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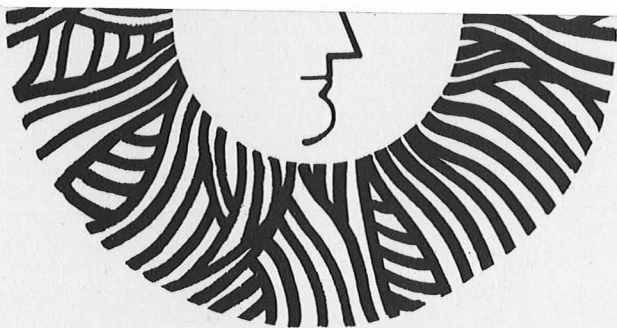SOOT IN THE ATMOSPHERE

T. Novakov

October 1980

SOOT IN THE ATMOSPHERE*

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Introduction

Carbon-, sulfur-, and nitrogen-containing particles account for most of the anthropogenically generated particulate burden in urban areas. Considerable attention has been given to understanding the origin and speciation of the sulfur and nitrogen components, but until recently relatively little effort has been directed toward the carbonaceous aerosol, which is often the single most important contributor to the submicron aerosol mass.

Carbonaceous particles in the atmosphere consist of two major components — graphitic or black carbon (sometimes referred to as elemental or free carbon) and organic material. The latter can either be directly emitted from sources (primary organics) or produced by atmospheric reactions from gaseous precursors (secondary organics). Black carbon, however, can be produced only in a combustion process and is therefore definitely primary. For the sake of clarity, we define soot as the total primary carbonaceous material, i.e., the sum of graphitic carbon and primary organics.

According to the view prevailing at the time our research was initiated (1972), it was postulated that most of the particulate material was produced by certain atmospheric photochemical reactions from gaseous hydrocarbons [1]. The products of these reactions were believed to be certain highly oxygenated hydrocarbons which condense into carbonaceous particles. Such highly oxygenated carbonaceous species, if present in sufficient concentrations, should be detected easily by

X-ray photoelectron spectroscopy (ESCA).

We have used ESCA extensively in attempts to chemically characterize particulate carbon [2-4]. In most instances the carbon (1s) peak of ambient particulates appears essentially as a single peak with a binding energy compatible with either elemental carbon or condensed hydrocarbons or both. As seen in Fig. 1, where the carbon (1s) spectrum of an ambient air particulate sample is shown, chemically shifted carbon peaks, due to suspected oxygen bonding, are of low intensity compared with the intense neutral chemical state peak. This and other similar experiments suggested that the oxygenated (i.e., secondary) species are not the major constituents of carbonaceous particles, even when the samples were collected under conditions of high photochemical activity.

We have also employed other supplementary measurements to estimate the relative abundance of primary particulate carbon [2-4]. This was attempted by comparing the carbon (1s) peak obtained from the sample at 25°C with the carbon (1s) peak from the sample at 350°C. The difference between the low-temperature and the high-temperature runs should give the fraction of volatile carbon. Figure 1 shows the result of one such experiment for a sample collected in 1975 from West Covina. This experiment suggests that most of the ambient particulate carbon is nonvolatile in vacuum at 350°C. Assuming that the secondary hydrocarbons will have a substantial vapor pressure at 350°C, we have suggested that a substantial fraction of the total particulate carbon is primary (sootlike) material.

The preliminary results on the origin and nature of carbonaceous particles were first reported at the First Annual NSF Trace Contaminants Conference at Oak Ridge National Laboratory in August 1973 [3], just one year after the start of our research. Additional results strengthening this hypothesis were reported in several publications from 1973 to 1975 [2,4]. From that time the complex set

of questions concerning the origin and the chemical and physical characterization of carbonaceous particulates has been central to the program of the Atmospheric Aerosol Research group at Lawrence Berkeley Laboratory (LBL). In this paper we will briefly review some of our recent work and attempt to estimate the concentrations and relative amounts of soot in several urban atmospheres.

Methodology

The principal goal of the research described here is to quantitatively assess the relative amounts of primary and secondary carbonaceous material in atmospheric aerosols and to differentiate between secondary carbonaceous species produced by photochemical and nonphotochemical reactions. The approach we have used most extensively involves the use of an optical attenuation technique, combined with total particulate carbon determination; it is based on the following rationale. The black component of soot, which is an unambiguous tracer for primary emissions, can be conveniently monitored because of its large and uniform optical absorptivity [5-8]. The black carbon content of the particles can easily be determined by an optical attenuation method developed in our laboratory [6,7]. Determination of total particulate carbon mass enables us to study the relations between the black and the total carbon content.

An important characterization of a particulate sample is given by the fraction of black carbon to total carbon. Measurements of this ratio of numbers of source samples give insights into the relative black-to-total-carbon ratio of primary emissions and the source variabilities. Secondary material will not contain the black component, but it will increase the total mass of carbon and will therefore reduce the black-to-total-carbon fraction.

Photochemical gas-to-particle conversion reactions should be most pronounced in the summer in the Los Angeles air basin, while in the winter 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 black carbon to total carbon of these particles. That is, under high photochemical conditions one would expect this ratio to be significantly smaller than under conditions obviously heavily influenced by sources.

This approach to the identification and quantitation of primary and secondary carbonaceous aerosols involves a systematic comparison of particulates collected from a wide range of ambient sites as well as combustion sources. Ambient particulates are sampled at sites that differ significantly in meteorology, photochemical activity, and source composition. Source samples have been obtained at a tunnel and a parking garage, and from direct source samplings.

In our field experiments the samples are collected in parallel on prefired quartz fiber and Millipore filter membranes. The Millipore filter is used for X-ray fluorescence (XRF) elemental analysis and for the LBL laser transmission technique described in detail elsewhere [6]. The latter technique gives a measurement that is proportional to the amount of light-absorbing (black) carbon present on the filter. The quartz filter is used for total carbon determination.

The LBL optical method [6] compares the transmission of a 633-nm He-Ne laser beam through a loaded filter relative to that of a blank filter. The relationship between the optical attenuation and the black carbon content can be written as:

$$[C_{black}] = (1/K) \times ATN , \qquad\qquad (1)$$

where $ATN = -100 \ln(I/I_0)$. I and I_0 are the transmitted light intensities for the loaded filter and for the filter blank.

Besides the black carbon, particulate material also contains organic material which is not optically absorbing. The total amount of particulate carbon is then:

$$[C_{tot}] = [C_{black}] + [C_{org}] . \qquad\qquad (2)$$

A fundamental characterization of a particulate sample can be given by its
attenuation per unit mass of total carbon, i.e., its specific attenuation, σ:

$$\sigma \equiv \frac{ATN}{[C_{tot}]} = K \times [C_{black}]/[C_{tot}] . \qquad\qquad (3)$$

The determination of specific attenuation therefore gives an estimate of black
carbon as a fraction of total carbon.

The proportionality constant K, which is equal to the specific attenuation
of black carbon alone, was recently shown to have an average value of 20 [9].
This value was obtained by determining the optical attenuation of 25 samples
for which the absolute concentration of black carbon was known. In principle
the percentage of soot (i.e., primary carbonaceous material) in ambient particles
can be determined from the ratio of ambient specific attenuation and an average
specific attenuation of major primary sources:

$$[Soot]/C = \sigma_{ambient}/\sigma_{source} . \qquad\qquad (4)$$

The approach for estimating the soot content depends on the validity of
using the optical attenuation as a measure of the black carbon content. That
this procedure is valid can be illustrated by the following example, involving
a direct analysis for total carbon and black carbon by thermal analysis [10,11]
Thermal analysis is used to obtain total carbon, black carbon, organic carbon,
and carbonate carbon. A schematic representation of the thermal analysis
apparatus used in our studies is shown in Fig. 2. The main components of this
apparatus are a quartz tube and a temperature-programmed furnace. The tube is
mounted axially inside the furnace. The particulate sample, collected on a
prefired quartz filter, is placed in the quartz tube so its surface is perpendicular

to the tube axis. The tube is constantly supplied with pure oxygen. The

excess oxygen escapes through an axial opening at the end of the tube, while

the remainder of the oxygen (and other gases evolved during analysis) passes

through a nondispersive infrared analyzer at a constant flow. In addition to

the variable temperature furnace, the apparatus also contains a constant tempera-

ture furnace, usually kept at about 850°C. The segment of quartz tube inside

the constant temperature furnace is filled with a copper oxide catalyst. The

purpose of the catalyst is to ensure that carbon-containing gases evolved from

the sample are completely converted to CO_2. This is especially important at

relatively low temperatures when complete oxidation to CO_2 does not occur.

The actual measurement consists in monitoring the CO_2 concentration as

a function of the sample temperature. The result is a "thermogram" — a plot of

the CO_2 concentration vs. temperature. The area under the thermogram is propor-

tional to the carbon content of the sample. The carbon content is quantitated

by calibrating with a calibration gas (CO_2 in oxygen) and by measuring the flow

rate through the system. This calibration is crosschecked by analyzing samples

of known carbon content. The thermograms of ambient and source aerosol samples

reveal distinct features in the form of peaks or groups of peaks that correspond

to volatilization, pyrolysis, oxidation, and decomposition of the carbonaceous

material.

To determine which of the thermogram peaks corresponds to black graphitic

carbon, the intensity of the light beam produced by a He-Ne laser is monitored

by a photomultiplier and displayed by the second pen of the chart recorder,

simultaneously with the measurement of the CO_2 concentration [11]. In actual experi-

ments the light penetrating the filter is collected by a quartz light guide and

filtered by a narrow band interference filter to eliminate the effect of the

glow of the furnaces. An examination of the CO_2 and light intensity traces

enables the assignment of the peak or peaks in the thermograms corresponding to the black carbon because they appear concomitantly with the decrease in sample absorptivity.

In Fig. 3, a complete thermogram of an ambient sample is shown. The lower trace represents the CO_2 concentration vs. the sample temperature, while the upper curve corresponds to the light intensity of the laser light beam that reaches the detector during the temperature scan. Inspection of the thermogram shows that a sudden change in the light intensity occurs concomitantly with the evolution of the CO_2 peak at about 470°C. The light intensity I_0, after the 470°C peak has evolved, corresponds to that of a blank filter. This demonstrates that the light-absorbing species in the sample are combustible and carbonaceous. We refer to these species as black carbon. The carbonate peak evolves at about 600°C; and as carbonate is not light absorbing, it does not change the optical attenuation of the sample. In addition to black carbon and carbonate, the thermogram in Fig. 3 also shows several distinct groups of peaks at temperatures below ∿ 400°C that correspond to various organics.

The thermogram in Fig. 3 was obtained with a 1.46-cm-diameter disc cut out of a sample collected on prefired quartz fiber filters. The temperature ramp rate was 10°C/minute. The integrated area under the CO_2 trace is proportional to the total carbon concentration. For this sample the total carbon concentration, determined by thermal analysis, was 17.9 µg (C)/cm^2. The black carbon, determined from the thermogram, composes 14% of the total carbon. This value can be crosschecked by using the optical attenuation and total carbon data. The specific attenuation for this sample, determined in a separate measurement, is $\sigma \equiv ATN/C = 3.00$. The estimated percentage of black carbon (as a percent of total C), determined from measurement of optical attenuation and total carbon only, is 100 x 3.0/20.0 = 15%. This value is in excellent agreement with the percentage of black carbon determined directly from the CO_2 thermogram.

Results and Discussion

The data presented in this paper consist of information obtained from analyses of 24-hr samples (collected weekdays) and multi-day samples (collected over weekends [9]. Table I lists the routine sampling sites with the beginning date of sampling.

Total carbon and optical attenuation. Figure 4 shows the variations of 24-hr total carbon (weekends excluded) at the Fremont, California, site. These data cover the period from July 1977 to January 1980. The 24-hr histogram superimposed on the bar diagram represents the monthly averages.

It is evident from Fig. 4 that there are significant day-to-day variations in total carbon. The maximum and minimum daily concentrations differ by an order of magnitude. The monthly averages are at peak values during the November-December periods of each year. The variations in optical attenuation for the same samples are represented in Fig. 5. The pattern of ATN values resembles that of total carbon and shows similar seasonal variations. The specific attenuation (ATN/C) variations represented in Fig. 6 are much less pronounced and show no clear seasonal variations. Similar features of total C, ATN, and ATN/C are also observed at the Berkeley and Anaheim sites.

At the New York, Gaithersburg, and Argonne sites, daily and monthly variations of total C and ATN are much less pronounced than at the three West Coast sites.

Correlations between total carbon and ATN. Statistical analysis of the data shows that there is a strong correlation (r > 0.85) between optical attenuation and total particulate carbon at every site studied [12,13]. Furthermore, a study of a number of source samples shows that there is also a strong correlation between optical attenuation and total carbon for these samples. The correlations between optical attenuation and total carbon for the three California sites, Argonne, and source samples are shown in Fig. 7 (a-e) [13].

Results obtained from ambient samples imply 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, however, there can be large variations in the ratio, reflecting the variations in the relative amounts of organic and black carbon. The least squares fit of the data shows regional differences which are related to the fraction of black carbon 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.

Concentrations of black carbon. Determination of specific attenuation, $\sigma \equiv ATN/C$, enables a straightforward estimation of black carbon. From relation (3) one can calculate black carbon as a percentage of total carbon, and the concentration of black carbon in $\mu g/m^3$. Table II lists the average specific attenuation and black carbon percentages for all samples (including multi-day samples) analyzed to date. In addition to the average values, the highest and lowest values are given. Based on this estimate, on the average 20% of the total carbon is black carbon. This fraction can on occasion be as high as 56% or as low as 6%. The latter occurs as a rule when total carbon concentrations are low. Table III lists the concentrations of total particulate carbon and estimated concentrations of black carbon for the same samples as Table II.

Concentrations of soot. Soot contains not only black carbon but also various organic material. Because the organic soot component does not absorb light, the specific attenuation of soot is much less than 20, the σ value of pure black carbon. Table IV lists the average and extreme values of specific attenuation and the black carbon fraction of a number of source samples.

The percentage of soot in ambient carbonaceous particulates can be estimated by comparing the σ of sources with that of ambient samples. The fraction of soot is given in equation (4). Table V lists the mean specific

attenuation of ambient samples (weekends excluded) in order of decreasing σ and soot fractions obtained by using equation (4) and σ_{source} = 5.85.

Based on this estimation, the New York City carbonaceous aerosol is essentially primary soot. A different value of σ_{source} would certainly change the estimated soot percentage. However, New York City's average soot content would nevertheless remain the highest, irrespective of the actual numerical value of σ_{source}. It is logical that samples from this location have the highest soot content because the site is representative of a heavily traveled street canyon. Fremont and Anaheim samples have on the average the smallest soot content, as may be expected, because both sites represent receptor sites. According to the above estimate, Denver has the smallest specific attenuation value. It is possible that high-altitude combustion results in increased emissions of primary organics; however, we note that the number of samples from this location is small compared to that from other sites, so these results should be taken with caution.

It is instructive to present the specific attenuation data in the form of histograms representing their frequency of occurrence. Histograms for New York and Fremont (Fig. 8) show that the occurrence of high specific attenuation samples is much greater for New York than for Fremont. In Fig. 9 the histogram of specific attenuations of a number of source samples is shown together with those for New York and Fremont. The distribution for sources looks similar to the distribution for New York. This supports the inference that the New York samples, on the average, consist almost entire of primary carbonaceous material. Histograms for other sampling sites are shown in Figs. 10 and 11.

Secondary Organics

Results in Table V suggest that the West Coast sites have an organic component that occurs in excess of sources of source-dominated organics. This

excess should be equal to the secondary organic material, which can be conveniently identified by the thermal analysis method.

We have already described how thermal analysis can be used to obtain the total carbon, black carbon, organic carbon, and carbonate carbon. The greatest strength of this method, however, is its ability to "fingerprint" source-produced carbonaceous particles and their contribution to the ambient aerosols. As an illustration, in Figs. 12 and 13 we show the thermograms of a sample collected in Manhattan (high σ) and one collected in Berkeley (low σ). The two thermograms are substantially different. Common features of both samples are the black carbon and the group of peaks below $\sim 250°C$, corresponding to volatile organic compounds. However, the Berkeley sample clearly shows the presence of other peaks which are absent in the thermogram of the New York sample. These peaks are not observed in samples collected in a highway tunnel and a parking garage and probably correspond to secondary species.

Secondary Organics and Ozone

It is clear from the results described so far that the ratio of black carbon to total carbon may vary on specific days. However, no large systematic differences are found as a function of the ozone concentration, which is viewed as an indicator of the photochemical activity [13]. This is graphically demonstrated in Fig. 14, 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 black carbon fraction. This places a low limit on the importance of secondary organic particulates formed in correlation with the ozone concentration.

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and by A.D.A. Hansen, H. Rosen, R.L. Dod, and T. Novakov, "Optical

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Table I. LBL aerosol sampling sites.

Site	Location	Date of first sample
Lawrence Berkeley Laboratory	Berkeley, California	1 June 1977
BAAQMD monitoring station	Fremont, California	15 July 1977
SCAQMD monitoring station	Anaheim, California	19 August 1977
Argonne National Laboratory	Argonne, Illinois	22 January 1979
DOE Environmental Measurements Laboratory	Manhattan, New York	22 November 1978
National Bureau of Standards	Gaithersburg, Maryland	23 January 1979
Denver Research Institute	Denver, Colorado	15 November 1978

Table II.   Specific attenuation (σ) and black carbon (BC)(% of total C) from
            ambient samples.

Site	Dates on file	# samples	Average σ	Average % BC	Highest σ	Highest % BC	Lowest σ	Lowest % BC
New York	Nov 78 - Apr 80	439	5.44	27%	11.1	56%	2.8	14%
Argonne	Jan 79 - Mar 80	438	4.30	22%	9.1	46%	1.1	6%
Gaithersburg	Jan 79 - Mar 80	381	4.33	22%	8.0	40%	1.8	9%
Denver	Nov 78 - May 79	141	3.23	16%	5.7	29%	1.4	7%
Anaheim	Aug 77 - Jan 80	852	3.70	19%	9.6	48%	0.8	4%
Fremont	Jul 77 - Mar 80	924	3.55	18%	8.3	42%	1.6	8%
Berkeley	Jun 77 - Apr 80	998	4.09	20%	9.2	46%	1.2	6%

Table III. Carbon concentrations ($\mu g/m^3$).

Site	Average C	Average BC	Highest C	Highest BC	Lowest C	Lowest BC
New York	15.2	4.2	53.1	12.6	3.4	0.6
Argonne	8.1	1.7	25.1	5.2	3.1	0.2
Gaithersburg	6.1	1.4	17.6	5.6	2.3	0.3
Denver	9.8	1.6	30.8	5.3	4.1	0.2
Anaheim	16.6	3.1	112.9	17.4	3.1	0.3
Fremont	12.0	2.1	75.6	9.2	3.4	0.3
Berkeley	6.7	1.3	31.7	5.2	3.0	0.3

Table IV. Specific attenuation (σ) and black carbon (BC)(% of total C)
of source samples.

Source	# samples	Average σ	Average % BC	Highest σ	Highest % BC	Lowest σ	Lowest % BC
Parking garage	12	5.4	27%	7.7	39%	2.25	11%
Diesel	6	5.6	28%	5.7	29%	3.5	18%
Scooter	9	5.1	26%	6.1	31%	4.2	21%
Tunnel	63	6.3	32%	12.5	63%	3.7	19%
Natural gas	6	2.6	13%	3.3	17%	1.9	10%
Garage and tunnel		5.85	29%				

Table V. Mean specific attenuation of ambient samples.

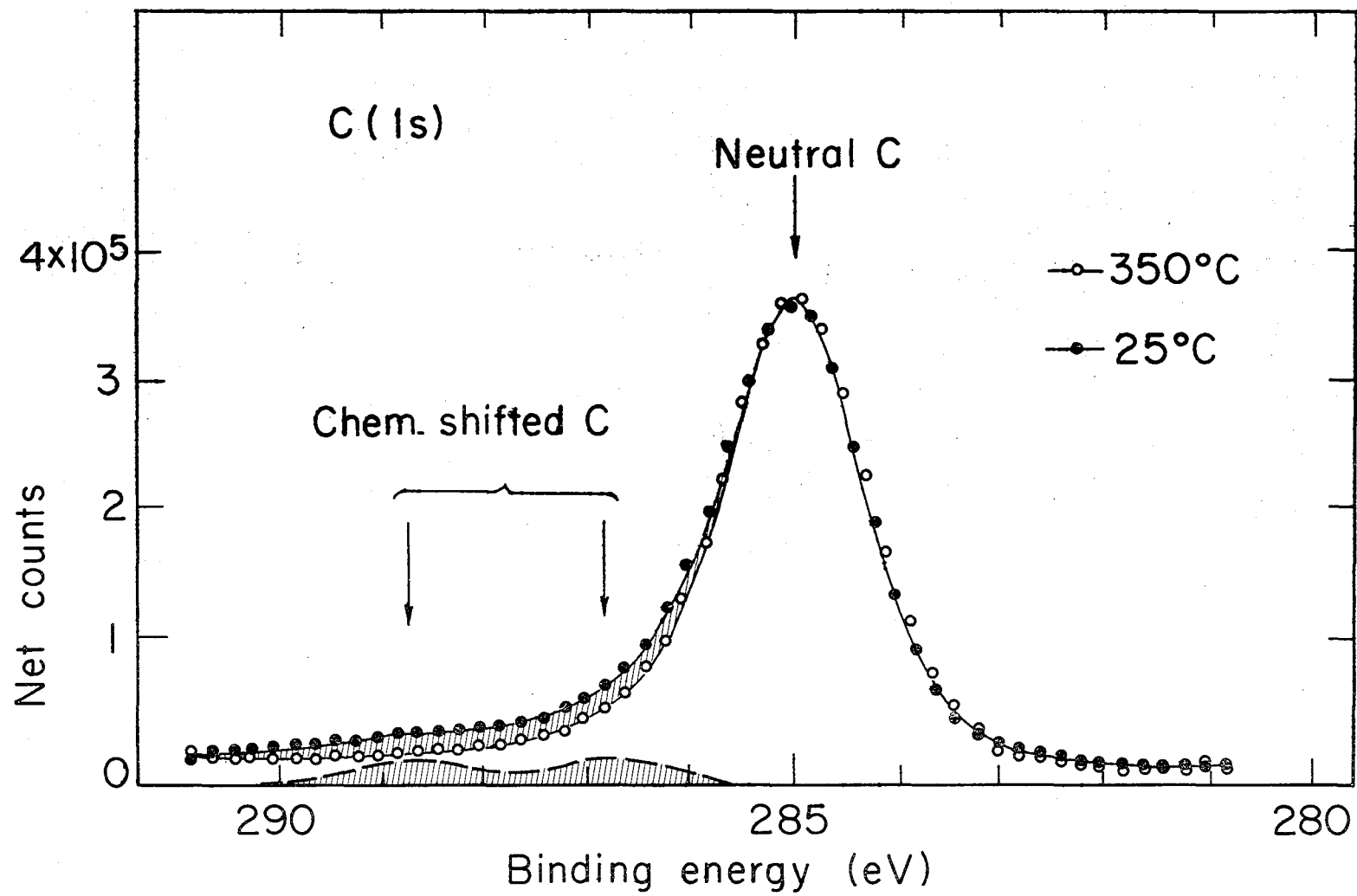| Site	# samples	$\bar{\sigma}$	SDEV	Soot (%)
New York	211	5.69	1.34	97
Gaithersburg	155	4.72	1.51	81
Argonne	221	4.35	1.64	74
Berkeley	513	4.28	1.47	73
Anaheim	444	3.99	1.71	68
Fremont	461	3.74	1.25	64
Denver	42	3.47	1.49	59

Figure Captions

Figure 1. Carbon (1s) photoelectron spectrum of an ambient (West Covina,
California) sample as measured at 25 and 350°C. The chemically shifted
peaks are of low intensity compared to the main peak. Most of the carbon
appears to be nonvolatile. The shaded area represents the difference
between low- and high-temperature spectra (from Ref. 2).

Figure 2. Schematic representation of the thermal analysis apparatus.

Figure 3. Thermogram of an ambient sample showing carbonate, black carbon,
and several forms of organic material.

Figure 4. Variations in the daily total carbon concentration at the Fremont,
California, site (from Ref. 9).

Figure 5. Variations in the optical attenuation at the Fremont, California,
site (from Ref. 9).

Figure 6. Variations in the specific attenuation at the Fremont, California,
site (from Ref. 9).

Figure 7. 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 (from Ref. 13).

Figure 8. Distribution of specific attenuation for the New York and Fremont
sites (from Ref. 9).

Figure 9. Distribution of specific attenuation for source, New York, and
Fremont samples (from Ref. 9).

Figure 10. Distribution of specific attenuation for Anaheim, California,
and Berkeley, California, sites (from Ref. 9).

Figure 11. Distribution of specific attenuation for Denver, Colorado, Argonne,
Illinois, and Gaithersburg, Maryland, sites (from Ref. 9).

Figure 12.   Thermogram of a New York sample with high specific attenuation.

Figure 13.   Thermogram of a Berkeley, California, sample with low specific

attenuation.

Figure 14.   Distribution of the ratios of specific attenuation 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 (from Ref. 13).

Figure 1

XBL 745-3308
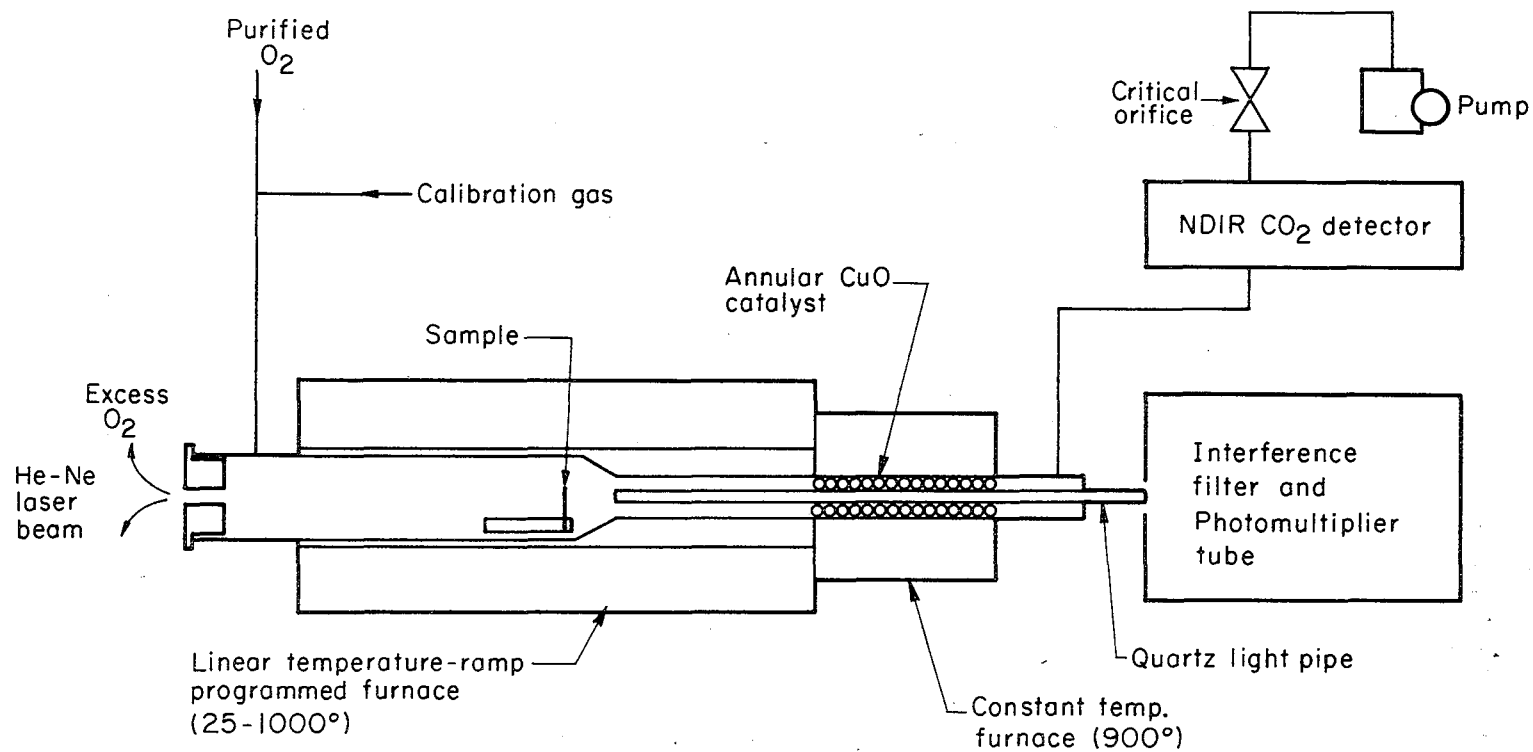
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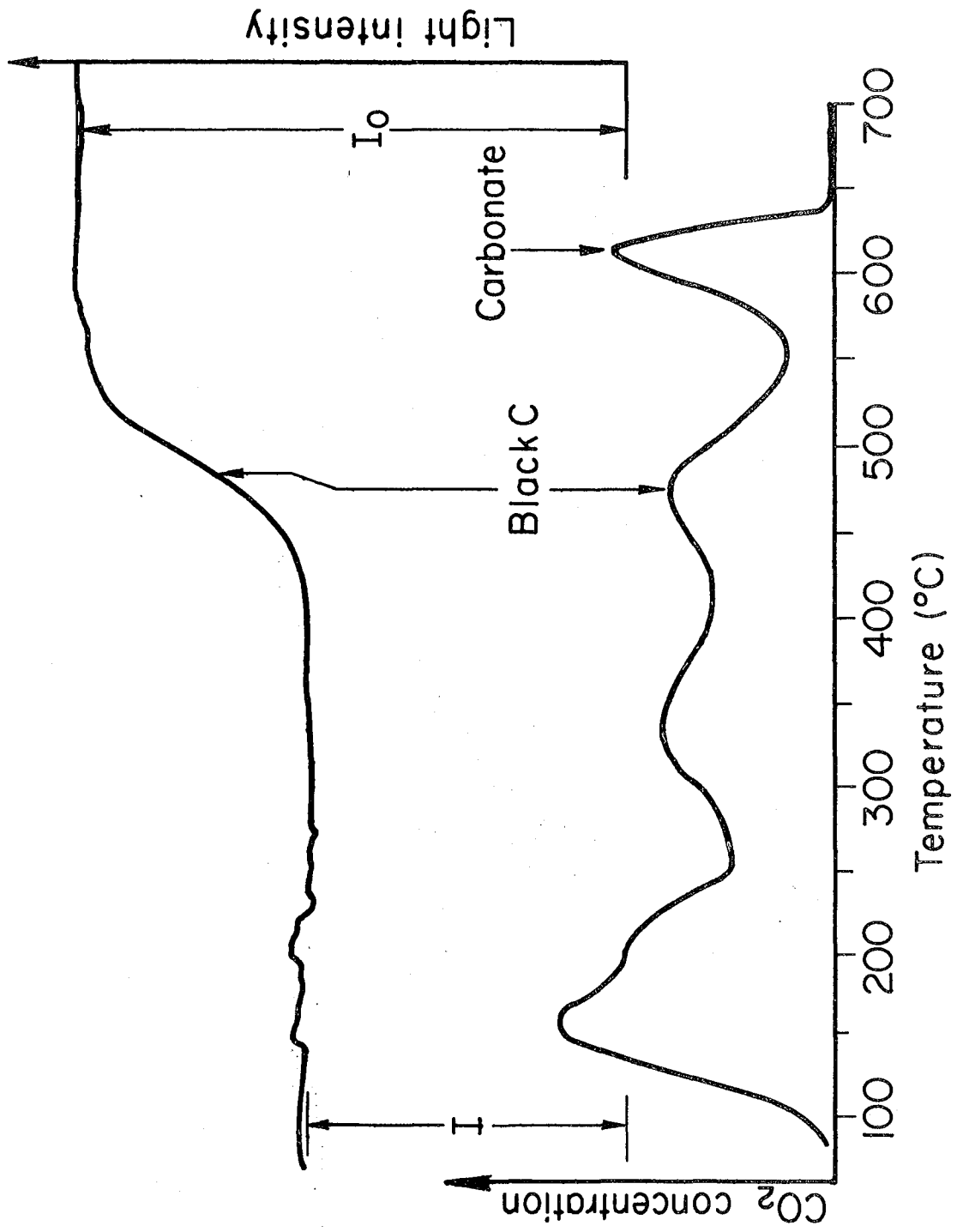
Figure 2

XBL 8012-13505

Figure 3

Figure 4

Figure 5

FREMONT : OPTICAL ATTENUATION

XBL 806-10536

FREMONT : SPECIFIC ATTENUATION
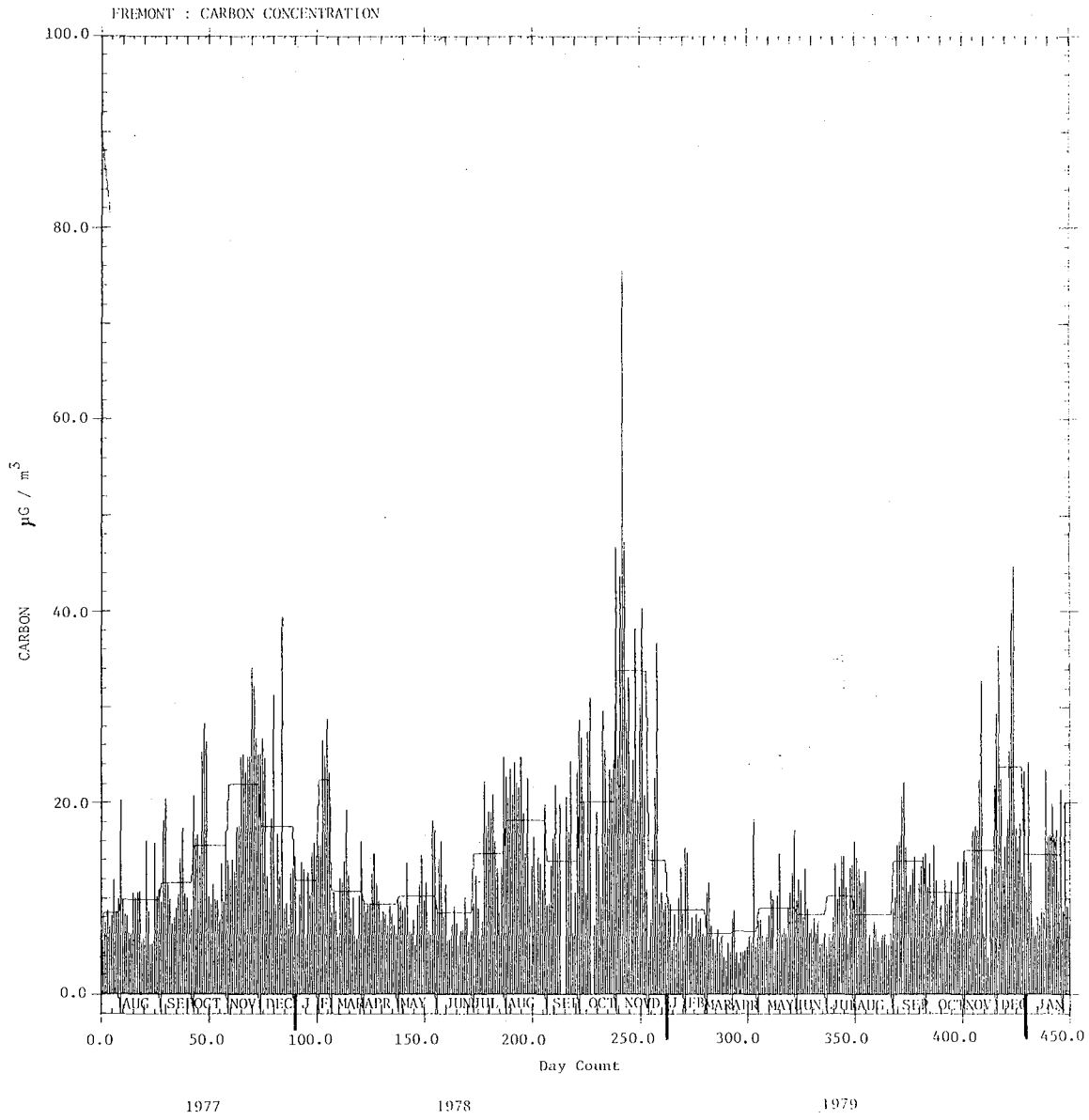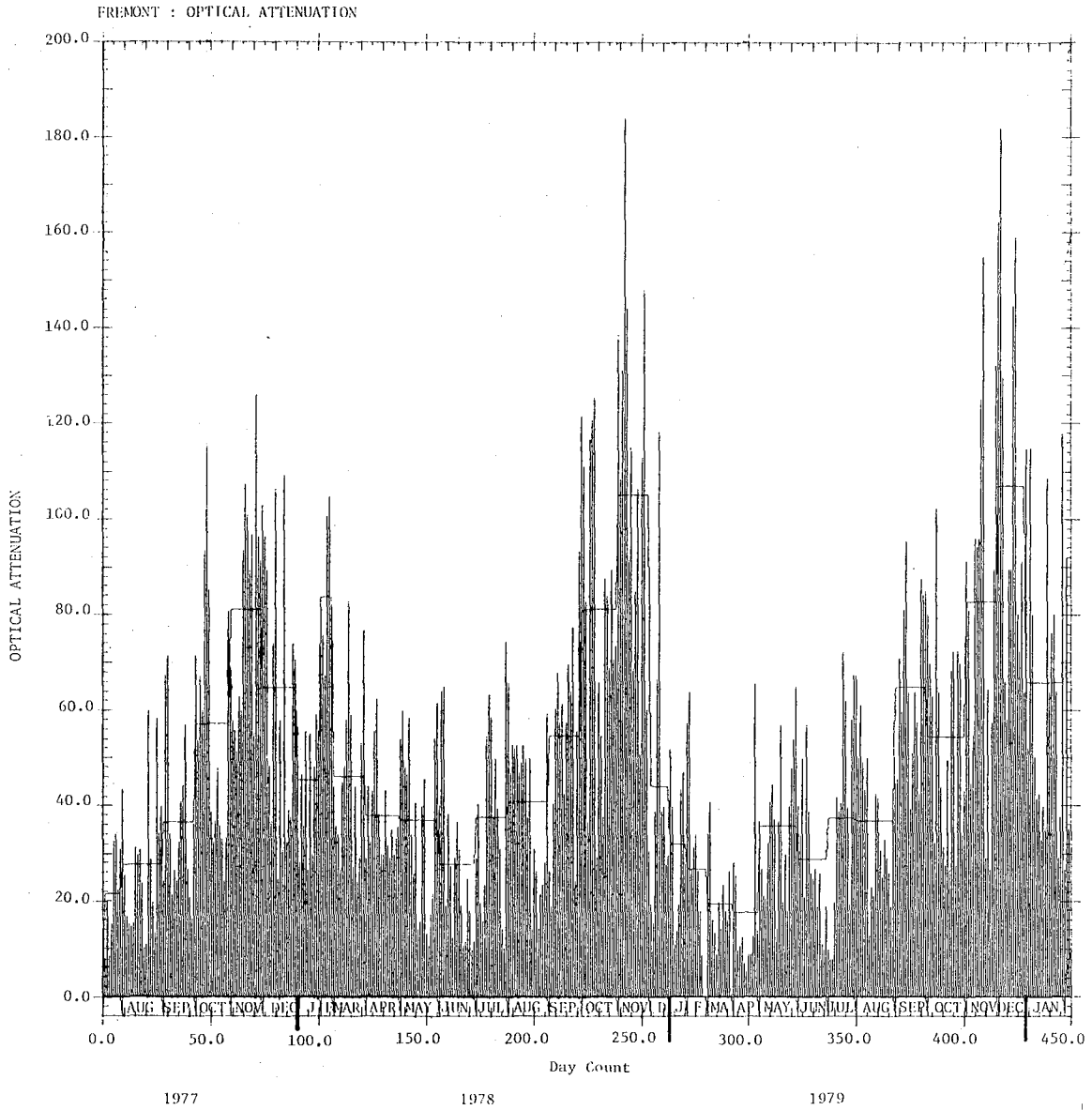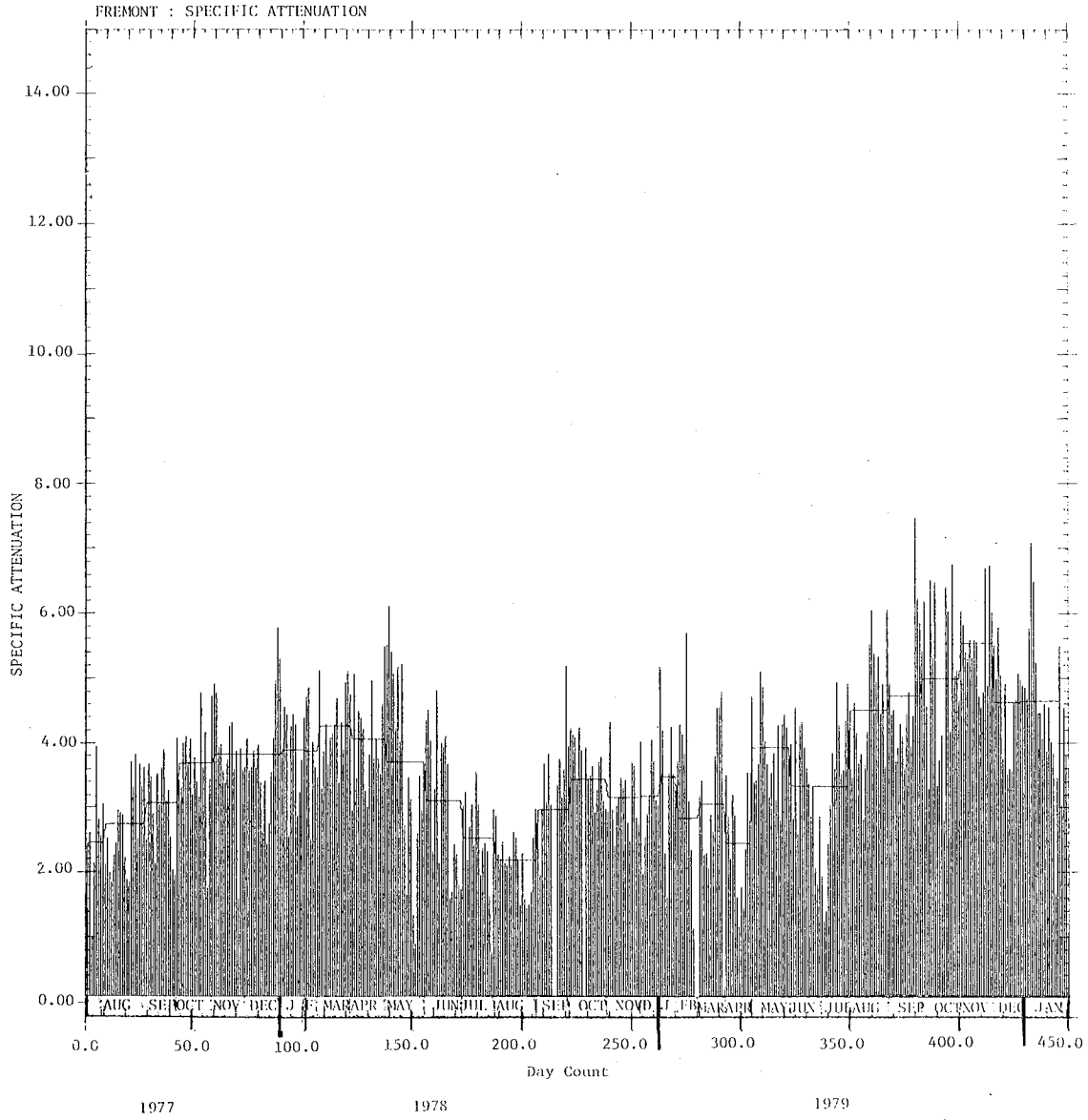
Figure 6

XBL 806-10537

XBL 796-1920A

Figure 7

HISTOGRAM OF ATN/ C FOR SITES NYC
FOR DATES 27 NOV 78 TO 14 APR 80
NPOINTS = 211   MEAN = 5.69   SDEV = 1.34   NO WKENDS

HISTOGRAM OF ATN/ C FOR SITES FRE
FOR DATES 18 JUL 77 TO 12 MAR 80
NPOINTS = 461   MEAN = 3.74   SDEV = 1.25   NO WKENDS

XBL 8010-12695

Figure 8

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HISTOGRAM OF ATN/  C FOR SITES GRG TUN SCT DSL NGS
FOR DATES  1 OCT 77 TO 12 APR 78
NPOINTS =  93    MEAN =  5.74    SDEV =  1.93

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     ..........*..........*..........*..........*..........*
      0.       2.00      4.00      6.00      8.00     10.00    ATN/  C


HISTOGRAM OF ATN/  C FOR SITES NYC
FOR DATES 27 NOV 78 TO 14 APR 80
NPOINTS = 211    MEAN =  5.69    SDEV =  1.34    NO WKENDS

    18 *
       .                              X
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       .                       XXXXXX XX
       .                       X XXXXXX XX
       .                       .XXXXXYXX XXX
       .              XX   XXXXXXXX.XXX X
       .              .XX.XXYXXXYXYXXXX XX
       .           .  .XXXXXXXXXXXXXXXXXXXX..  .    .
       .        X   X X XXXXXXXXXXXXXXXXXXXXXXXXX XX   X X
     ..........*..........*..........*..........*..........*
      0.       2.00      4.30      6.00      8.00     10.00    ATN/  C


    42 *
       .                     X
       .                     XX
       .                     YY.Y
       .              X   XXXX
       .              X..XXXXX.
       .            .X YXXXXYXXXX.
       .            XX XXXXXYXXXXX.
       .          X.XYXXYXXYXXXXYXXXX.X
       .         XXXXYXXYXXXXXXXXXXXXX  X ..
     ... ..X.XXXXYXXYXYXXXXXXXXXXXXXXX.XX...Y
     ..........*..........*..........*..........*..........*
      0.       2.00      4.00      6.00      8.00     10.00    ATN/  C

HISTOGRAM OF ATN/  C FOR SITES FRE
FOR DATES 18 JUL 77 TO 12 MAR 80
NPOINTS = 461    MEAN =  3.74    SDEV =  1.25    NO WKENDS
```
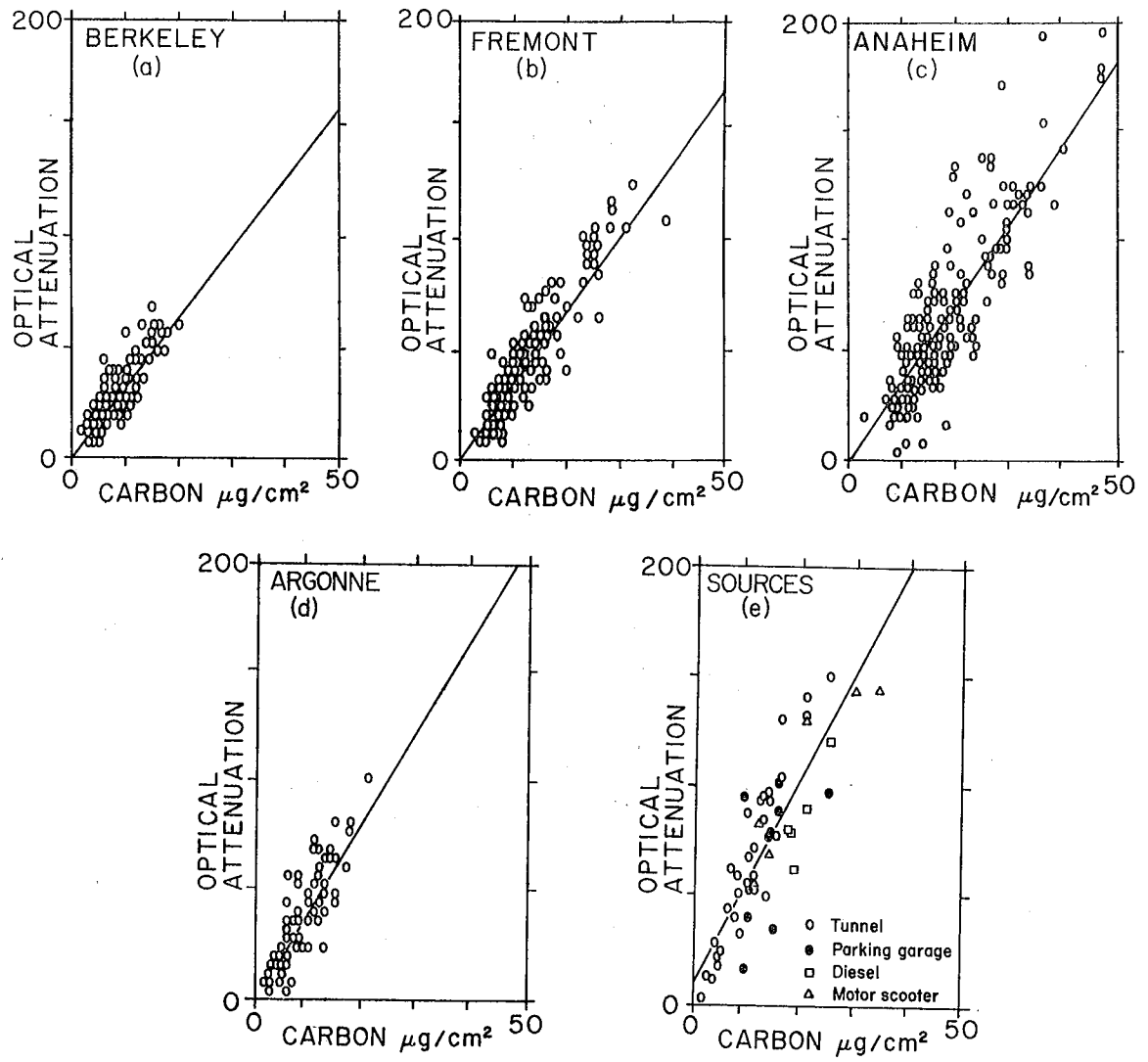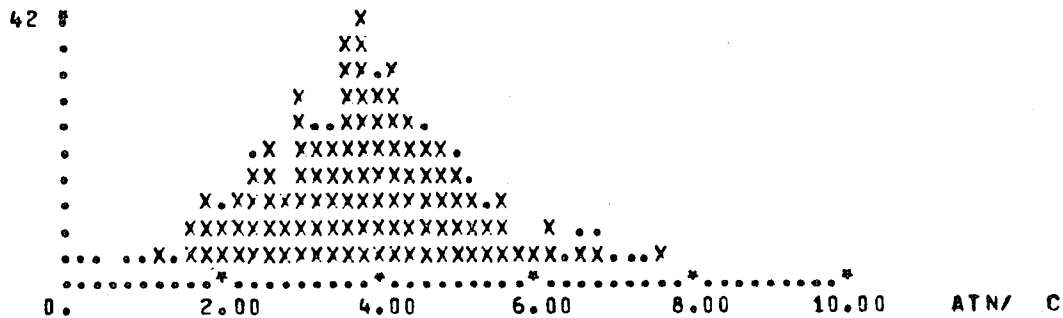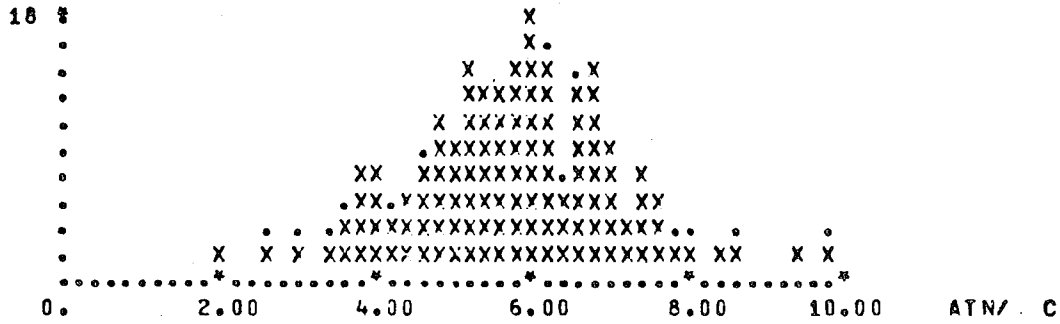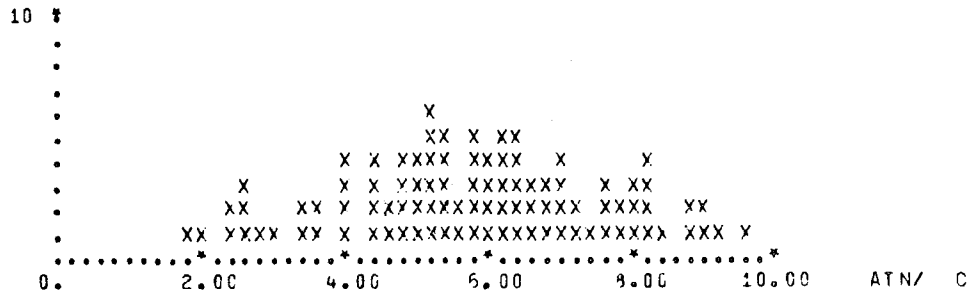
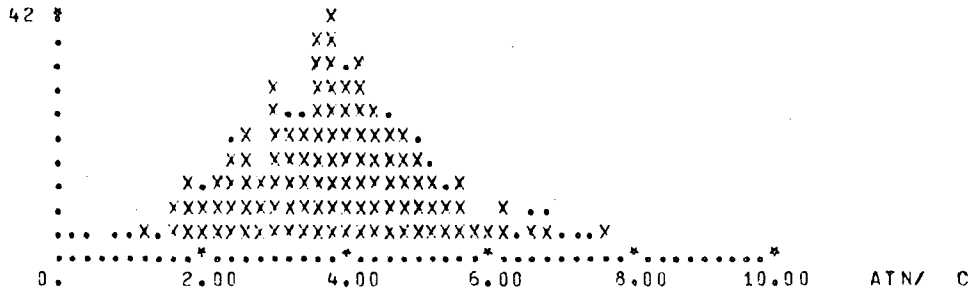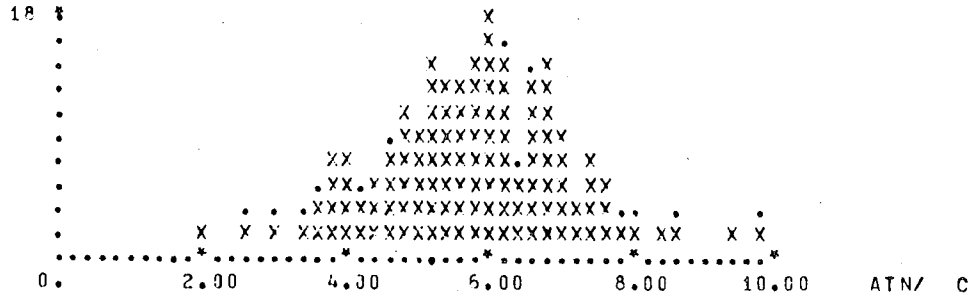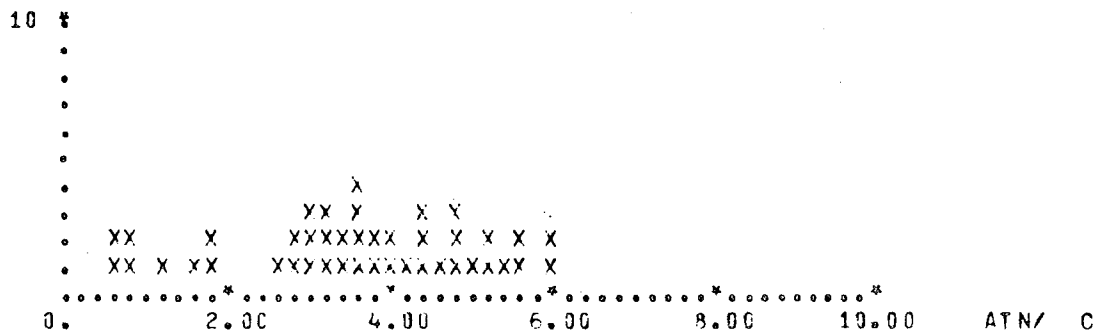XBL 8010-12697

Figure 9

```
HISTOGRAM OF ATN/  C FOR SITES ANA
FOR DATES 22 AUG 77 TO 29 JAN 30
NPOINTS = 444     MEAN =  3.99    SDEV =   1.71     NO WKENDS

    34 *                     X   .
       .                   . X  XX
       .                 .X.X X.XX
       .                 XYYX.XXXX
       .                 XYYXXXXYYX  . .
       .               X.XYYXXXXYXXXXXX
       .               XYXYYXXXXYXXYYX) .
       .              XYXXYXXXXXXXYYXYXX.XX X
       .              XXXYYXXXYXXXXXYXXXXYX X.
       .          XX  XYXYXYXXXYYYXYXXXX.XXXXXXXXX.... YX. ..X.. .
       .........................*............*.........*..........*
        0.        2.00       4.00       6.00       8.00      10.00     ATN/  C
```

```
    41 *                     X
       .                   ) X Y
       .                   YYY XX
       .                 . XXXY XXY
       .                 X XYXXXXXX X
       .                YY.YYYXXYXY.Y
       .                YXXXXXXXXYXXXXXXY.X
       .                XYYYXXXXYYYXXXXXXXX X
       .               .YXXXYYXYYYXXXXXXYYXXXXY  .    .
       .    . ....Y.XXXXYYXXXXYYYYXXXXYXYXXXXXXXX..X. X.. ...
       .........................*............*.........*..........*
        0.        2.00       4.00       6.00       8.00      10.00     ATN/  C
```

```
HISTOGRAM OF ATN/  C FOR SITES BRK
FOR DATES  1 JUN 77 TO 17 APR 80
NPOINTS = 513     MEAN =  4.28    SDEV =   1.47     NO WKENDS
```

Figure 10
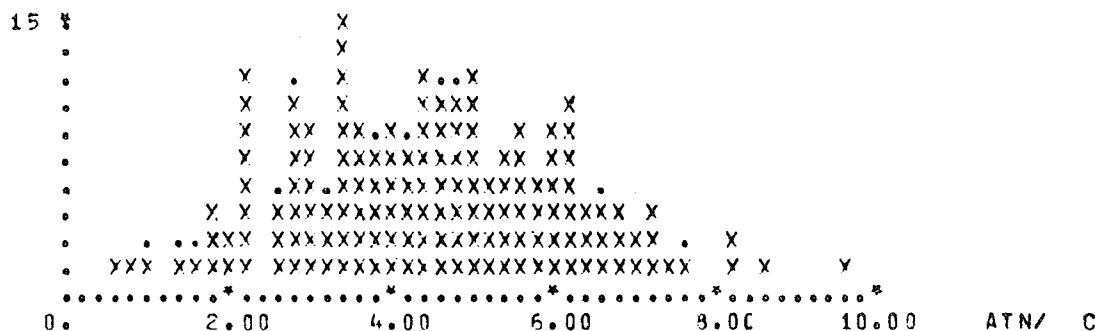
HISTOGRAM CF ATN/ C FOR SITES DNV
FOR DATES 16 NOV 78 TO 22 MAY 79
NPOINTS = 42   MEAN = 3.47   SDEV = 1.49   NO WKENDS

```
   10 %
      .
      .
      .
      .
      .
      .                     X
      .            YX Y     X X
      . XX    X       XXXXXXX X X X X X
      . XX X XX     XXYXXAXXXXAAXXAXX X
      ...........*..........*..........*..........*..........*
      0.       2.00       4.00       6.00       8.00      10.00     ATN/  C
```
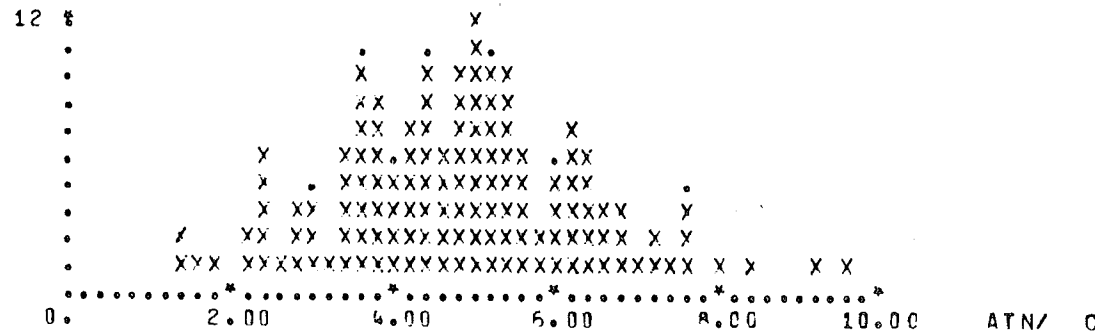
HISTOGRAM OF ATN/ C FCR SITES CHI
FOR DATES 23 MAR 78 TO 27 MAR 80
NPOINTS = 221   MEAN = 4.35   SDEV = 1.64   NO WKENDS

```
   15 %                   X
      .                   Y
      .          Y  .  X      X..X
      .          X  X  X    XXXX      X
      .          X  XX XX.X.XXYX  X XX
      .          Y  YY XXXXXXXXX XX XX
      .          X .XY.XXXXXX.XXXXXXXXX .
      .       Y  X XXYXXXXXXXXXXXXXXXXX X
      .      . ..XXX XXXXXXYXX.XXXXXXXXXXXXX .  X
      . YXX XYXXY XYYXXXXXXX.XXXXXXXXXXXXXXX  Y X    Y
      ...........*..........*..........*..........*..........*
      0.       2.00       4.00       6.00       8.00      10.00     ATN/  C
```

HISTOGRAM OF ATN/ C FCF SITES WDC
FOR DATES 23 JAN 79 TO 5 MAR 80
NPOINTS = 155   MEAN = 4.72   SDEV = 1.51   NO WKENDS
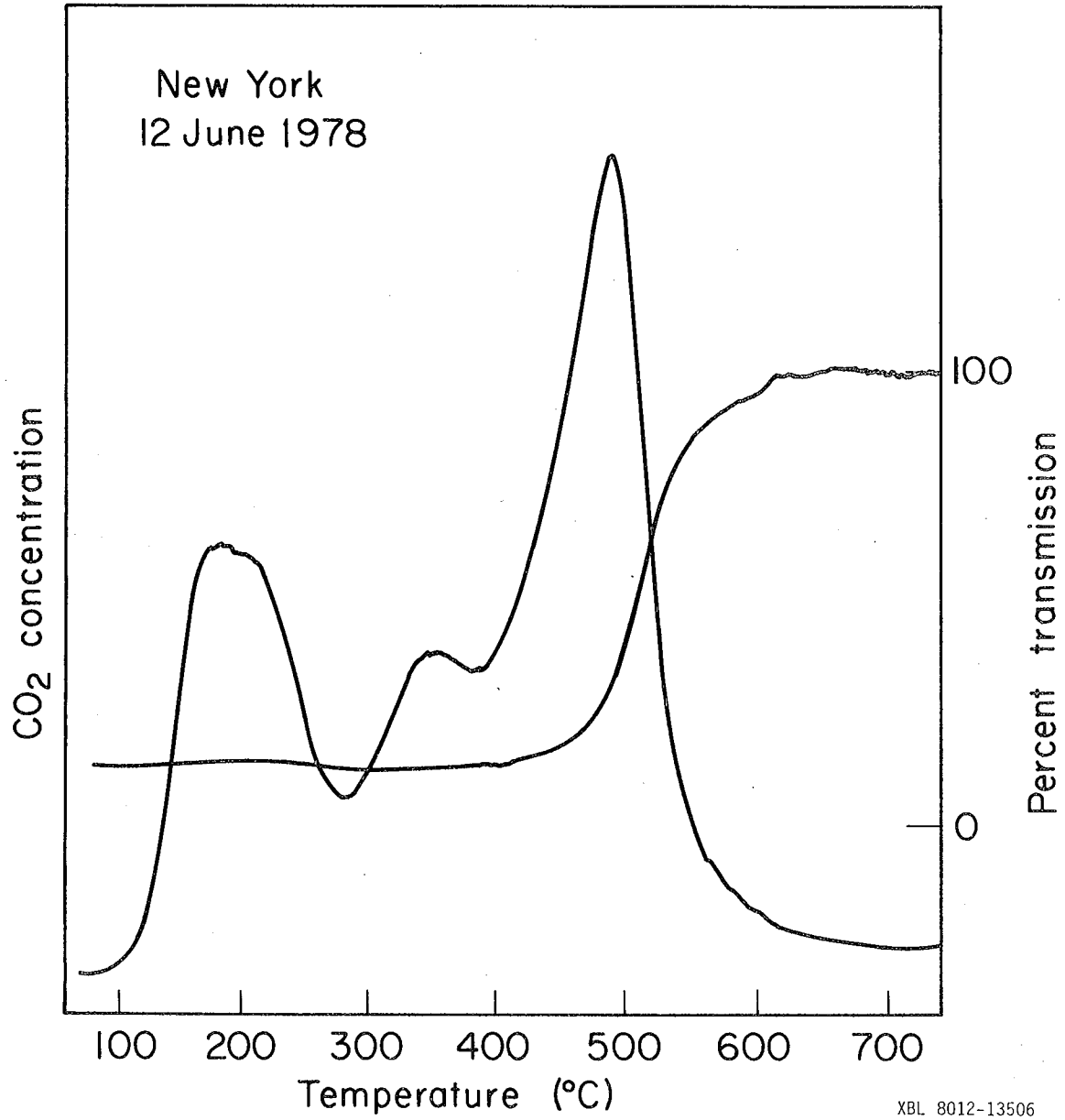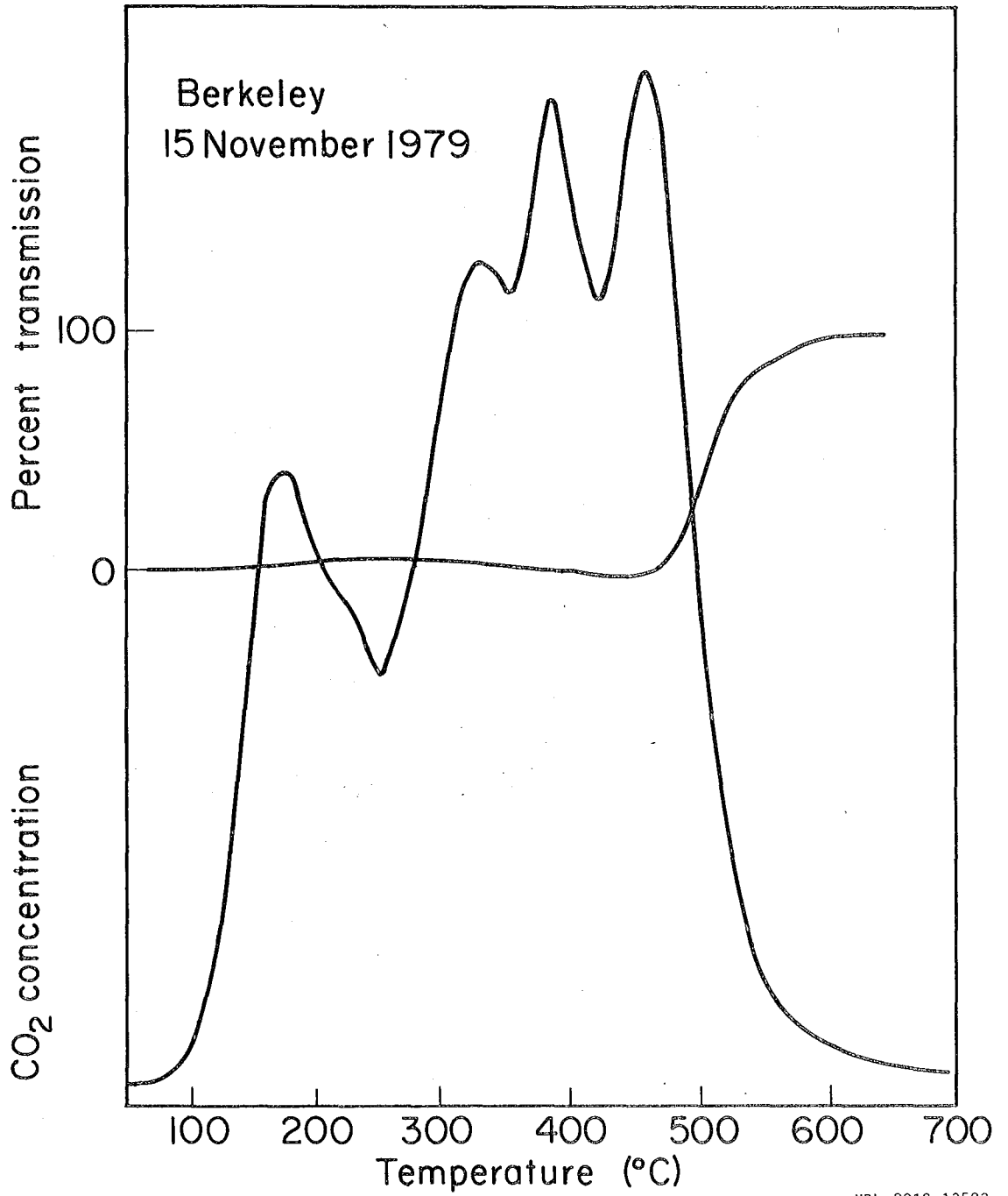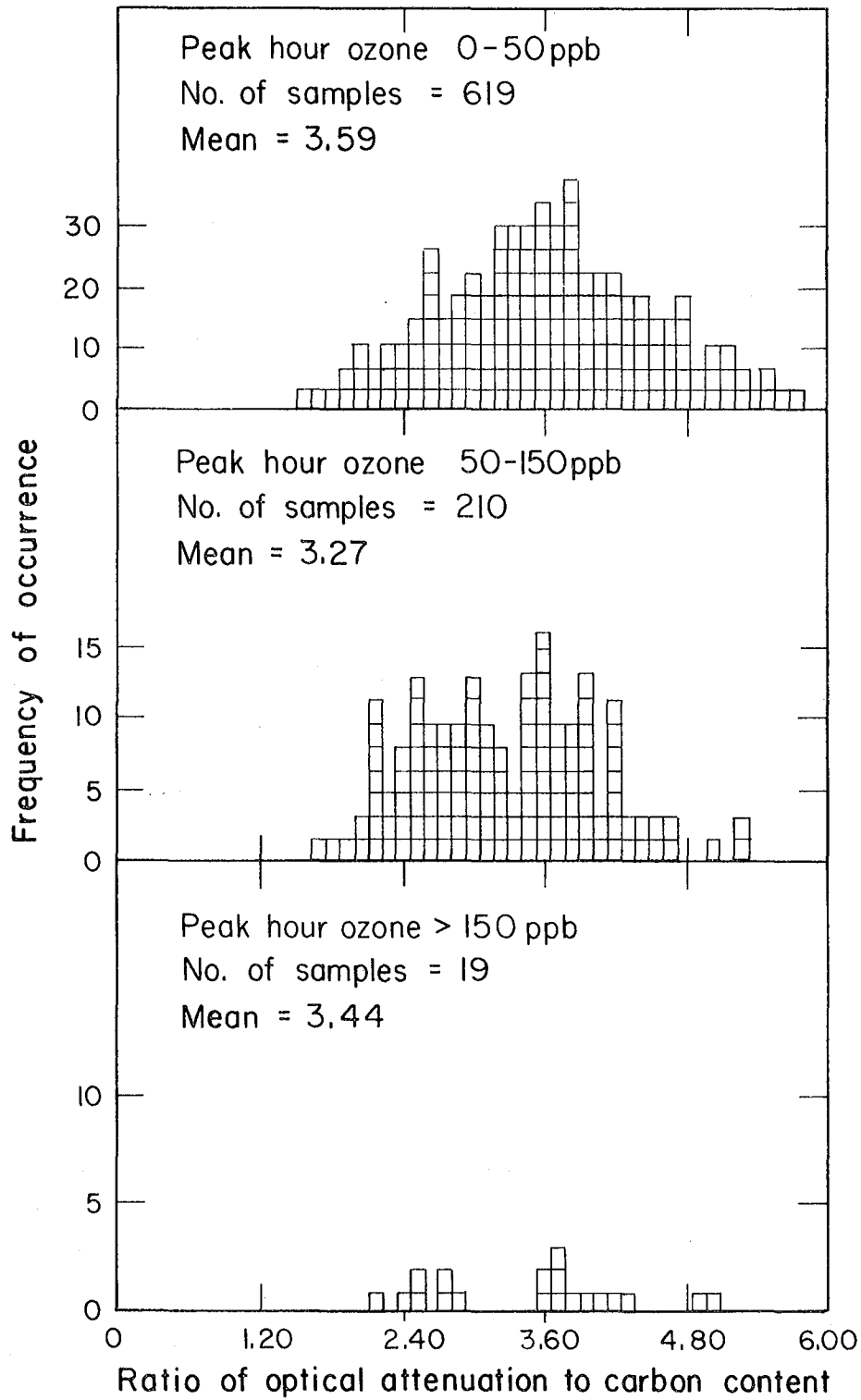
```
   12 %                     Y
      .              .   .  X.
      .              X   X XXXX
      .              XX  X XXXX
      .              XX XX YXXX    X
      .        Y     XXX.XYXXXXXX .XX
      .        Y  .  YYXXXXXXXXXX XXX          .
      .        X XY XXXXXX XXXXX  XXXXX     Y
      .      /   XX XY XXXXXXXXXXXXXXXXX X X
      .     XYX XYXXXYXXXYXXYXXXXXXXXXXXXXXXX X X   X X
      ...........*..........*..........*..........*..........*
      0.       2.00       4.00       6.00       8.00      10.00     ATN/  C
```

XBL 8010-12698

Figure 11

New York
12 June 1978

CO$_2$ concentration

Percent transmission

Temperature (°C)

XBL 8012-13506

Figure 12

Figure 13

Figure 14