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CHARACTERIZATION OF AMBIENT AND SOURCE PARTICLES
BY SOLVENT EXTRACTION

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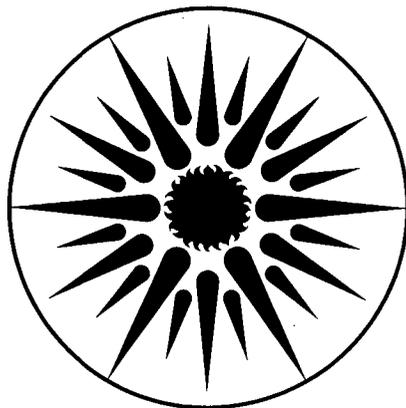
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CHARACTERIZATION OF AMBIENT AND SOURCE PARTICLES BY SOLVENT EXTRACTION*

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Abstract

The selective solvent extraction technique has been applied to source and ambient particulate matter collected during conditions of low photochemical activity. If the extraction technique correctly determines photochemically produced secondary compounds, it should yield very different results for aerosol samples collected during smog episodes than for samples collected during conditions of low photochemical activity. Nonpolar, polar, and unextractable fractions of total carbon from Berkeley and Los Angeles samples are 0.13, 0.37, 0.38 and 0.17, 0.40, $\leq$ 0.44 respectively. The polar to nonpolar ratio is approximately 3:1 for each site. There is no seasonal variation in this ratio for the Berkeley site. Vehicular exhaust and urban samples give comparable fractions of total extractable carbon (volatile + nonpolar + polar), but the polar to nonpolar ratio for these sources is close to 0.6:1. The results indicate that the contribution of ozone-related photochemical processes to production of particulate matter cannot be uniquely identified by application of selective solvent extraction.

Introduction

Ambient carbonaceous aerosols consist of black (or graphitic) carbon and organic material. The latter may be primary or secondary by origin, depending on whether it was directly emitted by sources or produced in the atmosphere by gas-to-particle conversion processes. Black carbon and primary organic species constitute the primary carbonaceous component, i.e., soot (Novakov, 1982). Atmospheric chemical reactions responsible for the formation of secondary organic material are not known with certainty. It has been proposed, however, that they are produced in gas-phase reactions between certain reactive hydrocarbons (especially olefins) and ozone (Grosjean, 1977).

Solvent extraction procedures have been used to demonstrate the photochemical origin of secondary organic species and to assess their contribution to the carbonaceous aerosol fraction. Based on his solvent extraction experiments, Grosjean (1975) concluded that much of the organic aerosol material consists of polar molecules. Appel et al. (1976 and 1979) applied similar techniques to the Los Angeles aerosol in an attempt to assess the relative contributions of primary and secondary carbonaceous matter. In this procedure the concentrations of primary and secondary particulate organics were equated with concentrations of nonpolar and polar compounds, respectively. An upper limit to the elemental carbon concentration was obtained from the difference between total carbon and total organic carbon. If the extraction technique correctly determines photochemically produced secondary carbon compounds, then it should yield very different results for aerosol samples collected during smog episodes in Los Angeles than for those collected in locations or conditions with low photochemical activity.

We have used this technique to characterize urban particulate matter from Berkeley and New York City (collected during low photochemical activity)

and from combustion sources. Results for particulate matter from these urban sites and sources are compared with results for carbonaceous particles sampled in the Los Angeles Basin in 1975 (Appel et al., 1979). What Appel et al. (1976 and 1979) have labelled as primary, secondary, and elemental carbon fractions are here referred to as nonpolar, polar, and unextractable carbon respectively.

Our results obtained from a number of 24-hr samples show that the ratio of polar to nonpolar fractions for typically nonphotochemical situations is similar to that of Los Angeles during episodes characterized by high ozone concentrations. Therefore, it is unlikely that solvent extraction can be used to uniquely determine the contribution of photochemically produced secondary species, or conversely, that other, possibly nonphotochemical, processes also contribute to the gas-to-particle conversion.

Experimental Methods

Particulate material was collected at 40 SCFM by high-volume samplers (Sierra Instruments Model 310R) on quartz fiber filters (Pallflex 2500 QAS) that had been fired at 800°C for 12 hours before use. Filter samples were wrapped in Al foil, manila envelopes, and plastic bags for storage at -5°C.

Twenty-nine 24-hr samples were collected at two sites in Berkeley between December 1977 and November 1979. One sampler was at the Lawrence Berkeley Laboratory (LBL), on a hillside above the city; and the other sampler was across from a major freeway that runs along the San Francisco Bay. Average total carbon loadings were 8 and 15 $\mu g\ m^{-3}$ for the LBL and freeway sites respectively. Two 24-hr hi-vol samples were collected in New York City during February 1978, with an average total carbon loading of 11 $\mu g\ m^{-3}$.

Samples were also collected in the Caldecott Tunnel (a highway tunnel) and in a parking garage to sample fresh vehicle exhaust. Emissions from a

small, idling diesel passenger bus were sampled by hi-vol sampler. Particulate matter from a natural gas boiler was sampled by suspending the hi-vol sampler above the boiler stack and operating it only while the burner was on. For sources, the sampling time was adjusted to give loadings in the range of 30-50 µg C cm^{-2}.

We have followed the procedure of Appel et al. (1977 and 1979) to determine the total amount of recoverable organic carbon in filter samples as the sum of the carbon content of the benzene and methanol-chloroform extracts per cm^2 of filter. Amounts of nonpolar carbon are obtained from the carbon content of cyclohexane extracts per cm^2 of filter. Amounts of polar carbon are determined from the difference between amounts of recoverable organic carbon and nonpolar carbon. While Appel et al. (1975, 1977, and 1979) calculated upper limits to the elemental carbon concentration as the difference between total carbon and recoverable organic carbon, we define the upper limits to the elemental carbon concentration as the amounts of unextracted carbon per cm^2 after benzene, methanol-chloroform extraction. Amounts of volatile carbon are obtained from the difference between total carbon and the sum of recoverable organic carbon and unextractable carbon as discussed below.

The Soxhlet extraction and carbon determination procedures were essentially the same as those used by Appel et al. (1977 and 1979). Using spectroquality solvents, one quarter of each filter was extracted in cyclolexane, while another quarter was extracted in benzene. The benzene-extracted filter was further extracted in a methanol-chloroform (1:2 v:v) mixture the next day. Extraction time was 6 hours for each step. Cycling time was 15 minutes. The three extracts were concentrated to 10 ml, and 1 ml of each was allowed to evaporate to dryness before carbon determination by combustion

(Mueller et al., 1972). Carbon content was also determined in the untreated filter and its extracted portions. Determination of the carbon content of the extracted pieces is an addition to the analytical procedure that permits comparison of the extract's carbon content with the carbon lost by the filter during the extraction step.

To monitor possible removal of insoluble particles during extraction, optical attenuation measurements were also performed on some of the filter samples, before and after extraction. The technique and apparatus have been described elsewhere (Rosen et al., 1978). The amount of black (elemental or graphitic) carbon in particulate samples has been shown (Rosen et al., 1978; Yasa et al., 1979; Gundel et al., 1981) to be proportional to the optical attenuation, which is defined as 100 ln I_0/I, where I_0 and I are the intensities of helium-neon laser light transmitted through blank and loaded filters respectively.

Results

Physical loss of particles from filters during extraction may be a source of error in measuring amounts of unextracted carbon. Optical attenuation measurements of the filter samples before and after extraction showed that cyclohexane and benzene extraction do not affect the attenuation values for a group of 8 source and 10 ambient filter samples. The methanol-chloroform extraction step leads to an average decrease of 8% in attenuation values for the ambient samples, which represents a physical removal of 3% of the total carbon. No such effect was observed for the source samples. Therefore, loss of nonsoluble particles during extraction does not appear to constitute a significant problem in use of the selective solvent extraction technique. No corrections for particle loss have been applied to the results of this study.

Cyclohexane and benzene extracts of ambient and source particles contain less carbon than has been removed from the filters during extraction. For both cyclohexane and benzene, the carbon loss is 13% of the total carbon for ambient particles and somewhat higher for combustion source samples (garage and tunnel, 15%; diesel, 73%). This carbon deficiency is not due to particle loss but may be accounted for by the escape of volatile compounds during extraction and evaporation of solvent from the extracts prior to carbon determination. Because the loss of nonpolar compounds is partly offset by a slight ($\sim$ 3% of total carbon for all samples) excess carbon content in the polar extracts, we define the concentration of volatile carbon as the difference between total carbon concentration and the sum of the concentration of organic (nonpolar + polar) and unextracted carbon. Volatile carbon accounts for approximately 10% of the total carbon for Berkeley-LBL, New York City, tunnel, and garage samples. The natural gas boiler particles sampled here contain no volatile carbon.

Evidence collected by Dod et al. (1980) shows that volatile carbonaceous compounds are adsorbed onto glass or quartz fiber filters from the gas phase. When ambient air is drawn at 20 SCFM for 24 hours through two prefired quartz or glass fiber filters arranged in series without physical contact, the second or downstream filter has a carbon content of 10-15% of the total carbon content of the particulate-laden filter (Dod et al., 1980). High-volume sampling at 40 SCFM with two quartz filters in the filter holder shows similar effects. Extraction of the back-up hi-vol filter by cyclohexane or benzene removes about 70% of the adsorbed material, but very little ($\sim$ 5%) of total carbon is recovered in the extract. These results suggest that volatile compounds adsorbed onto the filter material during sampling may account for at least part of the carbon lost during extraction.

Appel et al. do not find volatile carbon as defined above in urban filter samples for which this laboratory finds typical amounts (Gundel and Appel, 1982). The difference appears because Appel et al. recover slightly more carbon in the cyclohexane extracts than has been removed from the filters during extraction. The same methods applied in different laboratories appear to affect volatile compounds somewhat differently.

We have applied the selective solvent extraction method to 29 particulate-laden 24-hr hi-vol filters collected at the two Berkeley sampling sites between December 1977 and November 1979 and to 2 filters collected in New York City in February 1978. The results are shown in the top half of Fig. 1 and in Table 1. For comparison, results obtained by Appel et al. (1977 and 1979) from 12 14-hr hi-vol filters collected at three locations in the Los Angeles Basin are also shown. These samples were collected during four days of a photochemical episode in July 1975. Average ozone concentrations were 20, 25, and 240 ppb for Berkeley-LBL, Berkeley-freeway, and Los Angeles respectively.

Data are presented for volatile, nonpolar, polar, and unextractable carbon as fractions of the total carbon content. These fractions are similar for particulate matter collected during periods of both low and high ozone concentration. Nonpolar, polar, and unextractable fractions from extractions of Berkeley-LBL and Los Angeles samples are 0.13, 0.37, 0.38, and 0.17, 0.40, $\leq$ 0.44 respectively. Aerosol particles collected in both areas have roughly three times as much polar as nonpolar carbon; more than a third of the carbon is insoluble.

Particulate material collected close to a heavily used freeway in Berkeley contains a higher nonpolar carbon fraction than does the more aged particulate material collected at the LBL site. The polar to nonpolar ratio is 1:1. Results for winter New York City samples are qualitatively similar to

the freeway samples. They both contain a larger fraction of unextractable carbon than other California samples. No seasonal variations in nonpolar, polar, or unextractable carbon fractions are observed in Berkeley particulate material (Fig. 2). The Berkeley-LBL results are insensitive to the total carbon loading because there is no significant difference between extraction data for particles collected under clear ($\leq$ 6 μg C m^{-3}) and hazy ($\geq$ 15 μg C m^{-3}) conditions.

The vehicular exhaust samples (tunnel and garage) contain particulate matter with more nonpolar than polar carbon (Table 1 and lower half of Fig. 1). The nonpolar fraction is significantly larger for these particles than for Berkeley-LBL, Los Angeles, and New York City aerosols. The polar to nonpolar ratio is close to 0.6:1 for these sources, compared to approximately 3:1 for urban sites. Unextractable carbon levels are comparable for urban site, tunnel, and parking garage particles (38-55%). Natural gas soot contains mostly unextractable carbon (81%), while diesel bus samples contain mainly volatile carbon.

Conclusions

We have found that the organic particles from New York City and from Los Angeles and Berkeley, California, are very similar when characterized in terms of polar and nonpolar components by the selective solvent extraction - carbon analysis technique. Photochemical activity, as indicated by ozone level, was much less intensive in Berkeley and New York City than in Los Angeles, although fractions of polar and nonpolar carbon are very similar for the two locations. Although ambient particulate carbon collected under nonphotochemical conditions is similar to the particulate carbon collected during a photochemical episode, both differ from sources when characterized by selective solvent extraction. Automotive and diesel primary combustion

particles differ from ambient particles by enrichment in amounts of nonpolar carbon; however, significant fractions of polar carbon are also associated with all combustion sources here, which means that the polar fraction of ambient carbonaceous particles cannot be entirely secondary in origin.

Because Berkeley-LBL and Los Angeles organic particulate matter are similar, the contribution of ozone-related photochemical processes to production of particulate matter cannot be uniquely identified by application of selective solvent extraction. The fact that ambient particulate material from all locations contains larger fractions of polar organic carbon than combustion source particles do suggests that other transformation processes may exist in addition to photochemical gas-to-particle conversion.

Acknowledgments

References

Appel B.R., Colodny P. and Wesolowski J.J. (1976) Analysis of carbonaceous materials in southern California atmospheric aerosols. Envir. Sci. Technol. 10, 359-363.

Appel B.R., Hoffer E.M., Haik M., Wall S.M., Kothny E.L., Knights R.L. and Wesolowski J.J. (1977) Characterization of organic particulate matter. Final Report to California Air Resources Board, Contract No. ARB 5-682, NTIS Report PB 279 209/1 WP.

Appel B.R., Hoffer E.M., Kothny E.L., Wall S.M., Haik and Knights R.L. (1979) Analysis of carbonaceous material in southern California atmospheric aerosols, 2. Envir. Sci. Technol. 13, 98-104.

Dod R.L. et al. (1980) Investigations of sampling artifacts in filtration collection of carbonaceous aerosol particles. Atmospheric Aerosol Research, FY 1979, pp. 35-37, Lawrence Berkeley Laboratory report LBL-10735, Berkeley, California.

Grosjean D. (1975) Solvent extraction and organic carbon determination in atmospheric particulate matter: The organic extraction-organic carbon analyzer (OE-OCA) technique. Anal. Chem. 47, 797-805.

Grosjean D. (1977) Aerosols. Ozone and Other Photochemical Oxidants, pp. 45-123, Ch. 3, National Academy of Sciences-National Research Council, Committee on Medical and Biological Effects of Environmental Pollutants, Washington, D.C.

Gundel L.A. and Appel B.R. (1982) Unpublished interlaboratory comparison study.

Gundel L., Dod R. and Novakov T. (1981) Determination of black carbon by thermal analysis. Environmental Pollutant Studies, pp. 26-30, Lawrence Berkeley Laboratory report LBL-11986, Berkeley, California.

Mueller P.K., Mosley R.W. and Pierce L.B. (1972) Chemical composition of

Pasadena aerosol by particle size and time of day, IV, Carbonate and noncarbonate carbon content. J. Colloid Interface Sci. 39, 235–239.

Novakov T. (1982) Soot in the atmosphere. Particulate Carbon: Atmospheric Life Cycle, pp. 19–37 (G.T. Wolff and R.L. Klimisch, eds.), Plenum, New York.

Yasa Z., Amer N.M., Rosen H., Hansen A.D.A. and Novakov T. (1979) Photoacoustic investigations of urban aerosol particles. Appl. Opt. 18, 2528–2530.

Table 1. Selective solvent extraction results for ambient and source carbonaceous aerosols. Data presented as fractions of total carbon

	Volatile[a]	Nonpolar[b]	Polar[c]	Unextracted[d]	Number of samples	$[O_3]$ ppb
Urban particulate matter						
Berkeley, LBL	0.11±.08	0.13±.03	0.37±.08	0.38±.07	22	20
Berkeley freeway	0.04±.07	0.21±.04	0.26±.07	0.49±.08	7	25
New York City	0.09±.03	0.10±.03	0.26±.06	0.55±.01	2	— [e]
Los Angeles	— [e]	0.17±.02	0.40±.05	≤0.44±.05[f]	12	240
Source particulate matter						
Highway tunnel	0.10±.09	0.32±.04	0.17±.04	0.41±.05	6	—
Parking garage	0.11±.01	0.23±.04	0.19±.12	0.46±.08	3	—
Diesel bus	0.70±.08	0.17±.10	0.11±.02	0.02±.00	2	—
Natural gas boiler	0.00±.00	0.09±.04	0.10±.05	0.81±.06	3	—

[a] Volatile C = carbon fraction 1 - (nonpolar + polar + unextracted)

[b] Fraction of total carbon in cyclohexane extracts

[c] Fraction of carbon extracted by benzene and methanol-chloroform mixture — nonpolar (cyclohexane-extract) fraction

[d] Fraction of carbon remaining on filters after extraction

[e] Not available

[f] Fraction of total carbon not recovered in benzene and methanol-chloroform extracts (from Appel, 1977). This is an upper limit to the unextracted fraction.

Figure Captions

Figure 1. Selective solvent extraction results for carbonaceous particles
collected from urban sampling sites and from combustion sources. The
number in parentheses below the site or source label represents the
number of filter samples analyzed. Error bars represent standard
deviation. Los Angeles data are taken from Appel (1977 and 1979).(XBL 818-1252)

Figure 2. Variation in fractions of nonpolar and polar carbon during one
year for particulate matter collected in Berkeley, California.
(XBL 818-1110)
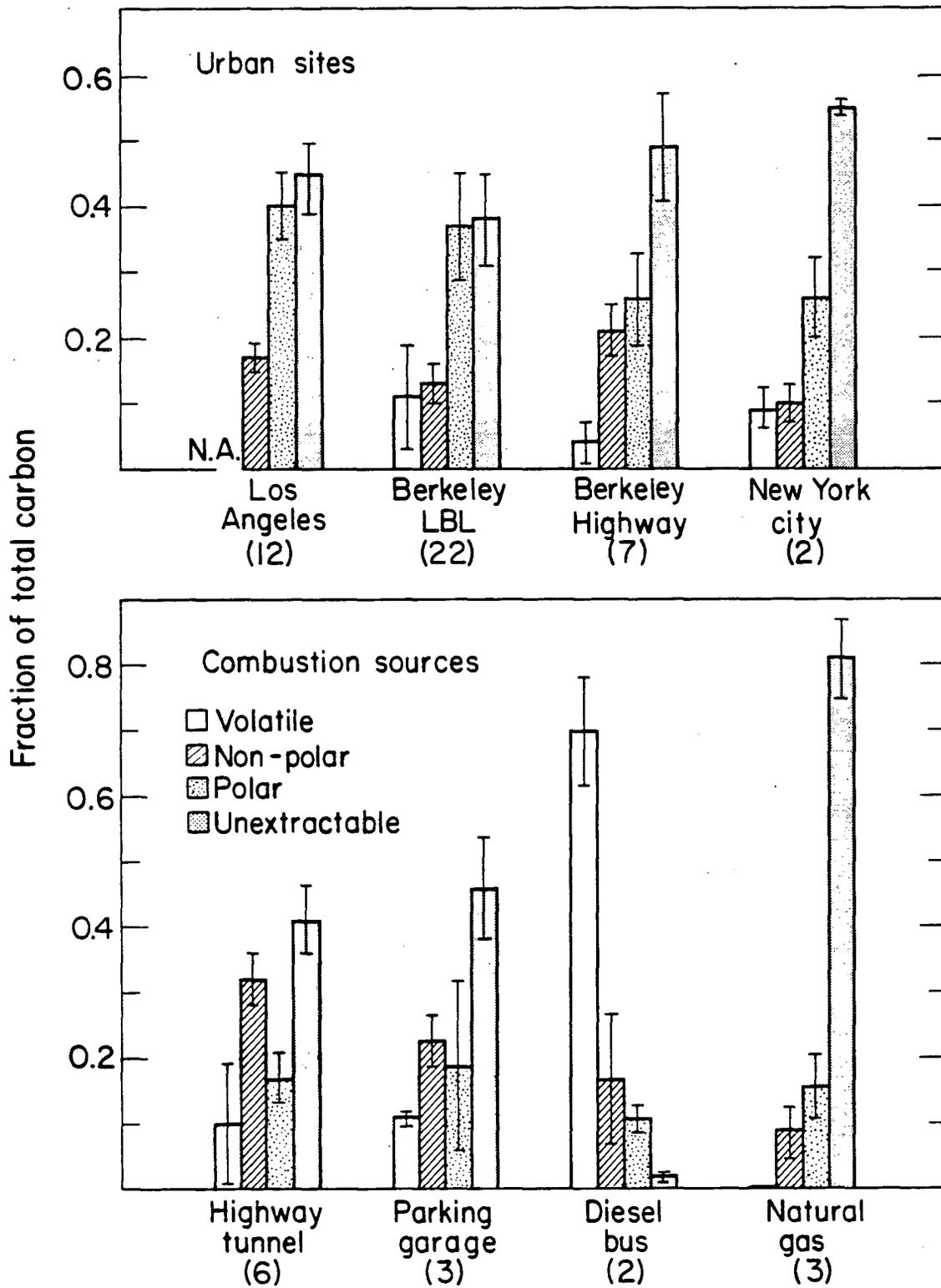
Figure 1

XBL 818-1252

BERKELEY(LBL) CARBONACEOUS PARTICLES

Figure 2

XBL 818-1110