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SOOT IN THE ARCTIC

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Abstract

Substantial concentrations of graphitic carbon and its associated large optical absorption coefficient are observed in the Arctic. The graphitic content shows a dramatic increase from late fall to early spring, reaching levels that can be comparable to those found in urban environments.

Recent studies in the Arctic[1,2] show the presence of large aerosol concentrations which significantly affect optical transfer through the atmosphere and lead to the phenomenon of Arctic haze, which was first reported by Mitchell.[3] In particular, the observation of substantial concentrations of particulate sulfur and vanadium at the NOAA-GMCC sampling station near Barrow, Alaska, has attracted considerable attention.[1,2] Questions have been raised as to the anthropogenic character, sources, and climatic impacts of these aerosols. In order to gain a better understanding of these issues, a study of the physical and chemical properties of the carbonaceous aerosol at Barrow was initiated in October, 1979.

Recent studies of the urban aerosol indicate the presence of substantial graphitic carbon concentrations. These graphitic species — identified by a variety of modern analytical techniques (Raman spectroscopy,[4] photoacoustic spectroscopy,[5] thermal analysis,[6] etc.) — are very effective absorbers of visible radiation and are responsible for the high optical absorption coefficients which have recently been observed in urban air.[7,8] The impacts of these highly absorbing particles on a regional or global scale have not been assessed so far, but they could be important, especially over regions with a high surface albedo like the polar icecaps. Furthermore, graphitic carbon can only be produced from combustion processes, and therefore it can offer a very attractive and convenient tracer for anthropogenic activity.

An aerosol sampler was constructed to collect parallel 47-mm quartz fiber and Millipore filter samples at a flow rate of $\sim$ 1.5 cfm. The sampler had two chambers — a lower chamber which contained the pumps and an upper chamber for collecting the aerosol samples. The upper chamber was warmed by several thermostatically controlled heatlamps, while temperature control in the lower chamber was achieved by using a thermostatically controlled fan and

heatlamps. The exhaust of the pumps was vented below the sampling platform. To minimize local contamination, the aerosol sampler was controlled by a wind sensor which was built by the University of Rhode Island group.[1] This allowed samples to be collected only when the wind was from the clean air sector at Barrow, between 0° North and 130° Southeast. Results obtained with and without the wind controller suggest that there is no significant influence from local sources. Approximately 50 filter pairs have been collected at sampling time intervals ranging from 2 days to 1 week. The quartz filters were used to determine the total carbon content of the aerosol by a combustion method,[9] and the Millipore substrate was used to determine the optical absorption coefficient of the aerosol by the LBL laser transmission method described elsewhere.[4,5, 8] The absorption coefficients reported here are consistent with the optical constants of graphitic carbon and are expected to have an accuracy of better than a factor of 2. The Millipore substrate was also analyzed by the X-ray fluorescence technique to determine the concentration of elements with $Z > 11$. The quartz blanks had a carbon loading of $< .5\ \mu g/cm^2$, while typical filter deposits corresponded to $15\ \mu g/cm^2$. Selected filters have been analyzed by Raman spectroscopy, thermal analysis, and solvent extraction techniques. The results of these analyses are described below.

Raman spectroscopy is a highly selective method of analysis which has been used to identify large concentrations of graphitic carbon in urban particulates.[4] This technique has been applied to the analysis of several samples collected at Barrow. The experimental arrangement and methods are described elsewhere.[4] The results are shown in Fig. 1, where the spectrum of an Arctic sample collected in December 1979 is compared to that of urban particulates, various source emissions, and carbon black. All these spectra show the presence of two intense Raman modes located at 1350 and 1600 cm^{-1}, which have been identified as being due to phonons propagating with graphitic planes.[10] This result shows that graphitic structures similar to carbon black and due to combustion processes

are present in the Arctic aerosol. Furthermore, the large intensity in these modes indicates that, just as in urban samples, the graphitic structures represent a major component of the aerosol.

The filters collected at Barrow from fall through late spring have a grey or black appearance similar to that found for urban particulates. For the urban samples, this optically absorbing component has been identified as graphitic carbon.[4] Preliminary measurements on a limited number of samples show that the optically absorbing species in the Arctic has a $1/\lambda$ wavelength dependence, is insoluble in a wide range of solvents, and has a high temperature stability with an oxidation threshold of approximately 500°C. These results are consistent with the properties of graphitic carbon and strongly suggest that indeed the optically absorbing species at Barrow is graphitic in nature.

The seasonal variation of the optical absorptivity (or graphitic carbon concentration) of the Barrow aerosol is shown in Fig. 2. The absorption coefficient changes by more than an order of magnitude from mid-October to early January and remains at a relatively high level throughout most of February, March, and April. It decreases substantially in May. The magnitude of the absorption coefficient during the winter and spring is comparable to that found in urban environments (Table I) (i.e., the peak values in February are only about a factor of 10 less than the average absorption coefficients in New York City and a factor of 3 less than those found in Berkeley, California, and Denver, Colorado). This absorption coefficient is large enough to produce significant optical effects. For example, an absorption coefficient of 5×10^{-6} m^{-1} extended over a pathlength of 10 km would produce an optical thickness of .05. This would be a large perturbation on the transfer of optical radiation through the atmosphere when the sun's irradiance is at a high level, as it is during part of these pollution episodes. In order to assess the importance of these

effects, more detailed measurements of the seasonal variation in the optical properties (visible and infrared) and the vertical and horizontal extent of the aerosols need to be determined.

The pollution episodes observed at Barrow are not a local phenomenon but appear to be areawide with similar seasonal variations occurring at widely spaced sites across the Arctic.[11,12] This is illustrated in Fig. 3, where a comparison of the monthly variations in the blackness of the filter deposits collected at Barrow and Mould Bay, Canada, are shown. (The samples from Mould Bay were provided by Dr. L.A. Barrie and Dr. P. Hoff of the Canadian Atmospheric Environment Service.) These sampling stations are widely separated, yet the initial onset and duration of the episodes observed at these two sites are almost identical.

Using the optical constants of graphitic carbon determined from our urban studies,[13] we can make an estimate of the graphitic carbon concentration at Barrow. These results are shown in Fig. 4, where we plot the graphitic carbon concentration as a fraction of the total carbon content of the aerosol for various periods of time during the year. The results show a strong enrichment of the graphitic fraction of the carbonaceous aerosol from early to late winter. The concentration of graphitic carbon in late February is almost 40% of the carbonaceous mass. Remarkably, this percentage is higher than that found in urban centers like New York City and Los Angeles.[14] After its peak in February, the fraction of graphitic carbon seems to level off to a value which is more typical of those found in urban environments. The interpretation of these interesting features in terms of transport, atmospheric chemistry, and deposition processes is complicated and will have to await more detailed analyses and further measurements.

In summary, these observations indicate that large graphitic concentrations

can develop at remote locations. If one ignores the possible contribution of natural burning processes (e.g., forest fires), which is expected to be small during these times of year in the northern hemisphere, this component can be attributed directly to the burning of fossil fuels. The source and the climatic effects of these highly absorbing species are uncertain and will have to await more systematic measurements and careful modelling.

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Table I.

Site	Date	Number of samples	Average absorption coefficient x 10^5 (m^{-1})	Average total carbon ($\mu g/m^3$)	Average graphitic carbon as percent of total carbon[a]
Barrow, Alaska	12/79-4/80	33	.4	1.2	24
Argonne, Illinois	1/79-3/80	438	2.8	8.1	22
Gaithersburg, Maryland	1/79-3/80	381	2.1	6.1	22
Denver, Colorado	11/78-5/79	141	2.4	9.8	16
Anaheim, California	8/77-1/80	852	4.9	16.6	19
Fremont, California	7/77-3/80	924	3.4	12.0	18
Berkeley, California	6/77-4/80	998	2.1	6.7	20
New York, New York	11/78-4/80	439	6.4	15.2	27

[a]Calculated from optical constants in Ref. 13.

Figure Captions

Figure 1. Raman spectrum of an Arctic sample compared to those of urban particulates, various source emissions, carbon black, and polycrystalline graphite.

Figure 2. Seasonal variations in the optical absorption coefficient in m^{-1} at Barrow from October 1979 to May 1980.

Figure 3. A comparison between the seasonal variation in the blackness of filter deposits collected at Barrow, Alaska, and Mould Bay, Canada, in 1979 and 1980. Mould Bay samples were provided by L.A. Barrie and P. Hoff of the Canadian Atmospheric Environment Service.

Figure 4. Seasonal variation of graphitic carbon as a percentage of the total carbon content of the aerosol at Barrow from October 1979 to May 1980. These values are compared to the average values obtained in New York City and Los Angeles.

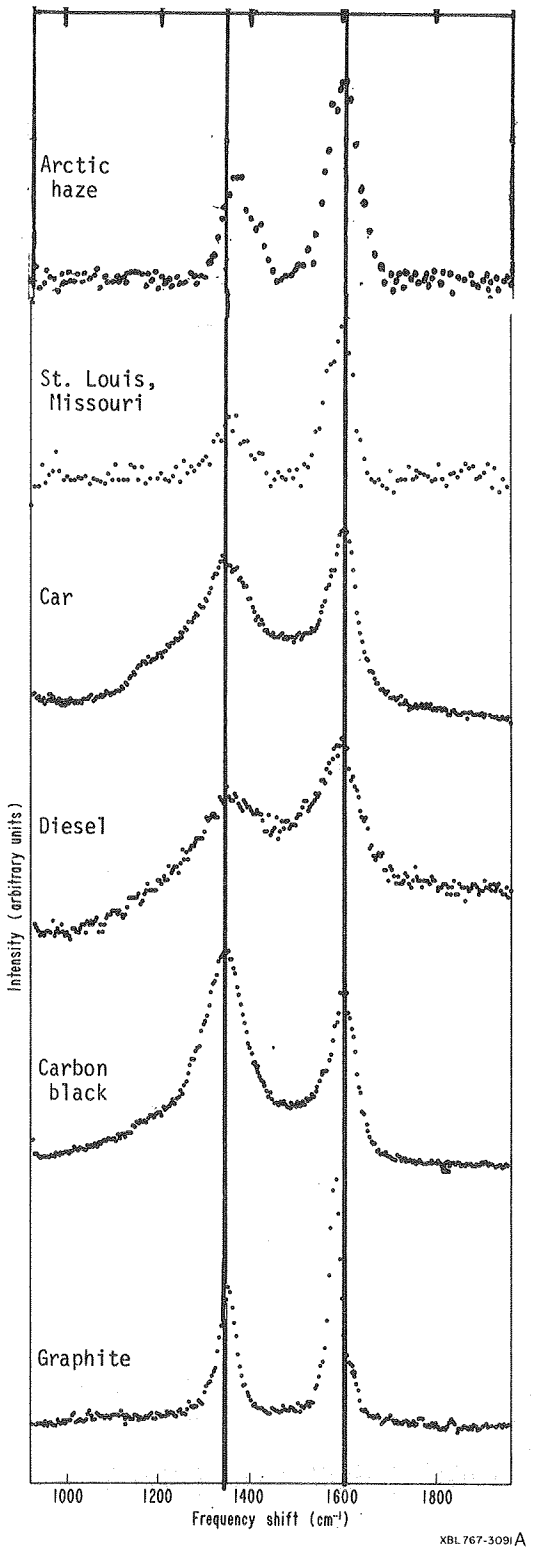
Arctic haze
St. Louis, Missouri
Car
Diesel
Carbon black
Graphite
Intensity (arbitrary units)
1000
1200
1400
1600
1800
Frequency shift (cm⁻¹)
XBL 767-3091A

Figure 1

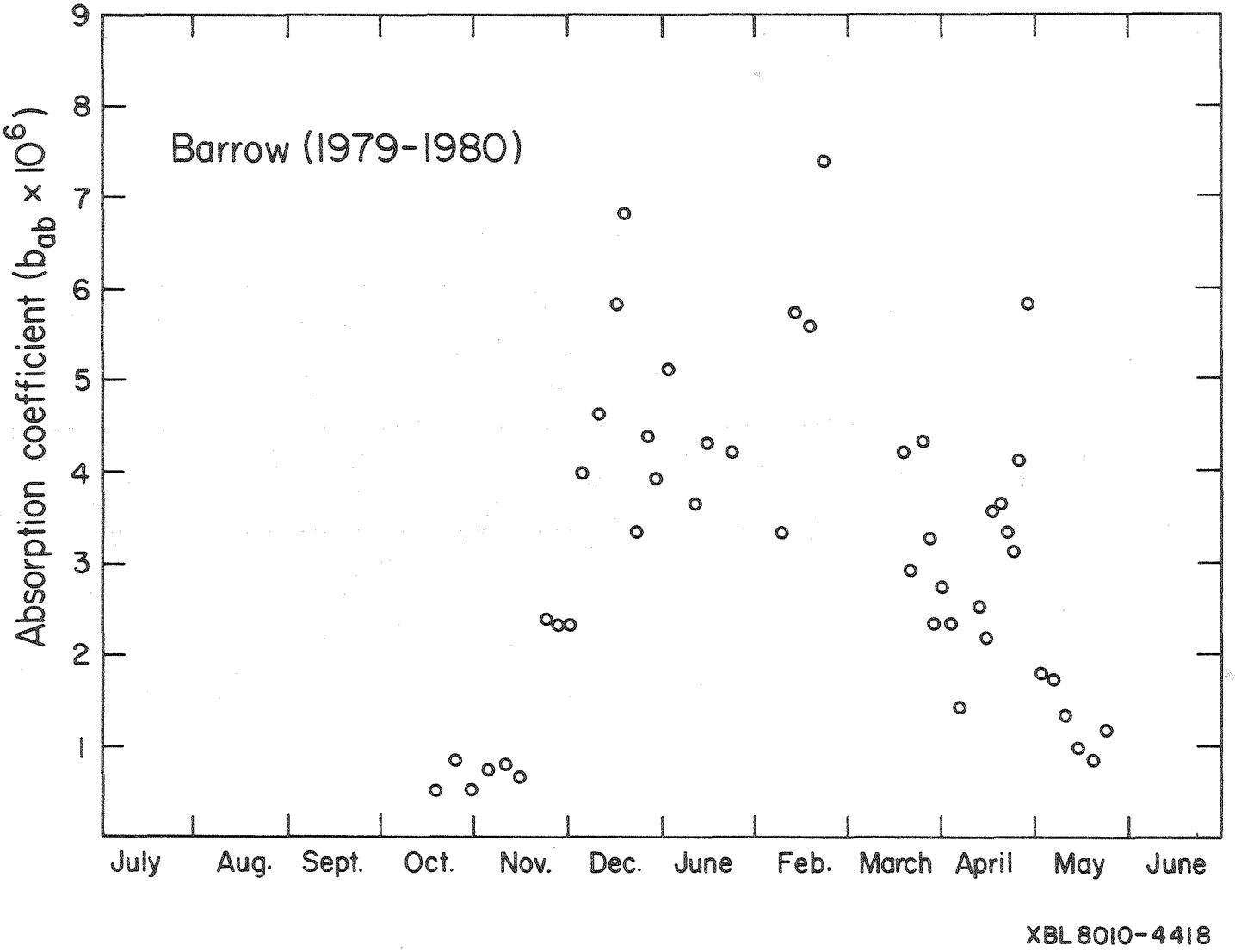
Barrow (1979-1980)
Absorption coefficient ($b_{ab} \times 10^6$)
9
8
7
6
5
4
3
2
1
July
Aug.
Sept.
Oct.
Nov.
Dec.
June
Feb.
March
April
May
June
XBL 8010-4418

Figure 2

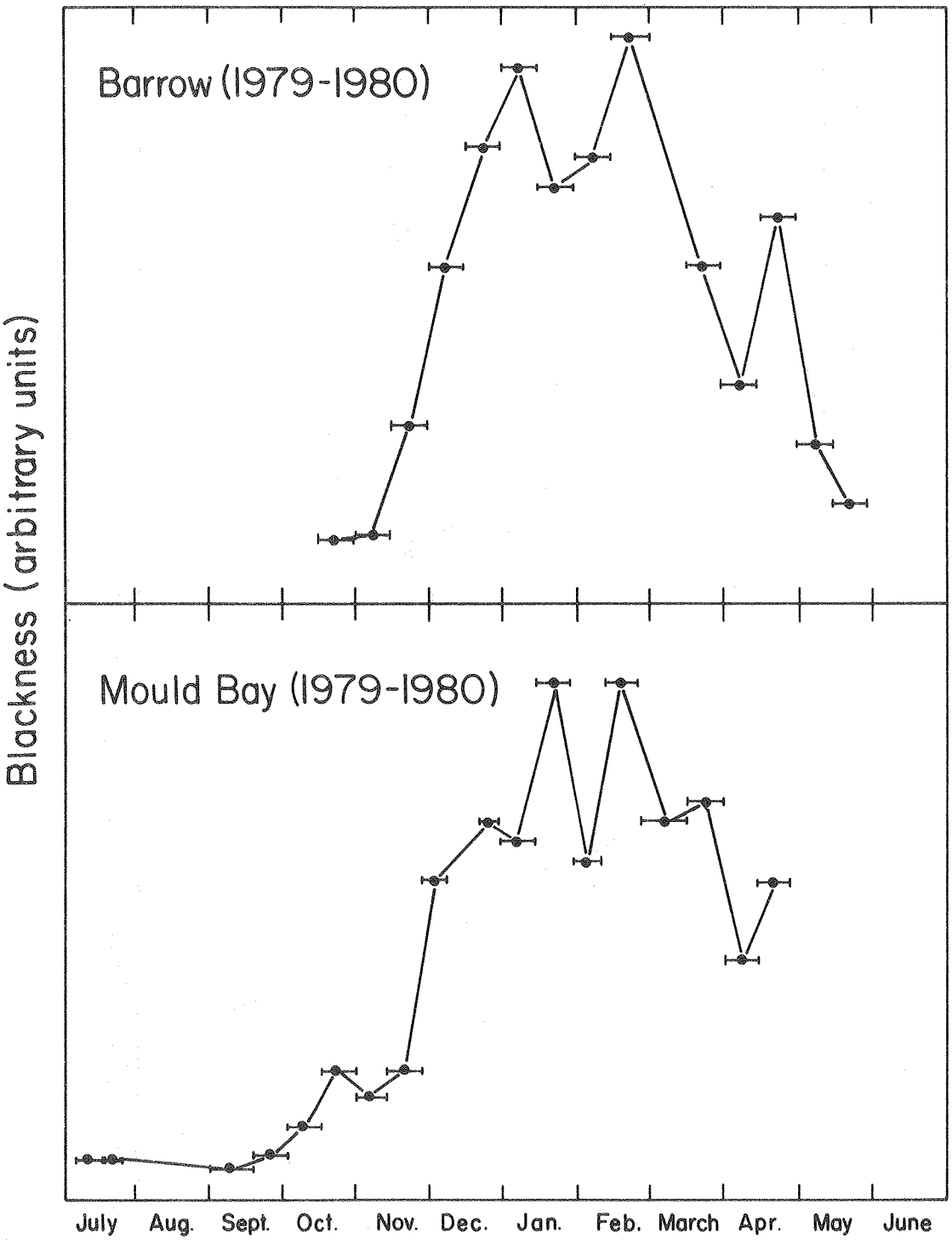

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Figure 3

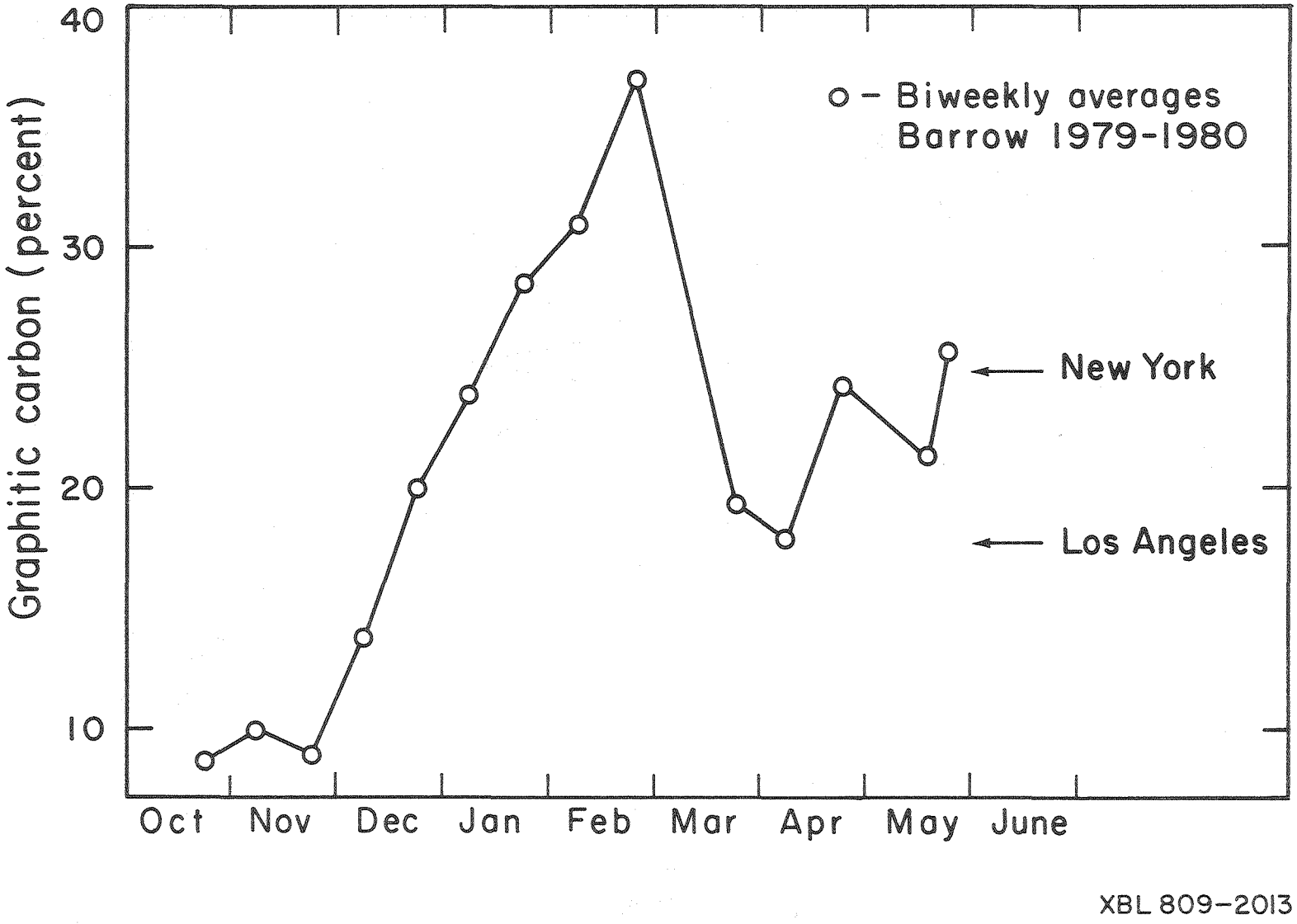

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Figure 4