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Visibility-reducing organic aerosols in the vicinity of Grand Canyon National Park: Properties observed by high resolution gas chromatography

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Abstract. Fine particle and total airborne particle samples were collected during August 1989 within the Grand Canyon (Indian Gardens (IG)) and on its south rim (Hopi Point (HP)) to define summertime organic aerosol concentration and composition as a function of elevation at Grand Canyon National Park. Inorganic chemical constituents were analyzed also to help place the relative importance of organics in perspective. Fine particle organic aerosols were approximately equal in concentration to sulfate aerosols at both sites. Monthly average mass concentrations for fine aerosol organics ranged from 1.1 μg m^{-3} (IG) to 1.3 μg m^{-3} (HP), while the organic aerosol concentration within total suspended particulate matter samples ranged from 1.9 μg m^{-3} (IG) to 2.1 μg m^{-3} (HP). Aerosol organics that could be evaluated by gas chromatography with flame ionization detection (GC-FID) (elutable organics) constituted 27% to 53% of the total organics mass collected as fine or total aerosol. At each site, roughly half of the elutable organics fine aerosol fraction was composed of highly polar organic compounds. Distributions of the elutable organics were compared to Los Angeles fine aerosol samples and to distributions of authentic sources of aerosol organics. It was found that the Grand Canyon organic aerosol during August 1989 did not resemble diluted aged Los Angeles organic aerosol, indicating that most of the organic particulate matter at the Grand Canyon at the time studied originated from other sources.

Introduction

Sulfates and carbonaceous aerosols are the largest contributors to the fine particle burden in the atmosphere near Grand Canyon National Park. While the effects of sulfate particles on visibility at the Grand Canyon have been studied extensively, much less is known about the nature and origin of the carbonaceous aerosols that are present [*Trijonis et al.*, 1990]. This disparity in understanding arises from at least two causes: (1) aerosol carbon data for the region are less plentiful, and (2) many of the sources that could contribute to that organic aerosol are both diverse and not well characterized. Measurement programs have been conducted over the past 20 years in remote desert regions of the southwestern U.S. (inclusive of the Grand Canyon) to further understand the role of airborne fine carbonaceous particles in visibility reduction [*Malm et al.*, 1994; *Committee on Haze in National Parks and Wilderness Areas and National Research Council*, 1990; *White and Macias*, 1989; *Macias et al.*, 1980, 1981a, b; *Tombach et al.*, 1985; *Macias and White*, 1985; *Trijonis et al.*, 1988; *Ouimette and Flagan*, 1982; *Saxena et al.*, 1995; *Vasconcelos et al.*, 1994, 1995; *McMurry et al.*, 1995; *Turpin et al.*, 1996]. For the most part, these field studies did not provide detailed organic chemical composition data needed to describe the origin of fine aerosol carbon but instead focused on bulk carbon ambient mass concentrations. One preliminary investigation was conducted on the origin of the organic aerosol at the Grand Canyon using molecular tracer methods [*Mazurek et al.*, 1991]. In that study, routine filter samples supplied by the SCENES air-monitoring network were examined. Evidence of plant waxes plus significant wood smoke input to the aerosol was observed both during the winter when wood was used for heating and during a summer period when forest fires were known to have occurred. However, the motor vehicle exhaust contribution to the aerosol could not be determined because analysis of SCENES network field blanks showed the presence of petroleum grease components [*Mazurek et al.*, 1988, 1991].

The organic aerosol data related in the present paper arise from a subsequent study of the origin of the carbonaceous aerosol at Grand Canyon National Park that is based on molecular tracer techniques which are applied to source and ambient samples collected specifically for this purpose. During the summer of 1989 an air-monitoring program was established both within the Grand Canyon and on its south rim to define summertime organic aerosol concentration and composition as a

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function of elevation in the canyon. Supporting information was collected on the composition of the inorganic portion of the atmospheric aerosol to help place the relative importance of the organics in perspective.

Aerosol carbon samples were analyzed by thermal evolution and combustion for elemental carbon (EC) and organic carbon (OC), by high-resolution gas chromatography with flame ionization detection (GC-FID), and by gas chromatography/mass spectrometry (GC/MS). In the present paper we report results of the EC/OC and GC-FID analysis of the ambient samples. Key information is developed relating to the quantity of polar organic compounds present in the airborne particulate matter. The patterns of elutable solvent-soluble organic species that result from our GC-FID analysis procedure are compared quantitatively to the patterns present in the elutable organics extracted from Los Angeles area fine particle ambient samples and from authentic emission source samples (e.g., motor vehicle exhaust) that we have examined previously using identical sampling and analytical procedures [*Mazurek et al.*, 1987, 1989; *Hildemann et al.*, 1991a, b, 1993, 1994b; *Rogge et al.*, 1993c, d, e; *Simoneit et al.*, 1993]. The interest in polar organics arises from their hygroscopic character and hence their ability to enhance light scattering and visibility reduction via incorporation of water into the aerosol. Comparison against the Los Angeles organic aerosol is sought in an effort to determine whether the Grand Canyon aerosol resembles long-distance transport of aged organics from cities like Los Angeles. In subsequent work using molecular marker techniques, the GC/MS analysis of samples from this experiment will be used to further identify the sources that contribute to organic aerosols at the Grand Canyon.

Ambient Sample Collection

Two monitoring sites were established at different elevations in Grand Canyon National Park: (1) Hopi Point on the south rim of the canyon, and (2) Indian Gardens, within the canyon itself. Indian Gardens is located at an elevation of about 3800 feet (1180 m) in the Upper Sonoran Zone of the canyon, on the Tonto Plateau, in an area containing scrub brush blending into Pinyon-Juniper woodland above [*Whitney*, 1982]. Hopi Point is on the south rim of the canyon, at an elevation of approximately 7000 feet (2174 m), in a transition zone between the Upper Sonoran and the Boreal Forest Zones, in an area influenced by Pinyon-Juniper woodland and Ponderosa Pine forests. Indian Gardens is located almost directly below Hopi Point; thus the data collected represent a nearly vertical transect through the canyon. The Hopi Point site was located in an area set aside for atmospheric sampling and closed to the public to minimize contamination due to visitors to the park. The Indian Gardens site was established on a hill above the cultivated oasis to separate the site to the extent possible from local sources of human activity and nonnative plant life.

Ambient 24-hour average samples of both fine (particle diameter, $d_p < 2.1$ μm) and total airborne particulate matter were collected daily at Hopi Point throughout August 1989. Consecutive 72-hour average samples of airborne fine particles ($d_p < 1.5$ μm) and total aerosol were taken at Indian Gardens over the same time period. In order to allow comparison to the ongoing work of other groups whose sampling schedule began daily at 0800 LT, sampling start times centered on that morning hour, commencing daily at 0600 LT at Hopi Point and at 0900 LT at Indian Gardens, the time difference necessitated by the time needed for the equipment operator to hike into the canyon from Hopi Point.

The aerosol-sampling systems employed are shown schematically in Figure 1. At Indian Gardens ambient air at a flow rate of 40 L min^{-1} was drawn through an American Industrial Hygiene Laboratory (AIHL)-designed cyclone separator [*John and Reischl*, 1980] that removed coarse particles larger than 1.5 μm in aerodynamic diameter. The output flow from the cyclone was then distributed to four 47-mm-diameter filter holders in parallel (filters A-D in Figure 1), each operated at a flow rate of 10 L min^{-1}. Each filter substrate was chosen to be compatible with a particular chemical analysis procedure. For the total aerosol samples (filters E-H in Figure 1) the same filter types were used in open-face filter holders that were protected from large-particle sedimentation and from rain by a Teflon-coated metal sheet. Critical flow orifices (Millipore, Bedford, Massachusetts) were used in series with each filter assembly to control the flow rate through each filter individually. Rotameters (Matheson, Secaucus, New Jersey) were used to measure actual flow rates onsite for each sampling period to take into account small differences in the calibration of each critical orifice. The rotameters had an accuracy known from calibration experiments to be ±3%. To compensate for the shorter sampling times at Hopi Point, higher overall air flow rates were used, in the range 13-19 L min^{-1} per filter, necessitating two cyclone separators and additional vacuum pumps at that site.

Two 47-mm-diameter Teflon membrane filters (Teflo, Gelman, Ann Arbor, Michigan) were used in each of the fine and total particle samplers. Filters with a pore size of 0.5 μm were used for the fine particle samples, whereas those with a pore size of 2.0 μm were used for the total particle samples to prevent clogging over the sampling period. Two 47-mm-diameter quartz fiber filters (Tissuquartz 2500 QAO, Pallflex, Putnam, Connecticut) also were used in each of the fine and total particle samplers. The quartz filters were baked at 520°C for 24 hours in individually wrapped aluminum foil envelopes to reduce their carbon blank levels. One Teflon filter sample in each paired set (one fine and one total at each site) was intended for measurement of particle mass and trace metals concentrations. The second Teflon filter was intended for analysis of sulfate, nitrate, chloride, sodium, magnesium, and ammonium ions. Ammonium nitrate volatilization from Teflon filters is commonly observed, and at high NH_4NO_3 concentrations, like those present in the Los Angeles Basin a denuder-based sampling system would be advised [*Hering et al.*, 1988; *Solomon et al.*, 1988]. However, at the very low concentrations and summer temperatures at the Grand Canyon during the present experiments, ammonium nitrate formation is not favored; ammonium nitrate concentrations are expected to be very low such that NH_4NO_3 volatilization artifacts are probably unimportant. One quartz filter in each set was used for bulk elemental carbon, carbonate carbon, and organic carbon particle determination by thermal evolution and combustion analysis, and the remaining quartz fiber filter was reserved for the detailed organics analysis that provided the principal motivation for this work. After use, the sampled quartz filters intended for organic compound analysis were stored in annealed glass jars with solvent-washed Teflon lid liners to prevent contamination. All other filters were stored in petri dishes with tightly fitting lids and sealed with Teflon tape. After collection, filters designated for inorganic analysis were returned to their respective dishes

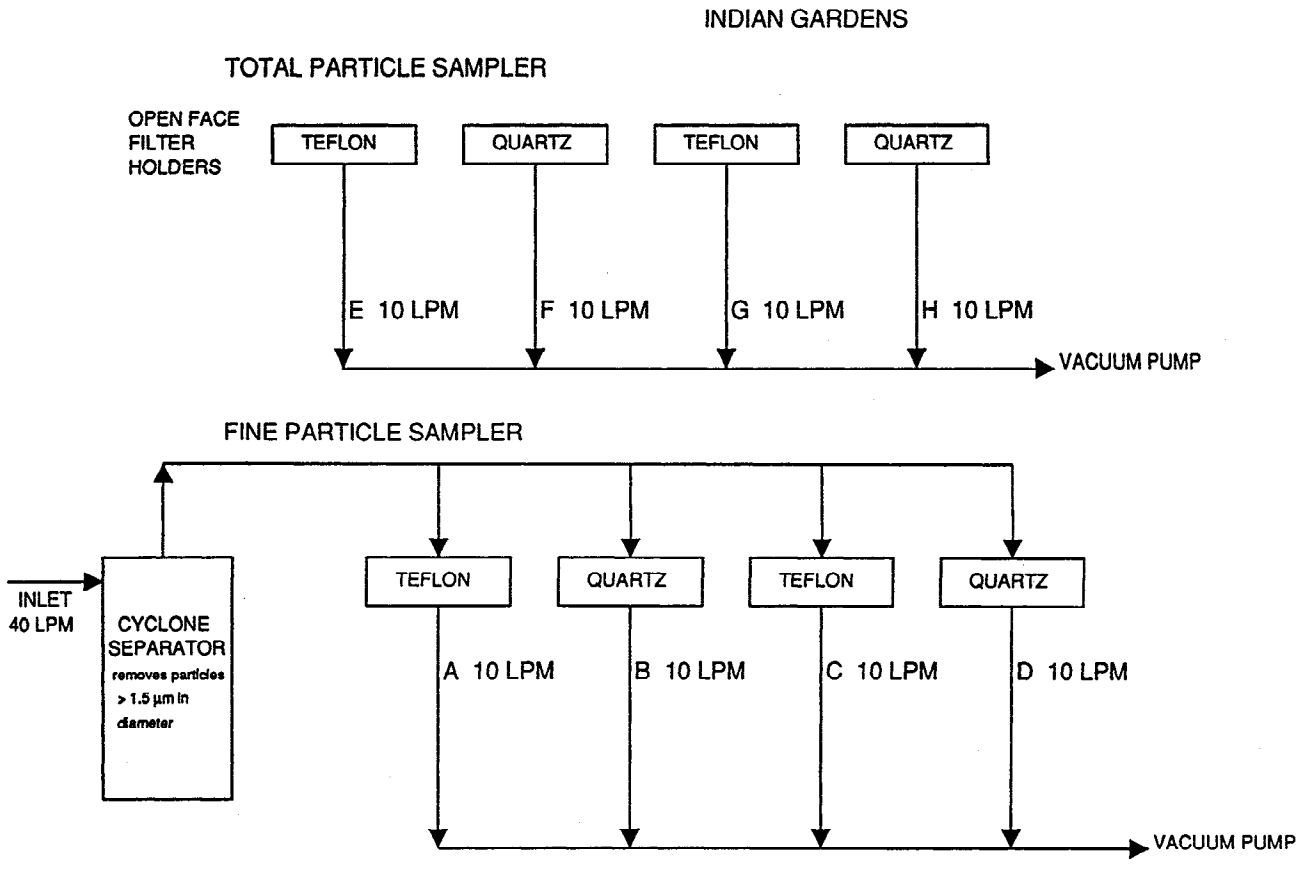

Figure 1. Schematic diagram of fine particle and total particle samplers used at Indian Gardens.

and sealed with Teflon tape. All filters were stored at -20°C within 1-3 hours after removal from the sampler and were then kept frozen until analysis in the laboratory.

Ambient particulate matter samples collected daily at Hopi Point from August 2 through August 27 were analyzed in combination with field blanks taken on July 29 (two blanks), August 28, and August 29. At Indian Gardens, 72-hour samples taken from August 2 through August 25 were used along with blanks taken on July 9 (two blanks), August 26, and August 28. The sampling schedule yielded 26 sampling periods at Hopi Point and 8 at Indian Gardens with nine blanks (counting lab blanks) for each of filters A-H. Half of the field blank filters were placed on the samplers for an entire sampling period but without turning on the pumps (static blanks). The other half of the field blanks were placed on samplers, the pumps were turned on for 10 seconds, and then the filters were removed (dynamic field blanks). All field blanks were processed in the same way as the regular samples.

Analytical Methods

Bulk Aerosol Composition

Teflon filters designated A and E (Figure 1) were analyzed for particle mass by weighing the filters before and after use on a Mettler model M-5S-A balance (Mettler Instruments, Hightstown, New Jersey) after equilibration for 24 hours in a temperature- and humidity-controlled room (22°C and 50% relative humidity). The precision of this instrument was <9 µg per filter, based on replicate measurements of samples and calibration filters. The same Teflon filters were measured subsequently for trace elements (Ag, Al, As, Ba, Br, Ca, Cd, Cl, Cr, Fe, Ga, Hg, In, K, Mn, Mo, Ni, P, Pb, Pd, Rb, S, Sb, Se, Si, Sn, Sr, Ti, V, Y, Zn, and Zr) using Xray fluorescence [*Dzubay*, 1977].

The second Teflon filter of each set was analyzed for ionic material. Each filter was placed in a plastic specimen cup where 250 µl of 100% ethanol was distributed evenly across the filter surface. Twenty milliliters of distilled water was then added along with a Teflon rod to keep the filter submerged. The cups were sealed and placed on a shaker table for 3 hours in a refrigerated room. The ethanol extracts were analyzed for ammonium ion by the indophenol colorimetric technique [*Bolleter et al.*, 1961] on an Alpkem model RFA-300 Rapid Flow Analyzer; for sodium and magnesium by flame atomic absorption (AA) on a Varian Techtron model AA-6 atomic absorption spectrophotometer; and for chloride, nitrate, and sulfate on a Dionex 2020i ion chromatograph (IC) (Dionex Corp., Sunnyvale, California). The detection limits were 0.4 µg per filter for ammonium ion; 0.1 µg for sodium; 0.2 µg for magnesium; and 0.1 µg, 0.2 µg, and 0.2 µg for chloride, nitrate, and sulfate, respectively. Analytical precisions were ±2% for ammonium ion, ±5% for sodium and magnesium, and ±1% for the species measured by ion chromatography.

Analysis of organic carbon, carbonate, and elemental carbon was obtained by a thermal evolution and combustion technique [*Johnson et al.*, 1981; *Cary*, 1987]. Detection limits for organic carbon, carbonate carbon, and elemental carbon were 0.9 µg per filter, with an analytical precision of ±3.5%. Actual uncertainties in the amount of organic aerosol in the atmosphere are higher than these analytical uncertainties. When sampling for organic aerosol by filtration, sample collection can be

affected by vapor adsorption onto the quartz fiber filters or by evaporative losses of semivolatile particulate matter [*McDow and Huntzicker*, 1990; *Hering et al.*, 1990]. When sampling the Los Angeles area organic aerosol described later in this paper, organic vapors adsorbed onto quartz fiber backup filters placed downstream of the quartz fiber particle filters were measured to monitor interferences due to vapor adsorption or particulate matter volatilization. These experiments showed organic carbon collection on the backup filters that averaged 17 of the nominal particulate organic carbon collected on the upstream particle filters [*Gray et al.*, 1986]. At the low concentrations present at the Grand Canyon the adsorption or volatilization artifact is probably small in an absolute sense but possibly two to three times larger as a percentage of the actual organic aerosol [*McDow and Huntzicker*, 1990].

Mass measurement errors were identified in the fine particle samples collected at Hopi Point on August 12 and 18, and the affected gravimetric mass values for those samples were discarded while retaining the chemical composition values for those days. Concentrations of Cu, Zn, Ag, and related trace elements in proportions characteristic of electrical brass were found in some Hopi Point ambient fine particle samples that were not present in the corresponding total particle samples (the fine particle and total particle samplers have separate inlets). This obvious anomaly was thought to arise from aerosol shed by the electrical motors used by the large number of air samplers operated at Hopi Point by several investigations in addition to our own. Metallic trace elements characteristic of electrical brass were not used in the data analyses that follow.

Organic Aerosol Characterization by Gas Chromatography

Sample preparation. The ambient aerosol samples collected on quartz fiber filters for organics analysis were grouped to form four single-month composites, each representing fine particles and total aerosol particles at Indian Gardens and Hopi Point. Static and dynamic field blank composites likewise were created for each site and particle size classification. Laboratory procedural blank samples were prepared by grouping unused prefired quartz fiber filters in numbers comparable to the number of filters in the ambient sample composites. Each group of filters was placed into a separate annealed heavy-walled borosilicate extraction bottle fitted with a Teflon-lined cap. A known quantity of perdeuterated tetracosane (n-$C_{24}D_{50}$) was spiked into each filter composite to serve as an extraction recovery standard. A ratio of 1 μg n-$C_{24}D_{50}$:150 μg C was followed as a guide to the approximate mass of surrogate standard to be added to each organic sample composite [*Mazurek et al.*, 1993]. The mass of total carbon contained in each filter composite was calculated from the results of the organic carbon analyses obtained by the cited thermal evolution and combustion technique for bulk atomic carbon species.

Sample extraction and derivatization. Aerosol organics were isolated from the insoluble particles and the quartz fiber sampling media using a previously described and validated extraction protocol [*Mazurek et al.*, 1987, 1993]. Samples were extracted successively in two 15-mL portions of hexane followed by three 15 mL portions of a 2:1 benzene/isopropanol mixture. Extraction conditions involved low intensity ultrasonic agitation at room temperature. After each extraction step the extract was filtered and transferred into a single boiling flask that contained ultimately all five solvent extractions for a given filter composite. The extracts were concentrated by rotary vacuum distillation followed by further vaporization of residual solvent into a slow stream of ultrapure nitrogen gas. Each extract was divided into two aliquots. One aliquot of each extract was derivatized by addition of diazomethane to convert organic acids to their methyl esters and acidic hydroxy compounds to their methoxy analogues, as the underivatized polar organic compounds do not elute from the GC column used. The underivatized aliquot was designated as the neutral organics fraction and the derivatized aliquot was designated as the acid+neutral organics fraction. The acidic organics fraction was calculated by difference by subtracting the mass of neutral organics from the mass of acid+neutral organics as measured by GC-FID analysis.

High-resolution gas chromatography. Characterization of the quantity of (1) nonpolar (neutral fraction) organics and (2) polar plus neutral organics (acid+neutral fraction) present in the Grand Canyon aerosol extracts was performed using a Varian 4600 high-resolution gas chromatograph (HRGC) fitted with a flame ionization detector (sensitivity 10^{-12} v) and a conventional Grob injector (injector temperature 300°C); 1-Phenyldodecane was used as a coinjection standard at a concentration of 5.6 ng μL^{-1}. The analytical column was a 30-m fused-silica DB-1701 column (bonded 86% dimethyl, 14% cyanopropylphenyl polysiloxane; 0.25-μm film thickness, 0.32-mm inside diameter; J&W Scientific, Folsom, California). Temperature programming consisted of injection at 65°C, isothermal hold at 65°C for 10 min, temperature increase of 10°C per min for 21 min, followed by an isothermal hold at 275°C for another 49 min. An external standard mixture containing 17 normal alkanes ($C_{10}H_{22}$ to $C_{36}H_{74}$, with concentrations of 9.7 ng μL^{1} to 15.7 ng μL^{-1} per compound) was injected on the GC either the same day or within 48 hours of injection of the Grand Canyon samples. The careful timing and sequencing of standard and sample injections was intended to verify consistent instrumental performance and chromatographic conditions needed for organics quantitation.

Results

Aerosol Chemical Composition

The average bulk chemical compositions of the four August monthly composites are shown in Figure 2, while the chemical compositions of individual sampling days can be examined in Figure 3. Organic compound mass concentrations shown in Figures 2, 3, and 5 are estimated as 1.4 times the organic carbon concentrations determined by thermal evolution and combustion analysis in order to account for the mass of oxygen, hydrogen, nitrogen, chlorine, and phosphorus present in the organic compounds. Mineral dust concentrations from minerals other than calcium carbonate were computed by converting the crustal elements such as Al, Si, Fe, Mn, Ti, and noncarbonate Ca to their common oxides and then summing the resulting masses.

At both Indian Gardens and Hopi Point the largest contributors to the fine aerosol consist of sulfate and associated ammonium ion plus aerosol carbon species. At Indian Gardens, sulfate and ammonium ion account for 24% and 8% of the fine aerosol, respectively, nearly equaled by the 30% of the sample composed of organic compounds and 1% contributed by elemental carbon. Mineral dust is present as a minor contributor to the Indian Gardens fine aerosol, with calcium carbonate equal to 5% of this sample composite and other crustal oxides

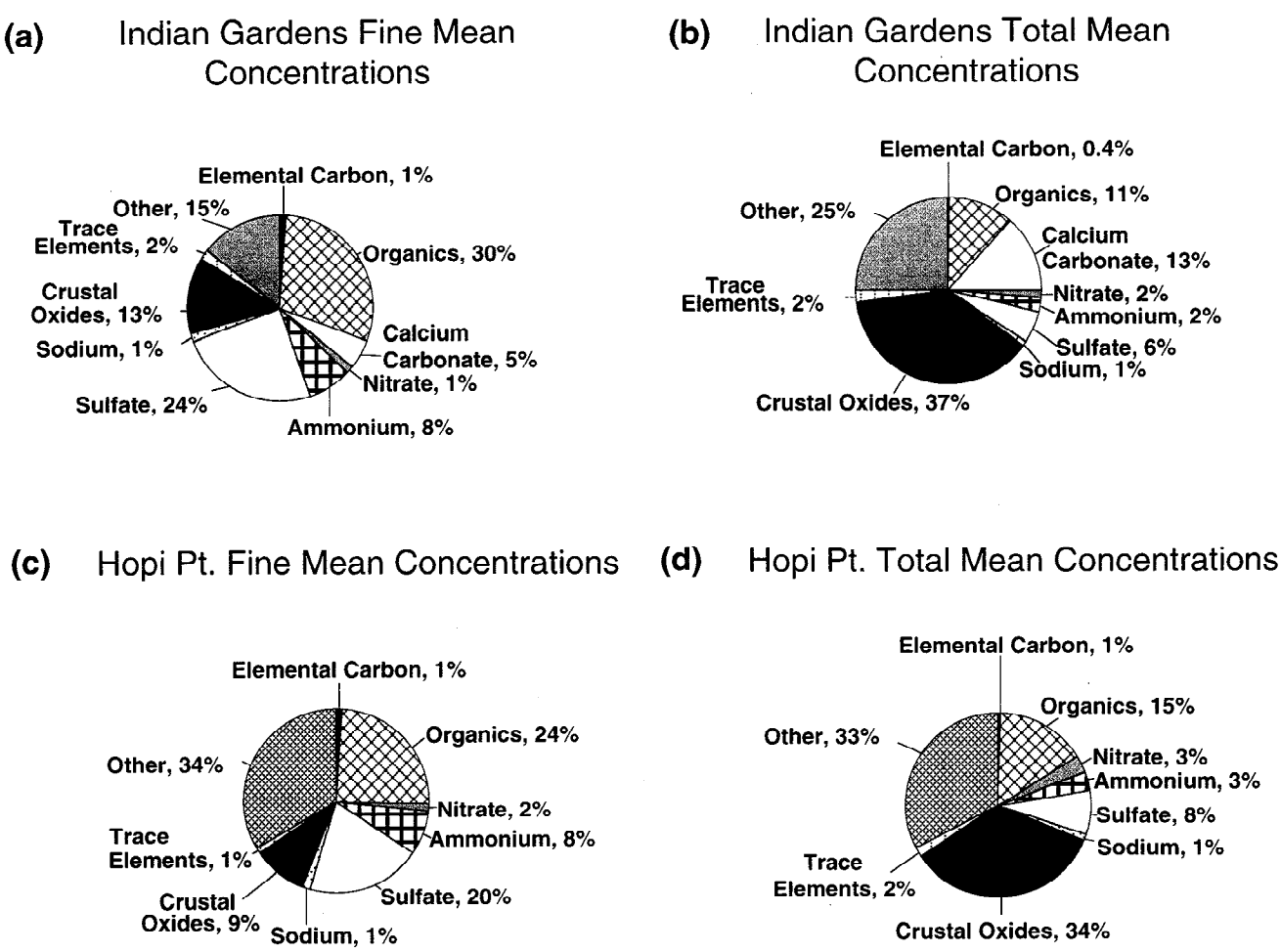

Figure 2. Average chemical compositions determined for atmospheric aerosol samples collected at Grand Canyon National Park during August 1989 for (a) Indian Gardens fine particles, (b) Indian Gardens total particles, (c) Hopi Point fine particles, and (d) Hopi Point total particles.

accounting for 13%. Somewhat more than half of the fine aerosol at Hopi Point can be explained by sulfate ion, ammonium ion, organic compounds, and elemental carbon, again with roughly equal mass concentrations due to the ionic versus carbonaceous components. Calcium carbonate is not found in the fine airborne particles at Hopi Point in large quantities, which helps to distinguish samples taken at this site from samples taken at Indian Gardens. Fine aerosol materials that could not be identified by chemical analysis ranged from 15% of fine mass at Indian Gardens to 34% at Hopi Point. A portion of this unidentified mass usually is due to bound water that is associated with deliquescent and hydrophilic aerosol chemical constituents. This mass of aerosol water is not fully removed from the samples despite desiccation prior to analytical workup and is not measurable by the methods employed here. Although the Grand Canyon is surrounded by an arid plateau, it receives precipitation during summer and, in fact, experienced significant rainfall on several days during this experiment.

The total aerosol samples differ from the fine particle samples in that much more mineral matter (e.g., coarse airborne soil dust) is present in these samples. Again, the Indian Gardens aerosol is distinguished from the Hopi Point aerosol by the large amount of calcium carbonate present in the total aerosol at Indian Gardens. Given the substantial amount of airborne carbonate at Indian Gardens, future routine monitoring of the organic aerosol at the Grand Canyon should not be based on a total carbon analysis but instead should be structured to distinguish carbonate carbon from organic carbon, as was done in the present work.

Approximate air mass trajectories arriving at the Grand Canyon during August 1989 were computed at Brookhaven National Laboratory. Trajectories of 48 hours' duration ending at 0400 and at 1600 PST daily were prepared by interpolation of 850-mbar winds. These trajectories are intended to track emissions that disperse into a thick polluted layer in the atmosphere. The 850-mbar winds produce trajectories within that mixed layer that travel over relatively low terrain until they are close to the canyon. Even though the 850-mbar level is below the elevation of the south rim of the canyon, these trajectories still provide a valuable qualitative guide to the general direction from which polluted air masses approached the Grand Canyon during August 1989. The origin of these trajectories is summarized in Table 1. Examples of the airmass trajectories are reproduced in Figure 4.

Fluctuations in the concentrations of each of the analyzed chemical components can be associated with changes in the wind trajectories. Sodium, magnesium, and chloride exhibit greatest variation (for the most part) with changes in wind direction that involve the ocean as a source with the highest

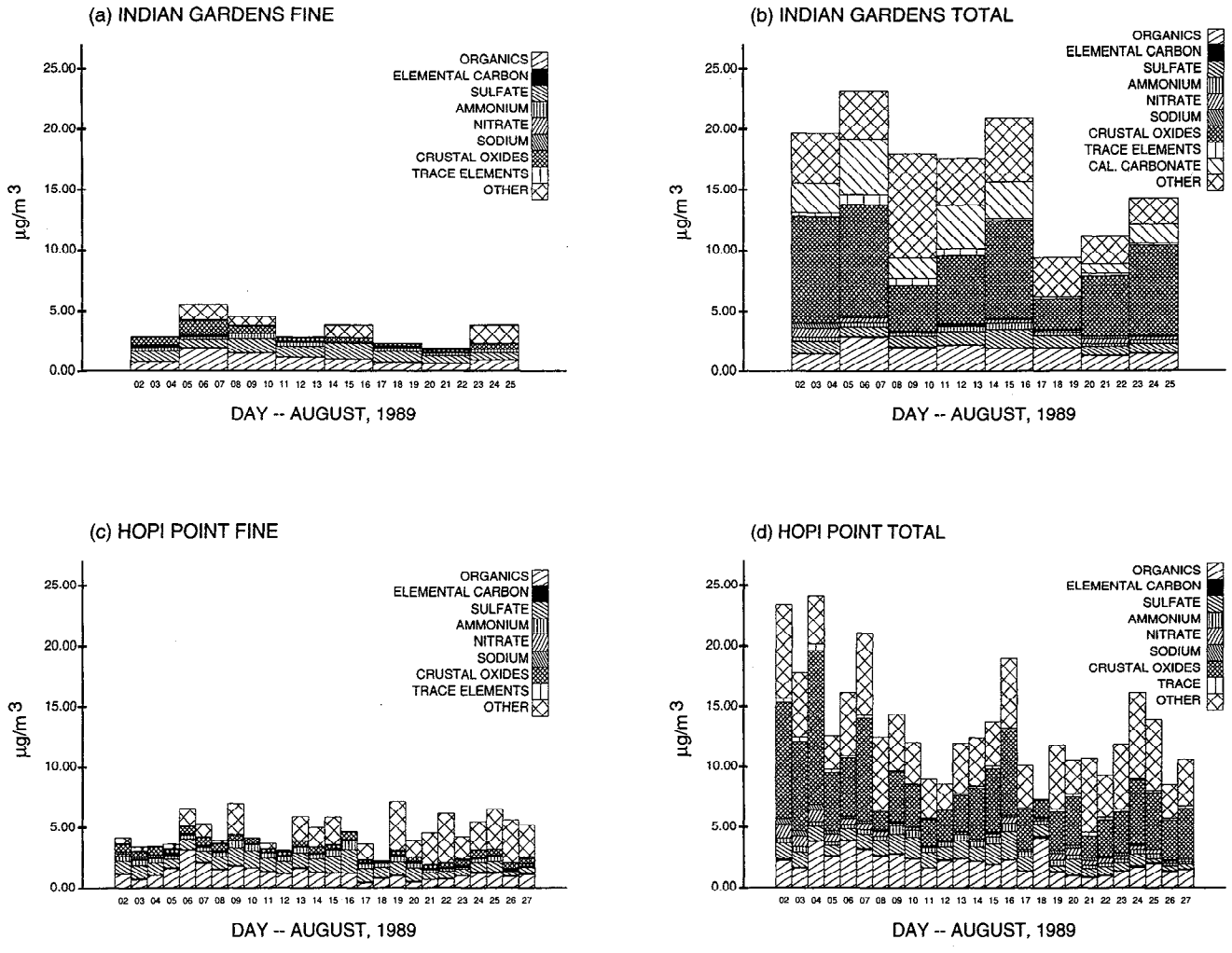

Figure 3. Concentration and chemical composition of aerosol samples for individual sampling periods at Grand Canyon National Park during August 1989: (a) Indian Gardens fine particles (72-hour samples), (b) Indian Gardens total particles (72-hour samples), (c) Hopi Point fine particles (24-hour samples), and (d) Hopi Point total particles (24-hour samples).

concentrations on days when air resided over the Pacific Ocean within the preceding 48 hours (particularly August 2-3 and August 19-24). The increase in ambient mass concentrations of these three chemical species is consistent with the known composition of sea-salt aerosol. Nitrate and sulfate concentrations are shown in time series in Figures 5a and 5b. Many of the highest nitrate levels recorded correspond to days when the prevailing wind trajectories passed near major west coast cities such as Los Angeles, San Diego, or Tijuana enroute to the Grand Canyon. The elevated nitrate trends are not surprising since nitrogen oxides are found in high concentrations in urban smog. Lower-than-average nitrate levels over the period August 9-18 generally are associated with transport over land from the south. Sulfur oxides are a major product derived from the combustion of sulfur-bearing fuels and also are emitted from smelter operations. The largest sulfate values coincide with wind trajectory patterns having southerly origins (particularly August 9-10 and August 16), suggesting that the sources most responsible for large increases in sulfate levels during August 1989 may lie to the south. One of the trajectories ending on August 16 shows a very short final segment of its trajectory, indicating possible stagnation in the vicinity of the Grand Canyon, and thus enhancing the influence of local emission sources. Fluctuations in ammonium ion levels correspond almost exactly to similar patterns in sulfate levels, suggesting that sulfate and ammonium ion are transported by atmospheric winds as one unit. Elemental and organic carbon concentrations are shown in time series in Figures 5c and 5d. Elemental carbon levels are found at mass concentrations nearly equal to the instrumental limit of detection employed here, so apparent fluctuations in these values are not a reliable indicator of the wind sector from which elemental carbon might be transported. The ratio of elemental carbon to organic carbon (EC:OC) at the Grand Canyon is very much lower than the roughly one part elemental carbon to two parts organic carbon seen in Los Angeles urban aerosol [*Gray et al.*, 1986; *Turpin et al.*, 1991; *White and Husar*, 1976]. Our measurements of the EC:OC ratio obtained for the Grand Canyon average ambient chemical profiles show an EC:OC ratio that ranges from 1 part EC to 22-30 parts OC. The dramatically reduced EC:OC ratios for Grand Canyon samples suggest that the aerosol is enriched in organics from sources other than primary urban aerosol that is typical of the metropolitan Los Angeles source region [*Hildemann et al.*, 1994b; *Gray et al.*, 1986; *Turpin et al.*, 1991;

Table 1. Approximate Origin (48 Hours Earlier) of Air Masses Arriving at The Grand Canyon During August 1989.

Date	Source of Air Mass
2	Pacific Ocean/San Diego/Los Angeles
3	Pacific Ocean/San Diego/Baja California
4	central Arizona
5	Baja California
6	Baja California
7	central Arizona
8	New Mexico/southern Arizona
9	central Arizona/California desert
10	central Arizona
11	Pacific Ocean/Baja California
12	Mexico/California desert
13	Nevada-Arizona border
14	Sierra Nevada Mountains, California
15	California desert
16	central Arizona/Baja California
17	California desert
18	central/southern Arizona
19	Baja California/Pacific Ocean
20	Pacific Ocean/Baja California
21	Pacific Ocean/Baja California/San Diego
22	Pacific Ocean/Baja California/San Diego
23	Baja California/San Diego/Pacific Ocean
24	Pacific Ocean/San Diego/Los Angeles/Nevada
25	Nevada/Pacific Ocean/San Diego
26	southeastern California/Pacific Ocean/ San Diego/Baja California
27	Pacific Ocean/San Diego

Pandis et al., 1992]. Finally, the organics levels fluctuate and do not appear to reach peak concentrations consistently with air mass transport from any one direction. Instead, organics levels peak on August 6, a day of relative air stagnation near the Grand Canyon (see short terminal trajectory segments in Figure 4 for the day of August 6 and the early morning of August 7). It is possible that the organics may be emitted primarily from local sources. In the present paper we employ GC-FID analysis of the organic compounds to characterize these organics in a way that can be compared to data from GC-FID analysis of urban Los Angeles area fine aerosol organics and from primary emission sources of organic aerosol reported earlier [*Mazurek et al.*, 1989; *Hildemann et al.*, 1991b, 1994b; *Rogge et al.*, 1993c, d, e; *Simoneit et al.*, 1993]. In future work a detailed chemical inventory of the individual organic compounds present in the Grand Canyon aerosol based on GC/MS analysis will be presented to more closely define the likely organic aerosol sources [*Mazurek et al.*, 1995].

Organics Characterization by High Resolution Gas Chromatography

Aerosol organics are complex mixtures of individual organic compounds, some of which can be measured quantitatively by GC-FID. The fraction of solvent soluble aerosol organics that are identified by GC-FID are referred to as elutable organics. Figure 6 shows the relationship of elutable organics mass concentration to the total particle mass and various other forms of aerosol carbon present in the fine particle and total particle samples collected at the two Grand Canyon sites. These carbon inventories are based on ratios constructed from the following mass determinations: total particle mass, organics mass, elutable organics mass, neutral elutable organics mass, and acidic elutable organics mass. The total particle mass was determined by the gravimetric measurement procedure described above. The organics mass used to construct Figure 6 was calculated very carefully using the mass of organic carbon (OC) determined for each filter composite by thermal evolution and combustion analysis, followed by multiplication of the OC masses by conversion factors constructed to account for the mass of elements other than carbon present in the organic compounds. These conversion factors were calculated from the atomic mass compositions of those organic compounds present in these samples that could be identified by GC/MS analysis of the elutable organics fraction [*Mazurek et al.*, 1995]. The conversion factors varied between the samples studied, ranging from 1.38 to 1.46, and reflect in addition to carbon atoms the mass concentrations of hydrogen, of oxygen, and of trace amounts of nitrogen, chlorine, and phosphorus present in the organic compounds.

Elutable organics constitute 2% to 11% of the fine particle or total particle ambient mass concentrations, but comprise 27% to 54% of the total mass of aerosol organics (Figure 6). Organics that are either insoluble or that will not elute from the GC analytical column used in our analytical protocol comprise the largest share of aerosol organics in most cases. These nonelutable organics are carbonaceous substances which cannot be analyzed by our GC-FID procedure due to extremely high compound polarity and/or to high molecular weight (e.g., polymeric organic compounds, cellulose). One other important bulk chemical characteristic of the elutable organics is the acidity or relative polarity of the organic components that can be studied by GC-FID. As seen in Figure 6, the mass concentration of acidic elutable organics is nearly equal to the mass of neutral elutable organics. Recall that in this GC-FID application, the acidic elutable organics fraction contains those organic compounds which are detected by FID only after undergoing a chemical derivatization step that selectively targets acidic hydrogen atoms attached to either aliphatic or aromatic carboxyl groups or to aromatic hydroxyl groups. Our GC-FID analysis of acidic organics provides a mechanism for evaluating selectively the ambient mass concentrations and chemical distribution of the polar organic fraction.

Besides measurement of the mass of neutral and acid+neutral fractions of aerosol organics, GC-FID analysis permits quantification of the elutable compounds as a function of retention time if chromatographic and instrumental conditions remain constant from one injection to the next. We have employed such retention time analysis in earlier studies of Los Angeles organic aerosol [*Mazurek et al.*, 1987, 1989, 1993; *Hildemann et al.*, 1991b, 1994b; *Rogge et al.*, 1993e] and in studies of urban sources of fine organic aerosols which included, among other fine particle emission sources, motor vehicle exhaust [*Rogge et al.*, 1993a], wood smoke [*Simoneit, et al.*, 1993; *Hildemann*, 1990], road dust [*Rogge et al.*, 1993b], and surface abrasion products from urban vegetation [*Rogge et al.*, 1993c] in order to construct "fingerprints" for the effluent from different sources that can be compared to a similar analysis of the ambient samples. In this technique, histograms are constructed by summing the mass concentrations of all of the organic compounds that elute between the successive elution points of the C_n to C_{n+1} normal alkanes over the range from *n*-C_{10} to *n*-C_{36}. Details of the mass quantitation procedure were

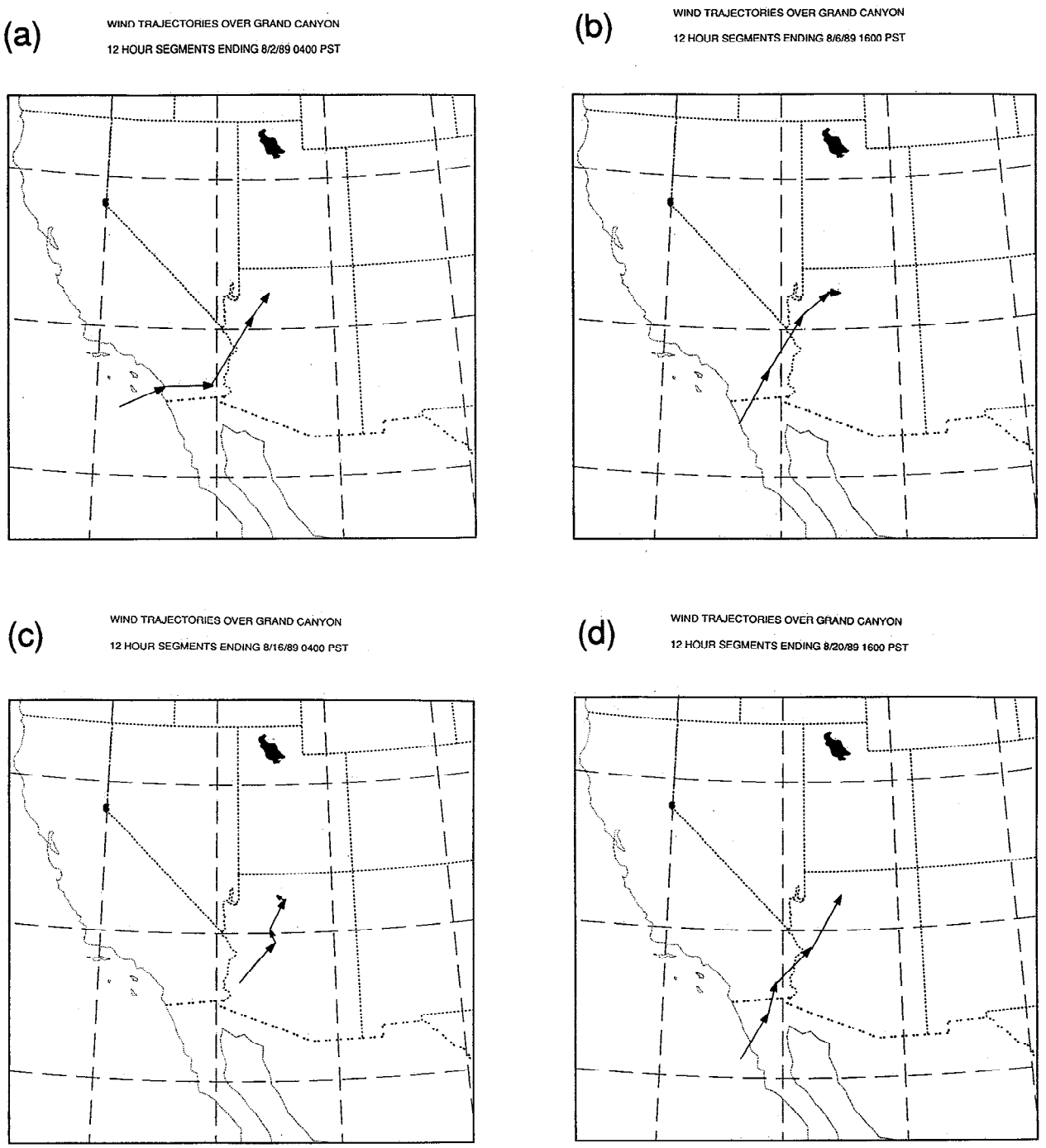

Figure 4. 48-hour backward trajectories for air masses arriving at the Grand Canyon on selected days during August 1989.

reported by *Hildemann et al.*, [1994b]. The technique employs GC-FID response factors that correspond to 17 individual *n*-alkanes ranging from $C_{10}H_{22}$ to $C_{36}H_{74}$. The mass response factors that are generated by the *n*-alkane standard series are applied to 17 mass intervals, each containing a single *n*-alkane standard homolog. By dividing up the mass of complex elutable organics into successive mass intervals (i.e., retention volumes) having separate mass response factors, more accurate measurement of the mass of total elutable organics is achieved [*Hildemann et al.*, 1994b; *Lee et al.*, 1984]. Conversion of GC-FID area counts to organic mass concentrations is calculated as follows:

Mass eluting between C_n and C_{n+1} (including the C_n alkane itself) =

$$\frac{\text{mass } nC_{24}D_{50} \text{ added to sample}}{\text{area counts } nC_{24}D_{50}} \times \frac{\text{area counts between } C_n \text{ and } C_{n+1}}{RRF_{nC_{24}D_{50}}} \times RRF_{C_n} \quad (1)$$

where $RRF_{nC_{24}D_{50}}$ is the relative response factor for $nC_{24}D_{50}$ and RRF_{C_n} is the relative response factor of alkane C_n. The RRF values for individual compounds were calculated as

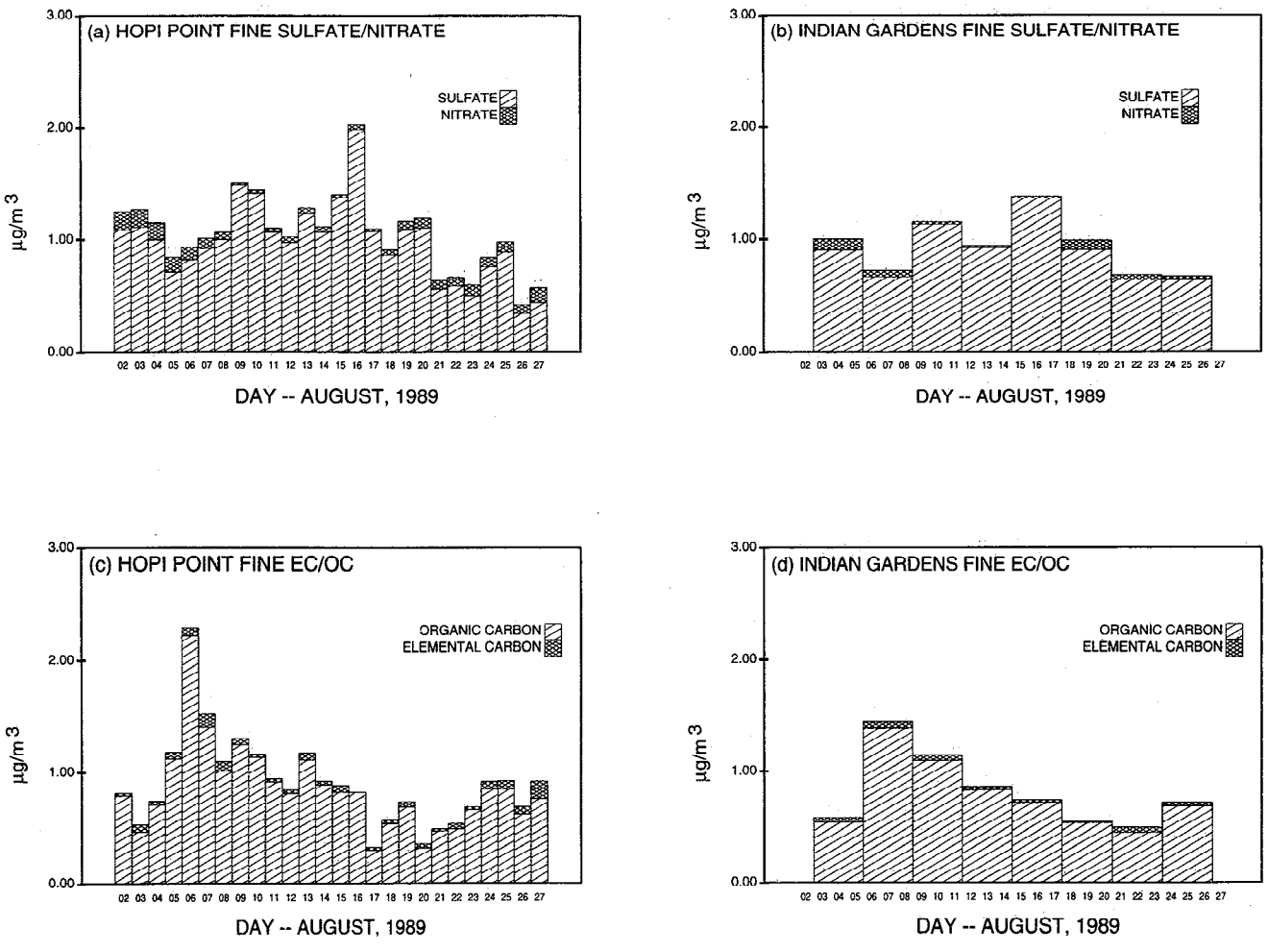

Figure 5. Fine particle sulfate and nitrate concentrations collected at (a) Hopi Point and (b) Indian Gardens, and fine particle organic carbon and elemental carbon concentrations collected at (c) Hopi Point and (d) Indian Gardens during August 1989.

$$RRF_{C_n} = \frac{\text{area counts 1-phenyldodecane}}{\text{mass 1-phenyldodecane}} \times \frac{\text{mass compound A}}{\text{area counts compound A}} \quad (2)$$

The calculations are applied to each GC-FID analysis of neutral and acid+neutral extraction aliquots. The mass of acid elutable organics for each mass interval is obtained by subtracting the mass of neutral elutable organics from the mass of acid+neutral elutable organics.

Figure 7 shows the elution order distributions of acid and neutral elutable organics that were isolated from the ambient particle samples collected during the August 1989 experiment at Grand Canyon National Park. Each bar in Figure 7 states the quantity of all of the organics that elute between the elution points of the C_n and C_{n+1} alkanes, including the C_n alkane itself, where the alkane carbon number (n) is stated below each bar. Several features are noteworthy. First, the carbon number maxima for all samples peak roughly near the interval that contains the n-C_{20} alkane, with generally unimodal distributions, except for a single spike near the elution point of the n-C_{15} alkane that is present in all samples. As will be seen shortly, this carbon number maximum occurs at a much lower carbon number than is the case for an airshed where the aerosol is dominated by petroleum residues from motor vehicle traffic (e.g., downtown Los Angeles, Figure 8b). However, for the case of the Grand Canyon aerosol examined here, the carbon number maxima near the elution point of the C_{20} n-alkane could be related to emissions from vegetation. In particular, gymnosperm species such as those present in abundance at Hopi Point, contain substantial quantities of monoterpenoid (C_{10} compounds), sesquiterpenoid (C_{15} compounds), and diterpenoid (C_{20} compounds) molecular species [*Poucher*, 1991; *Simonsen*, 1947, 1949, 1952; *Pinder*, 1960]. As part of the overall analysis scheme for the origin of organics at the Grand Canyon, we prepared quantitative standard mixtures of monoterpene and diterpene compounds. The elution points for the monoterpenes coincided with those of the C_{12} to C_{15} n-alkanes, and the diterpenes standard compounds eluted within the same range as C_{20} to C_{25} n-alkanes. Although a sesquiterpene standard was not prepared, given the intermediate molecular weights, sesquiterpene compounds would elute within the C_{15} to C_{20} n-alkane range under the chromatographic conditions adopted for this study. Further evidence of emissions from vegetation in the form epicuticular waxes is seen vaguely in the mass intervals defined by the n-C_{34} to n-C_{36} alkanes for the total particle samples at Indian Gardens. The predominance of the mass

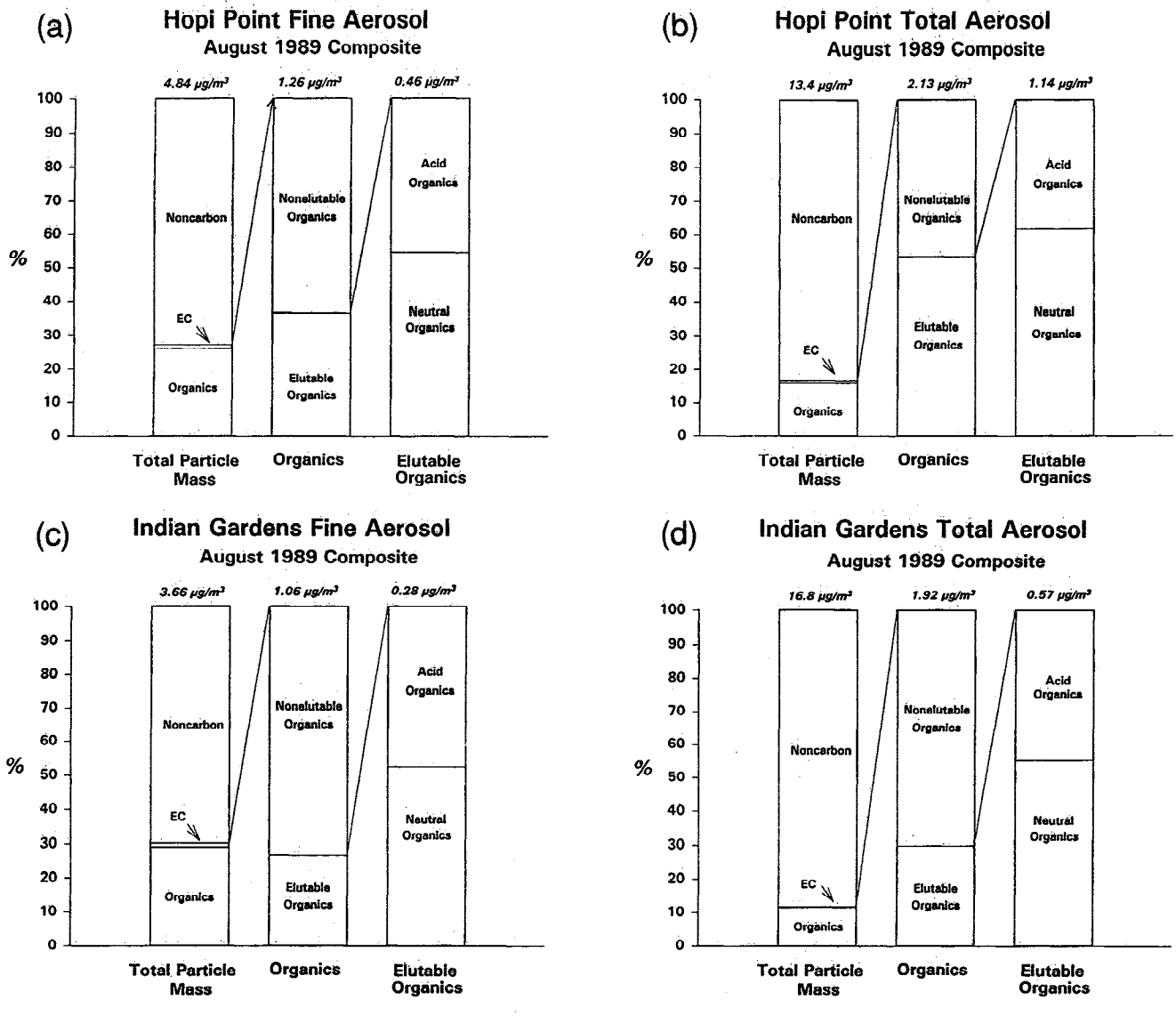

Figure 6. Carbon species material balances determined for (a) Hopi Point fine particles, (b) Hopi Point total particles, (c) Indian Gardens fine particles, and (d) Indian Gardens total particles; August 1989 monthly composites.

interval that contains the n-C_{35} alkane over the adjacent n-C_{34} and n-C_{36} mass intervals suggests the presence of high molecular weight n-alkanes that are characteristic of surface waxes found in desert vegetation [e.g., *Martin and Juniper*, 1970; *Cox et al.*, 1982]. The presence of epicuticular plant waxes from vegetation at Hopi Point is not as evident from the GC-FID mass interval plots in Figures 7a and 7b as was the case at Indian Gardens. The n-alkane distribution from dominant vegetation in the more temperate lifezones of the Grand Canyon such as the pinyon-juniper and Ponderosa pine woodlands (Hopi Point vicinity) are shifted slightly to the lower mass intervals defined by the C_{27} to C_{31} n-alkanes [*Simoneit and Mazurek*, 1982b] where their characteristic odd-to-even carbon number predominance is masked by the presence of other compounds.

For all Grand Canyon samples, the range defined by the elution points of the n-C_{10} to n-C_{20} alkanes that encompasses the elution points corresponding to monoterpenoid, sesquiterpenoid, and some diterpenoid species also contains the highest proportions of acidic/polar elutable organics. Molecular studies of the composition of photochemically generated aerosols formed by the oxidation of principally monoterpene precursors show abundant oxidized organic compounds in the form of monocarboxylic acids, dicarboxylic acids, ketones, aldehydes, and lactones [*Schuetzle and Rasmussen*, 1978; *Altshuller*, 1983; *Arnts and Gay*, 1979; *Martin et al.*, 1991; *Grosjean et al.*, 1992; *Pandis et al.*, 1991; *Grosjean and Seinfeld*, 1989; *Yokouchi and Ambe*, 1985; *Kotzias et al.*, 1990; *Hatakeyama et al.*, 1989]. Our derivatization step prior to GC-FID analysis is selective for hydrogen atoms attached to carboxylic acid groups and to phenolic-type hydroxyl hydrogen atoms and thus promotes chromatographic separation of these known biogenic secondary organic acids. However, the selective derivatization procedure, when combined with GC-FID alone, cannot distinguish aerosol organic acids which result from primary emissions (chiefly from combustion of organic matter) from those which are produced in the atmosphere by chemical reaction (secondary organic acid compounds). In a subsequent paper we will report the molecular composition of the polar organics present in the same Grand

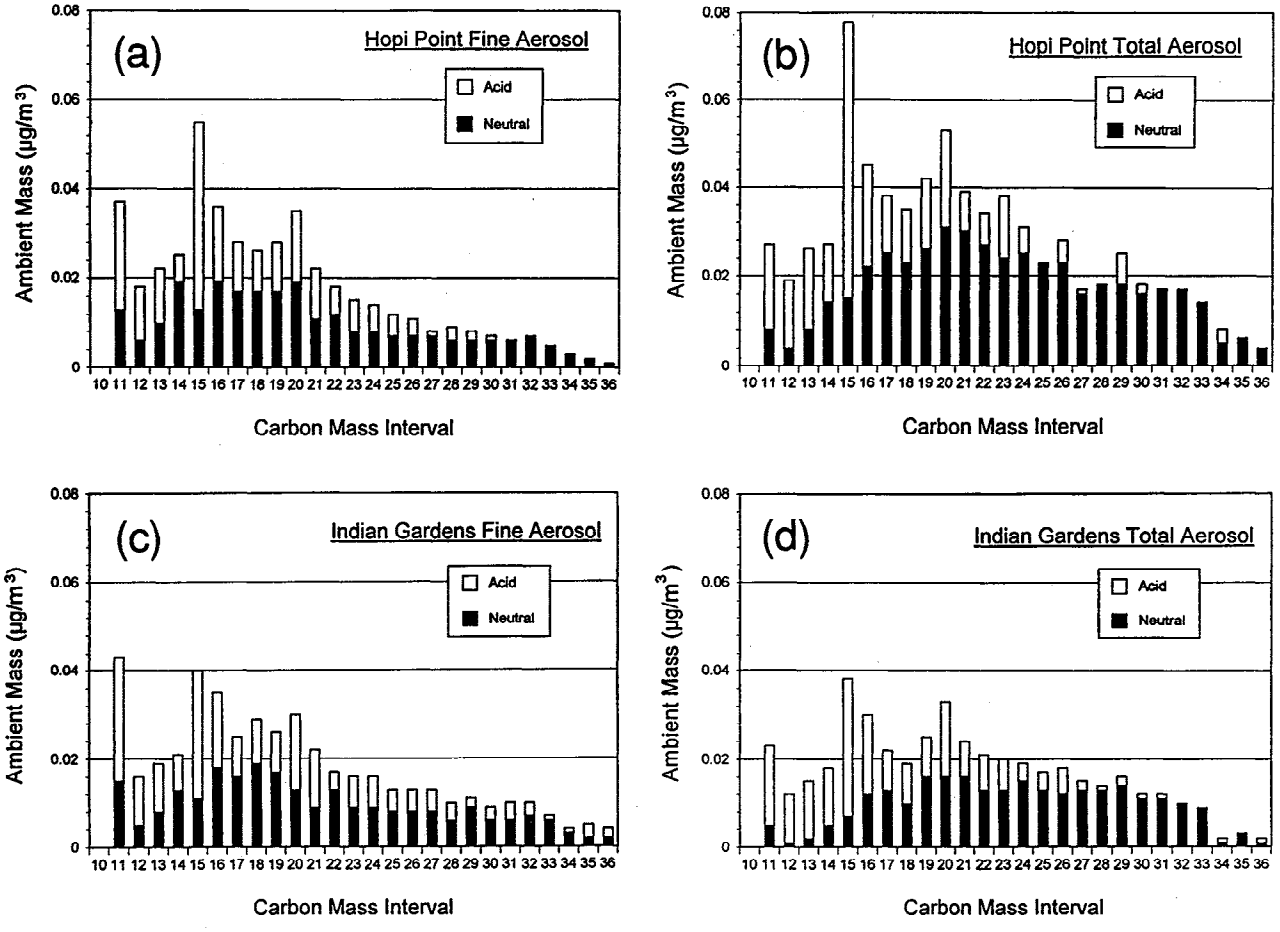

Figure 7. Distributions and ambient mass concentrations of acid and neutral elutable organics obtained from GC-FID analyses of (a) Hopi Point fine particles, (b) Hopi Point total particles, (c) Indian Gardens fine particles, and (d) Indian Gardens total particles; August 1989 monthly composites. Each bar shows the quantity of all organics that elute between the elution points of the C_n and C_{n+1} n-alkanes, including the C_n alkane itself, where the alkane carbon number (n) is stated below each bar.

Canyon ambient samples based on GC/MS analysis [*Mazurek et al.*, 1995]. Using GC/MS analysis the acidic organic compounds derived from atmospheric chemical reactions can be distinguished from directly emitted combustion products.

The ambient mass distributions of elutable organics from the Grand Canyon aerosol samples shown in Figure 7 can be compared with those obtained by *Hildemann et al.* [1990, 1991b, 1993] for August 1982 monthly composites of fine particle (d_p < 2.1 µm) samples taken at four sites located in the Los Angeles basin and at San Nicolas Island, a background sampling site located offshore and predominantly upwind of the Los Angeles metropolitan area. Figure 8 shows the ambient mass distributions of elutable organics measured at downtown Los Angeles, Pasadena, west Los Angeles, Rubidoux, and San Nicolas Island. With the exception of San Nicolas Island, ambient mass interval concentrations in the Los Angeles area are on the order of 10-20 times higher than those observed for the Grand Canyon ambient samples, a result that is consistent with earlier determinations of elutable organics measured for SCENES network samples collected at Hopi Point during the summer and winter seasons [*Mazurek et al.*, 1991].

The distributions of organics between the adjacent elution zones defined here for all Los Angeles area samples are clearly different from the those of the Grand Canyon ambient samples. These compositional differences, which are apparent in the carbon mass interval distributions (Figures 7 and 8), suggest disparate origins for the elutable organics present at Grand Canyon versus those present in metropolitan Los Angeles, as did the earlier dissimilarities noted in the EC:OC ratios determined for the Grand Canyon versus those measured in the Los Angeles area. The San Nicolas Island summer composite shows a bimodal distribution with the dominant maximum between the elution points of the C_{15}-C_{17} n-alkanes and a smaller maximum between the elution points of the C_{26}-C_{29} n-alkanes. This lower molecular weight maximum corresponds to a marine source of organic compounds which elute in the range of the C_{15}-C_{17} n-alkanes and is characteristic of marine algal lipids [e.g., *Martin and Juniper*, 1970; *Simoneit*, 1986; *Air Pollution Foundation of Southern California*, 1954; *Hahn*, 1980; *Simoneit and Mazurek*, 1982b; *Marty et al.*, 1979]. A higher molecular weight maximum located in the range of the elution points of the C_{28}-C_{32} n-alkanes, especially evident for downtown Los Angeles and Pasadena, is typical of the distributions of elutable organics observed for fine particulate matter sampled from motor vehicle exhaust [*Simoneit*, 1984, 1985, 1986; *Boyer and Laitinen*, 1975; *Pierson et al.*, 1983; *Black and High*, 1979]. Earlier work has shown that these two urban Los Angeles sites are influenced heavily by emissions from motor vehicle exhaust

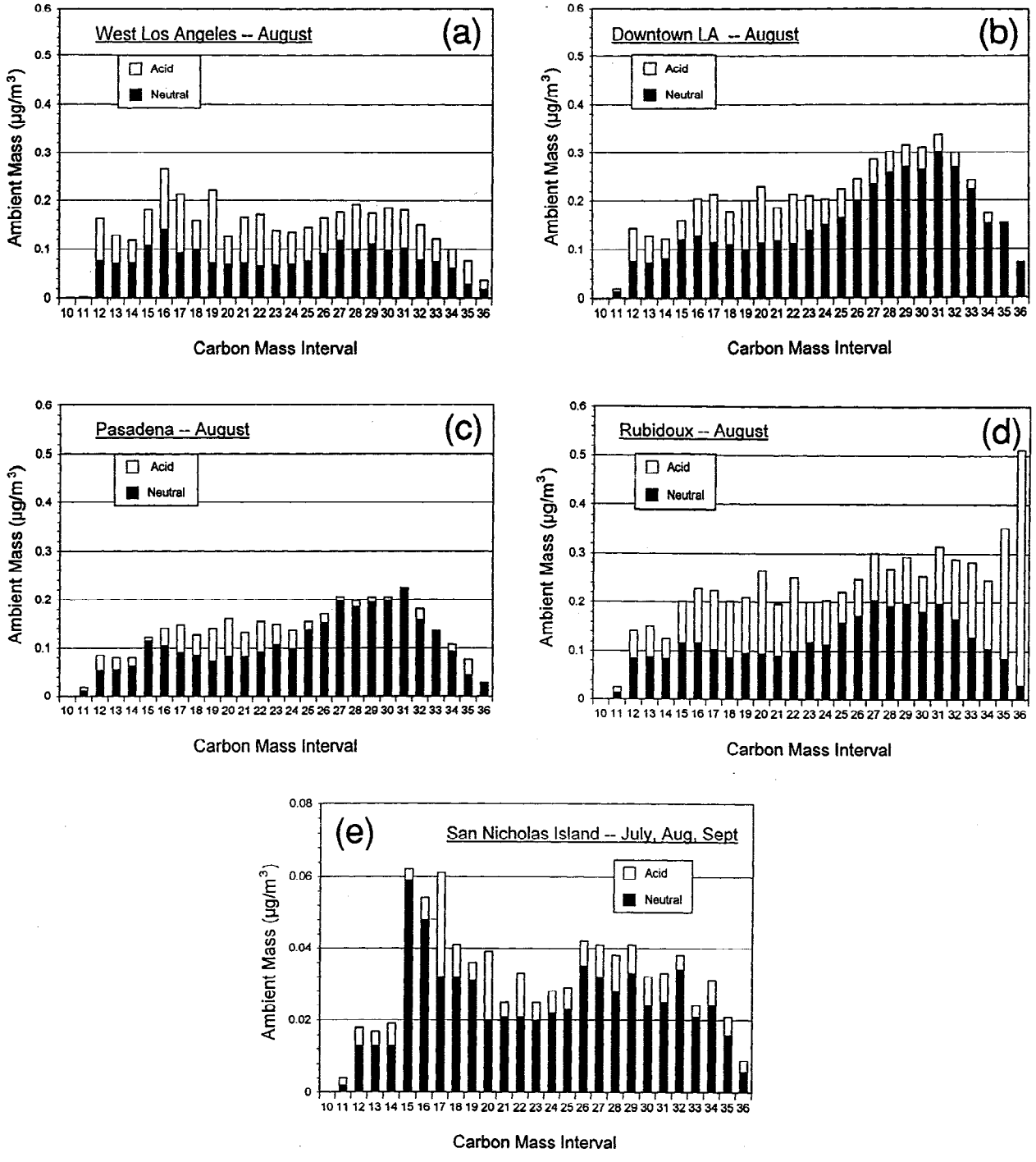

Figure 8. Distributions and ambient mass concentrations of acid and neutral elutable organics obtained from GC-FID analyses of (a) west Los Angeles, (b) downtown Los Angeles, (c) Pasadena, (d) Rubidoux, and (e) San Nicolas Island fine particles; August 1982 monthly composites (adapted from *Hildemann* [1990] and *Hildemann et al.* [1994]). Each bar shows the quantity of all organics that elute between the elution points of the C_n and C_{n+1} *n*-alkanes, including the C_n alkane itself, where the alkane carbon number (*n*) is stated below each bar.

[e.g., *Cass et al.*, 1982; *Gray*, 1986; *Gray et al.*, 1986; *Hildemann et al.*, 1993, 1994a; *Fujita et al.*, 1994; *Trijonis*, 1984; *Watson et al.*, 1994; *Pratsinis*, 1994]. The west Los Angeles August fine particle composite (Figure 8a) is intermediate in carbon mass interval distribution, exhibiting a mixture of both marine lipid and motor vehicle fine particle emission sources. Of the four urban sites shown, west Los Angeles is located nearest the Pacific coast (approximately 7 miles inland) and is the site most influenced by onshore breezes. At the other extreme, the Rubidoux site (approximately 60 miles inland) is farthest east and receives significant levels of secondary organic aerosols which have been advected from source regions nearer to the central portions of metropolitan Los Angeles [*Turpin et al.*, 1991; *White and Husar*, 1976; *Pandis et*

al., 1992; *Appel et al.*, 1978, 1980; *Schuetzle et al.*, 1975; *Cronn et al.*, 1977]. It is important to note (Figure 8d) that the Rubidoux site exhibits the highest concentration of organics relative to the other Los Angeles locations and has the highest proportion of acidic organics relative to the total mass of elutable organics. Moreover, the distribution of neutral elutable organics at Rubidoux carries the distinctive imprint of the mass distribution and carbon number maxima seen for vehicular exhaust (see Figure 8b, downtown Los Angeles; see also *Hildemann et al.* [1991b], *Boyer and Laitinen* [1975], *Pierson et al.* [1983], and *Black and High* [1979]) along with partially oxidized vehicular exhaust components present in the acidic fraction. We consider the Rubidoux August (Figure 8d) elutable organics distribution as an example of aged Los Angeles aerosol and ask if that aged Los Angeles aerosol looks like the organic aerosol arriving at the Grand Canyon vicinity during August 1989. We are unable to identify a mechanism which could produce the elutable organics mass distributions seen in the Grand Canyon ambient samples from material like that seen at the eastern end of the Los Angeles area at Rubidoux at that time of the year. The vehicle exhaust-like collection of high molecular weight neutral organics seen to peak in the range of the elution points of the C_{27}-C_{32} normal alkanes in the Los Angeles and Rubidoux aerosol is present as no more than a minor portion of the Grand Canyon fine aerosol shown in Figures 7a and 7c. Furthermore, as discussed earlier, the Rubidoux fine carbonaceous aerosol contained black elemental carbon in amounts equal to about 30% of the total aerosol carbon during the 1980's [*Gray et al.*, 1986], while the August 1989 Grand Canyon aerosol contains only traces of elemental carbon when compared to organic carbon (see Figures 2 and 5). Therefore it is evident that the Grand Canyon organic aerosol in August is not simply diluted aged Los Angeles area urban organic aerosol. The reader is cautioned that this conclusion applies only to the specific August 1989 sampling period studied here and cannot necessarily be extrapolated to other time periods.

Conclusions

Fine particle organic aerosols are approximately equal in concentration to sulfate aerosols at the Grand Canyon during the summer period examined here. This is true both at Hopi Point, on the south rim of the canyon, and within the canyon itself at Indian Gardens. At each site, roughly half of the elutable organics in the fine aerosol fraction is composed of highly polar organic compounds that could be observed by GC-FID only after chemical derivatization prior to analysis. Our GC-FID analysis of acidic organics measures the ambient mass concentrations and elution schedule of polar organics at the Grand Canyon, which otherwise have not been inventoried in earlier studies of the aerosol composition for this background continental United States site. The polar organics fraction is of great significance since the acidic nature of hydrogen atoms associated with this aerosol component may interact with atmospheric water vapor via hydrogen bonding to water molecules, thereby enhancing condensation of atmospheric water vapor which in turn could lead to increased light scattering by particles. Consequently, measurement of the polar organics fraction is an important step in understanding the role that organic carbon particles may play in visibility reduction within the remote airsheds of the southwestern United States.

The distributions of elutable organics present at Grand Canyon during August 1989 as measured by GC-FID show pronounced compositional differences when compared to the distributions of the elutable organics isolated from fine particle samples collected during August 1982 at four Los Angeles sites and at San Nicolas Island. The Los Angeles-area samples have elutable organics mass distributions which show the input of marine (minor influence) and vehicular exhaust (dominant influence) sources. The Grand Canyon samples show little evidence of motor vehicle exhaust inputs and instead have mass distributions of elutable organics which are consistent with those mass distributions of freshly emitted and partially oxidized monoterpene, sesquiterpene, and diterpene compounds.

Although all aerosol organics cannot be fully identified on a molecular level at the Grand Canyon at this time, we have chemical evidence in the form of EC:OC ratios and elutable organics mass distributions which allows us to compare August 1989 Grand Canyon organic aerosol samples to Los Angeles area August fine aerosol organics samples. First, the EC:OC ratios obtained for the Grand Canyon fine particle and total particle samples (e.g., 1 part EC to 22-30 parts OC) indicate a substantial addition of aerosol organics beyond the 1 part EC to approximately 2 parts OC present during the 1980s in Los Angeles primary aerosol emissions. Second, the distribution of elutable organics obtained for all Grand Canyon samples shows an abundance of low molecular weight carbon species without the high proportion of higher molecular weight elutable organics characteristic of the vehicular exhaust profiles which dominate the overall chemical composition of Los Angeles area elutable organics. Given this chemical evidence, we see no significant input of aged aerosols transported from Los Angeles area sources to Grand Canyon during August 1989. The lack of chemical equivalence between the Grand Canyon and Los Angeles-area ambient samples based on GC-FID mass distributions and on EC:OC ratios suggests that sources of organic aerosol other than from the Los Angeles urban area must affect air quality at Grand Canyon under the specific August 1989 summertime conditions studied. Since organic aerosols make contributions to fine aerosol mass concentrations (and hence to light scattering) that are comparable to those of sulfate aerosols at the Grand Canyon, determination of the identity and origin of these other organic aerosol components is important. In future work the identity of these sources will be described by use of GC/MS analytical data for the individual organic compounds that are present.

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