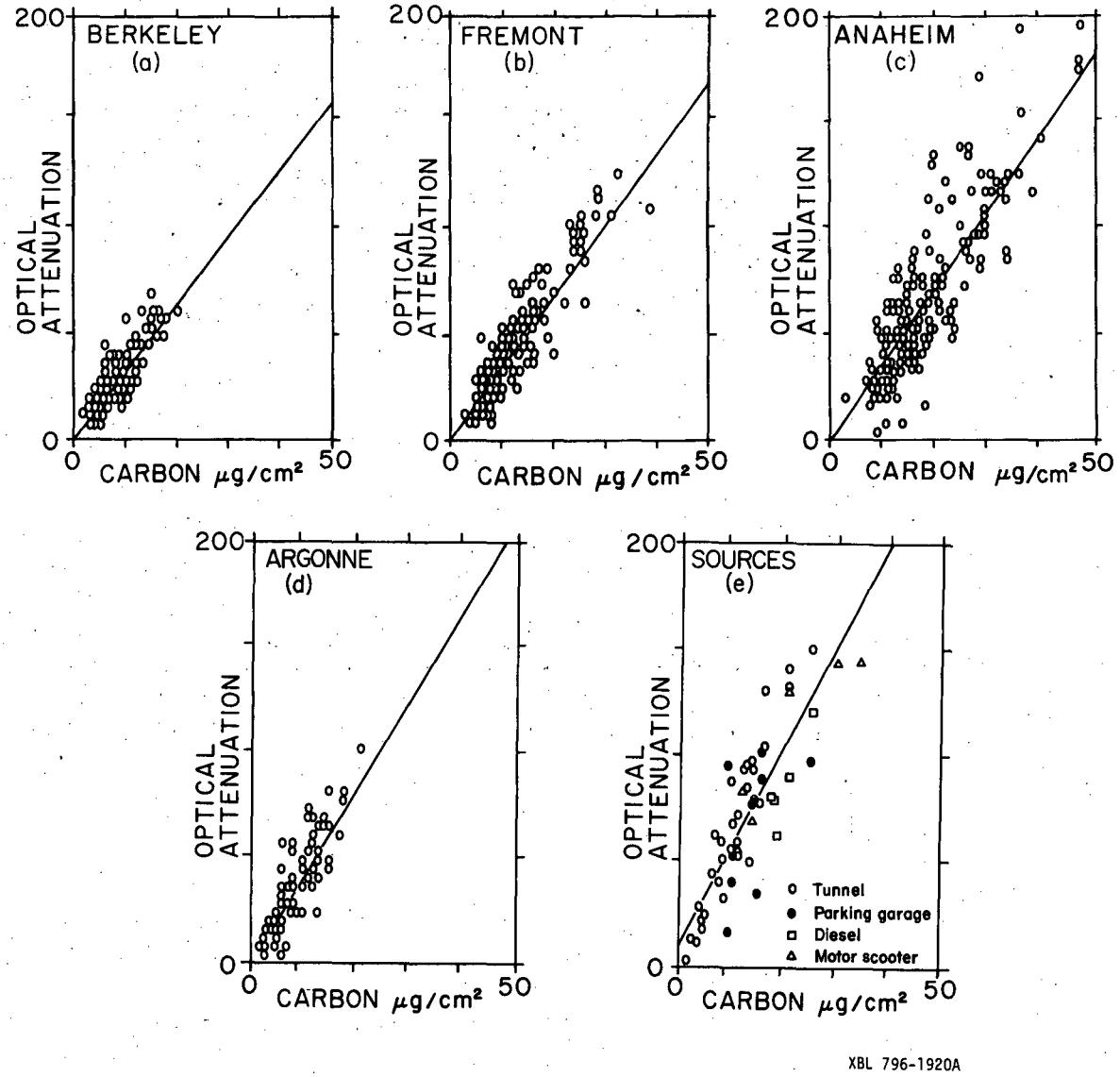
10. L. Gundel, G.E. Mason, and T. Novakov, in Atmospheric Aerosol Research Annual Report 1977-78 (Lawrence Berkeley Laboratory Report LBL-8696, 1979), p. 68.

11. See, for example, B.R. Appel, E.M. Hoffer, E.L. Kothny, S.M. Wall, M. Haik, and R.L. Knights, Environ. Sci. Technol. 13, 98 (1979).

Figure Captions

Figure 1. Plots of optical attenuation versus carbon loading in $\mu g/cm^2$ for particulate samples collected at Berkeley, Fremont, Anaheim, and Argonne, and from various combustion sources. The solid line represents the least squares fit of the data points.

Figure 2. Distribution of the ratios of optical attenuation to total carbon content in $\mu g/cm^2$ subdivided according to the peak ozone concentration. Note that the means of the distributions are only marginally smaller at larger ozone concentrations, which puts a rather low limit on secondary organics produced in correlation with ozone.


BERKELEY
(a)
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200
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Motor scooter
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Figure 1

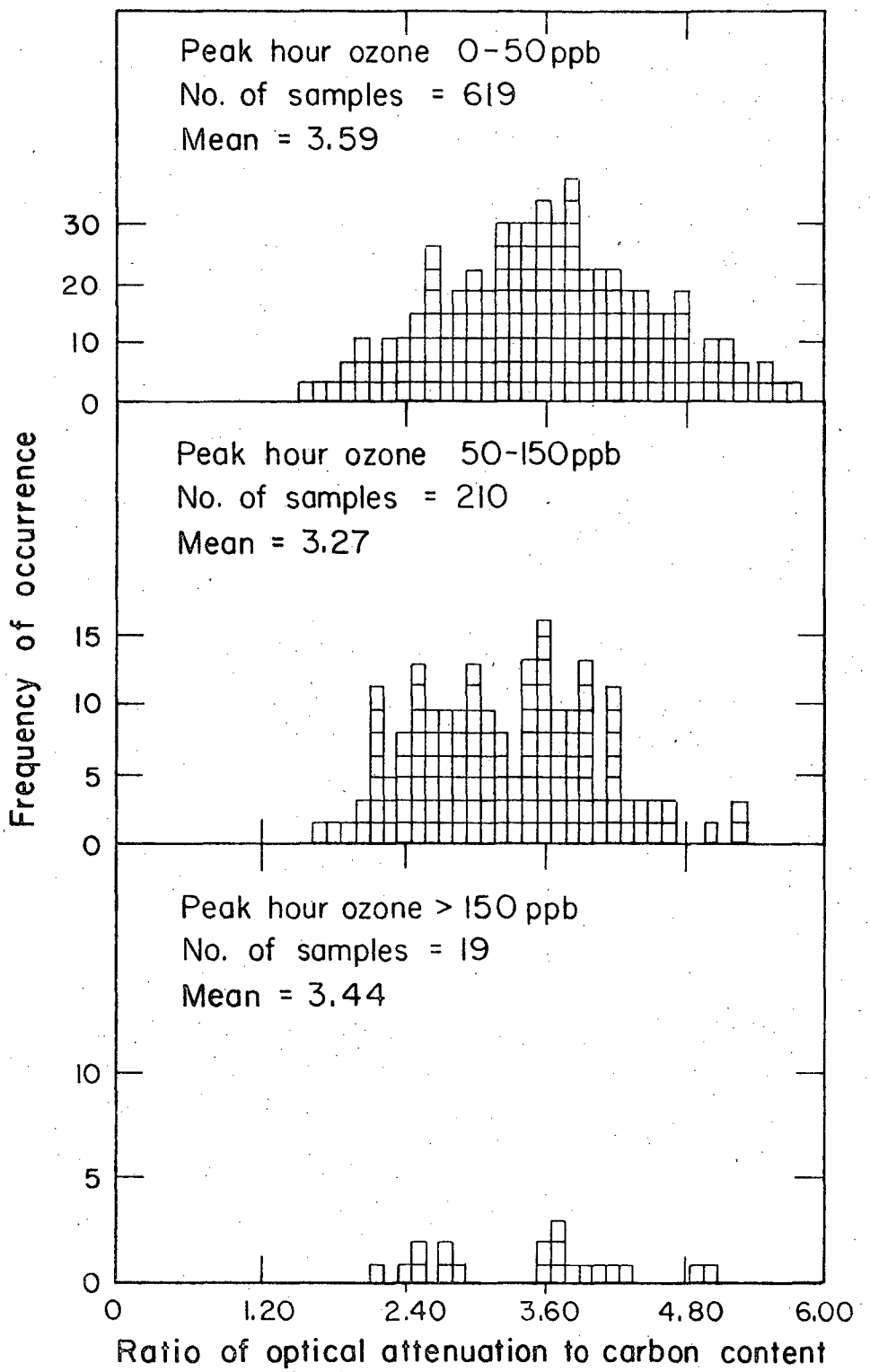


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Figure 2

0 0 0 3 5 0 4 5 9 3

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