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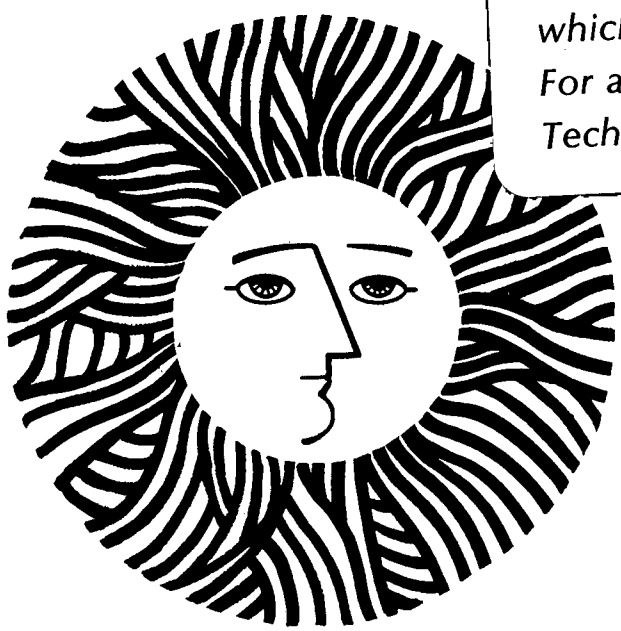

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DISCLAIMER

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ABSTRACT

Introduction

Carbonaceous particles in the atmosphere contain graphitic or black carbon in association with organic compounds. Particulate organic material is labelled primary when its origin is direct emission from combustion sources. Secondary particulate organic material may be gaseous when it is emitted into the atmosphere but subsequently reaches the particulate phase through transformation processes.[1] Black carbon plays a significant role in the physics and chemistry of atmospheric aerosols because of its optical absorptivity, adsorption capacity, and surface characteristics. These properties affect the composition and chemical behavior of the associated organic material.

Characterization of Carbonaceous Aerosols

Gas chromatographic and mass spectral studies[2-4] indicate that particulate organic material contains unburned and partially oxidized fuel hydrocarbons, polynuclear aromatic hydrocarbons, and polyfunctional oxygenated compounds which may be formed in the atmosphere by reactions of hydrocarbons with atmospheric or pollutant gases. This is not an exhaustive list.

We characterize carbonaceous aerosols using combustion evolved gas analysis (thermal analysis) with simultaneous optical attenuation measurements[5] and selective solvent extraction.[6-8] Thermograms of urban aerosols typically exhibit three broad peaks when evolved CO_2 concentration is plotted versus heating temperature. Sample thermograms are shown in Figure 1. The low temperature peak represents combustion of primary organic material; part of the middle peak represents the combustion of secondary organic material. Primary and secondary classifications are based on an operational definition from solvent extraction studies.[6] The high temperature peak represents combustion of some secondary carbon in addition to the combustion of optically absorbing black carbon.[8] Thermograms of extracted filter samples are used to measure concentrations of black carbon in urban and combustion-source particulate matter.[9] The thermal analysis technique is also used as a tool in chemical studies of the role of black carbon in the chemistry of carbonaceous aerosols.

Our field and characterization studies indicate that 1) the ratios of secondary to primary carbon in urban particulate matter are similar for samples collected in Berkeley, Los Angeles, and New York City, irrespective of the level of photochemical activity at the sampling sites[7]; and 2) the fraction of black carbon to total carbon in urban carbonaceous particles is approximately constant, independent of sampling location or time of year.[10]

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Black Carbon in Atmospheric Particles

The graphitic structure of black carbon is responsible for its large optical absorptivity.[11,12] The micron and submicron size range of atmospheric particles also affects the optical properties of black carbon.[11] The heating of carbonaceous particles by light absorption may influence the chemical composition and reactivity of particulate organic material which is associated with black carbon. We have studied the volatilization of primary organic material when ambient particles on filter substrates are exposed to sunlight. Loss of primary organics appears to be related to enhanced heating in the presence of black carbon.

The adsorption capacity of model black carbons (carbon black and activated carbon) is due to their porosity, surface area, aromatic electronic structure, and to partial surface oxidation.[13] Nonpolar compounds adsorb by interaction with the aromatic structure of these model black carbons. Polar compounds adsorb by interaction with carbonyl, hydroxyl, and related oxygenated functional groups on the surface of activated carbons. The possibilities for hydrogen bonding and ionic interactions in the presence of water enhance the ability of activated carbons to remove polar organic compounds from solution.[13] Our work on the characterization of source and ambient particles indicates that atmospheric black carbon has adsorption properties which parallel those of model black carbons. Primary organics display nonpolar adsorption behavior, while secondary organics interact more strongly with black carbons. Surface oxidation of black carbon may be responsible for this effect.

Model black carbons have been shown to catalyze several kinds of organic reactions[14-16] which may occur in combustion plumes or in the atmosphere. Preliminary studies in our laboratory indicate that aromatic aldehydes can be oxidized to acids in the presence of activated carbon or kerosene soot and water. Other workers have shown that activated carbon catalyzes the oxidation of benzoyl peroxide[15] and of cyclohexene.[16] Surface oxygen complexes on the carbon substrate are involved in the oxidation mechanism for these types of reactions.[13] If similar reactions occur in the atmosphere, they may contribute to transformation processes which generate secondary organic particulate material.

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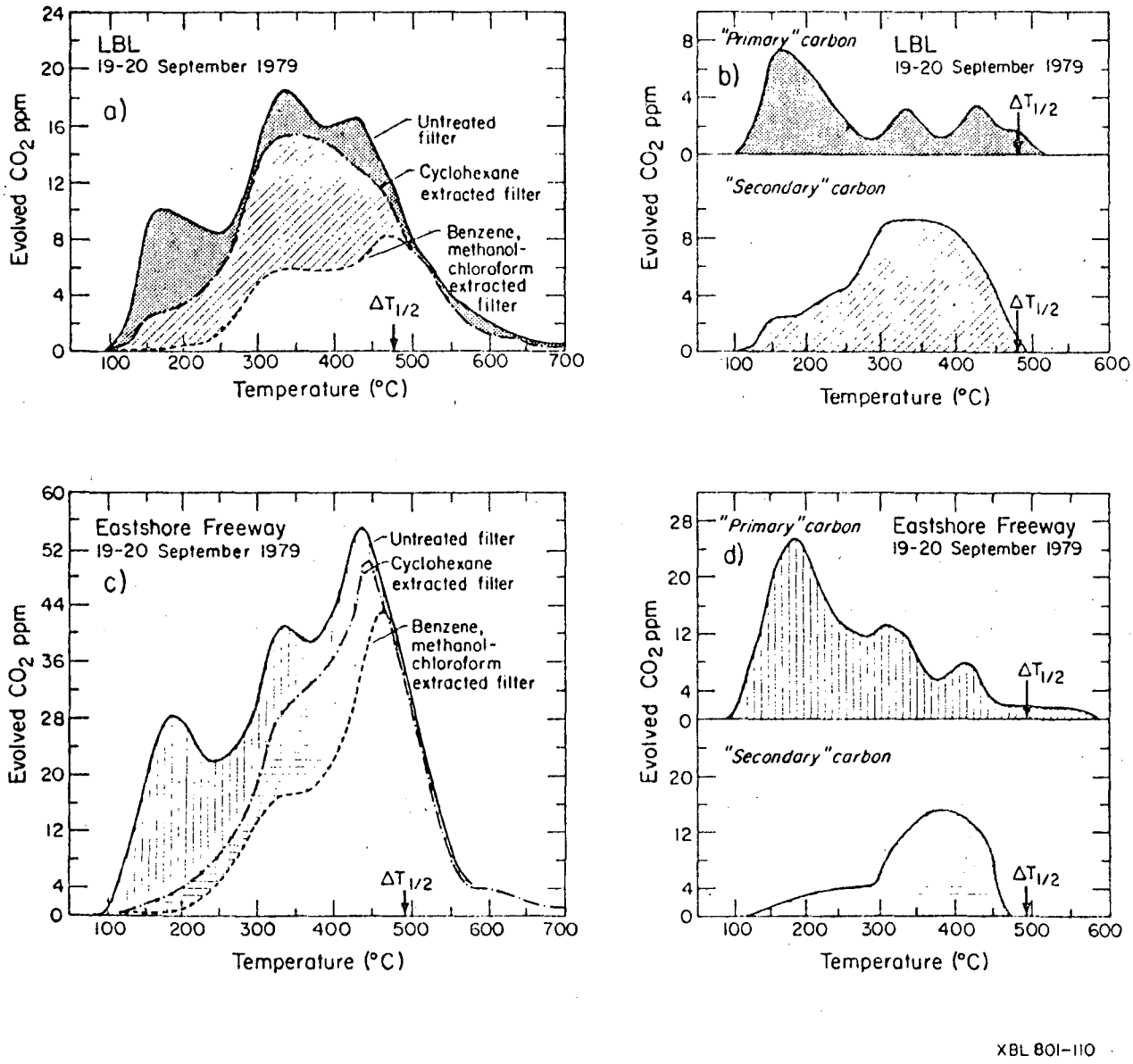

Figure 1. Thermal analysis results for particulate matter collected at two sites in Berkeley, California. The temperature midpoint in the optical transmission change is indicated as ΔT 1/2.

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