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INTERIM FINAL REPORT

Identification of Source Contributions to Visibility - Reducing Organic Aerosols in the
Vicinity of Grand Canyon National Park

By

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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 has been extensively studied, much less is known about the nature and origin of the carbonaceous aerosols that are present. This disparity in understanding arises from at least two causes: aerosol carbon data for the region are less plentiful and many of the sources that could contribute to that organic aerosol are both diverse and not well characterized.

Atmospheric carbon particles are emitted from both anthropogenic and biogenic sources (Cass et al, 1982; Gray, 1986; Hildemann et al., 1991). Motor vehicle exhaust and stationary source fuel combustion contribute aerosol fossil fuel residues to the atmosphere. Biomass combustion, including wood smoke from fireplaces and wood stoves, forest fires, structural fires and even cigarette smoke, adds to the organic particle emissions. Fugitive dust containing organic carbon is generated as particles are shed from tire and motor vehicle brake wear. Food cooking operations produce organic aerosols containing carbon of recent biogenic origin. In addition, truly natural sources of non-fossil carbon particles exist and include plant fragments. To these primary emissions that arise as particulate matter emitted directly from sources is added secondary organic aerosols that are formed by condensation in the atmosphere of the low vapor pressure atmospheric reaction products of gas phase organics. Effluents from many of these sources contain little other than carbonaceous materials, and thus appear identical if only a bulk carbon content determination is made via combustion analysis.

Considerable insight into the source origin of atmospheric organic aerosols can be achieved if the molecular, rather than elemental, composition of the particles is examined. Molecular markers can be defined in the form of organic compounds that are characteristic of some sources but not others. Resin acids and retene can be used to identify the wood smoke contribution to the aerosol (Standley, 1988; Ramdahl, 1983); hopanes and steranes can be used to identify the amount of vehicle exhaust present, for example (Rogge et al., 1993a).

A preliminary investigation of the origin of the organic aerosol at the Grand Canyon based on molecular tracer methods has been described by 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 is 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 that were not collected from ambient air (but that instead came from sampler parts, from anti-bounce coatings used in fine particle cyclones in the samplers, or from sample handling).

The objective of the present study is to examine the origin of the carbonaceous aerosol at Grand Canyon National Park during the summer season based on molecular tracer techniques applied to source and ambient samples collected specifically for this purpose. An air monitoring program will be established both within the Grand Canyon and on the South Rim to define summertime organic aerosol composition as a function of elevation in the canyon. Supporting information on the composition of the inorganic portion of the atmospheric aerosol will be collected to help place the relative importance of the organics in perspective. Source samples likewise will be collected from several of the most likely local organic aerosol sources at the Grand Canyon, including wood smoke from local pine, smoke from combustion of local vegetation, plant fragments abraded from local vegetation and local soil dust samples. Both source and ambient samples will be examined by methods identical to those used previously to characterize the upwind Los Angeles urban aerosol and urban sources (e.g. Rogge et al., 1993ab) such that organic aerosol components typical of motor vehicle exhaust and other human activities can be identified, if present, in the Grand Canyon summer atmosphere by reference to the previously measured composition of urban sources.

Experimental Methods

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. As seen in Figure 1, Indian Gardens is located at an elevation of about 3800 ft (1180m) in the Upper Sonoran Zone of the canyon, on the Tonto Plateau, in an area containing scrub brush blending into Pinyon-Juniper woodland above. Hopi Point is on the south rim of the canyon at an elevation of approximately 7000 ft (2174m), in a transition zone between the Upper Sonoran and the Boreal Zones, in an area influenced by Pinyon-Juniper woodland and Ponderosa Pine forests. Indian Gardens is

LIFE ZONES AND PLANT COMMUNITIES OF THE GRAND CANYON

Source: S. Whitney, 1982

Figure 1. Life zones and plant communities of the Grand Canyon. approximate location of Sampling sites, Indian Gardens and Hopi Point are indicated. Source: Whitney (1982).

located almost directly below Hopi Point, such that 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 oasis to separate the site to the extent possible from the local source of human activity and non-native plant life.

Ambient 24-hour average samples of both fine (particle diameter, $d_p < 2.1 \mu\text{m}$) and total airborne particulate matter were collected daily at Hopi Point throughout the month of August, 1989. Consecutive 72-hr average samples of airborne fine particles ($d_p < 1.5 \mu\text{m}$) 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 8 a.m., sampling start times centered on that morning hour, commencing daily at 6 a.m. at Hopi Point and at 9 a.m. 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 Figures 2 and 3. At Indian Gardens ambient air at a flow rate of 40 lpm was drawn through an AIHL-design cyclone separator (John and Reischl, 1980) that removed coarse particles larger than $1.5 \mu\text{m}$ in aerodynamic diameter. The output flow from the cyclone was then distributed to four 47mm diameter filter holders in parallel (filters A-D in Figure 2), each operated at a flow rate of 10 lpm. Each filter substrate was chosen to be compatible with a particular chemical analysis procedure. For the total aerosol samples (filters E-H in Figure 2), the same filter types were used in open-face filter holders that were protected from large particle sedimentation and rain by a Teflon-coated metal sheet. Critical flow orifices (Millipore, Bedford, MA) were used in series with each filter assembly to control the flow rate through each filter individually. Rotameters (Matheson, Seacaucus, NJ) were used to measure actual flow rates on-site for each sampling period to take into account small differences in the calibration of each critical orifice. The rotameters had an accuracy known from previous experiments to be $\pm 3\%$. To compensate for the shorter sampling times at Hopi Point, higher overall air flow rates were used, necessitating two cyclone separators and additional vacuum pumps at that site, as shown in Figure 3.

Figure 2. Schematic diagram of fine particle and total particle samplers used at Indian Gardens.

Figure 3. Schematic diagram of fine particle and total particle samplers used at Hopi Point.

Two 47mm diameter Teflon membrane filters (Teflo, Gelman, Ann Arbor, MI) 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 2.0 μm pore size filters were used for the total particle samples to prevent clogging over the sampling period. Two 47mm diameter quartz fiber filters (Tissuquartz 2500 QAO, Pallflex, Putnam, CT) were also used in each of the fine and total particle samplers. The quartz filters were baked at 750 C for 4 hours 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. Another Teflon filter sample in each set was intended for analysis of sulfate, nitrate, chloride, sodium, magnesium, and ammonium ions. 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 filters were used for the detailed organics analysis that provides the principal motivation for this work. Filters intended for organics analysis by gas chromatography/mass spectrometry were stored before and after use in annealed glass jars with solvent-washed Teflon lid liners to prevent contamination. All other filters were stored in petri dishes with tight-fitting lids and sealed with Teflon tape. The petri dishes containing quartz fiber filters were lined with aluminum foil that had been baked to prevent contamination from any organics. After collection, filters were put back in their respective dishes and sealed with Teflon tape. The filters were then kept frozen until analysis in the laboratory. This was done to prevent sample volatilization and chemical degradation.

Ambient particulate matter samples taken daily from August 2 through August 27 were acquired at Hopi Point along with field blanks taken on July 29 (2), 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 29 (2), August 26 and August 28. This results in 26 sampling periods at Hopi Point and 8 at Indian Gardens with 9 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. The other half of the field blanks were placed on samplers, the pumps were turned on for 10 seconds, and then the filters were taken off. All of these field blanks were processed in the same way as the regular samples.

Analytical Methods

Bulk Aerosol Composition:

Teflon filters designated A and E in Figures 2 and 3 were analyzed for particle mass by weighing the filters before and after use on a Mettler Model M-5S-A balance (Mettler Instruments, Highstown, NJ) after equilibration for 24 hours in a temperature and humidity controlled room (22 C and 50% relative humidity). The precision of this instrument is known (based on replicate measurements of samples and calibration filters) to be < 9 micrograms per filter. These same filters were then analyzed 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, Zr) using X-ray fluorescence (Dzubay, 1977) at NEA, Inc., Beaverton, OR.

The second Teflon filter of each set was analyzed for ionic material. Each filter was placed in a plastic specimen cup where 250 microliters of 100% ethanol was distributed evenly across the filter surface. Twenty ml of distilled water was then added along with a Teflon rod to keep the filter submerged. The cups were then sealed and placed on a shaker table for 3 hours in a refrigerated room. These extracts were then 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, CA). 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, 0.2, and 0.2 µg for chloride, nitrate and sulfate respectively. Analytical precisions were $\pm 2\%$ for ammonium ion, $\pm 5\%$ for sodium and magnesium, and $\pm 1\%$ for the species measured by ion chromatography.

One quartz fiber filter of each set was used for analysis of organic carbon, carbonate carbon, and elemental carbon at Sunset Laboratory by the thermal evolution and combustion technique of Johnson et al. (1981) as modified by Cary (1987). Detection limits for organic, carbonate, and elemental carbon were 0.9 micrograms per filter, with an analytical precision of $\pm 3.5\%$.

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. Unexpectedly high concentrations of Cu, Zn, Ag and related elements in proportions characteristic of electrical brass were found in some Hopi Point ambient fine particle samples but not in the corresponding total particle samples. This obvious anomaly is thought to arise from aerosol shed by the electrical motors used by the large number of air samplers operated there by several investigations in addition to our own. Metallic elements characteristic of electrical brass were not used in the data analyses that follow.

Organic Compound Determination

Sample Preparation:

The ambient aerosol samples collected on quartz fiber filters for organic compound determination were grouped to form four monthly composites, representing fine particles and total aerosol at Indian Gardens and Hopi Point, respectively. Static and dynamic field blank composites likewise were created for each site and particle size range. Laboratory procedural blank samples were prepared by compositing 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 top. A known quantity of perdeuterated tetracosane ($n\text{-C}_{24}\text{D}_{50}$) was spiked into each filter composite to serve as an extraction recovery standard.

Sample Extraction and Derivatization:

The extraction protocol described previously by Mazurek et al. (1987) was employed. Samples were extracted successively in three 15 ml portions of hexane followed by three 15 ml portions of a 2:1 benzene/iso-propanol mixture. Extraction occurred at room temperature assisted by mild ultrasonic agitation. After each extraction step the extracts were transferred to a volumetric flask, filtered and combined. 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.

GC/MS Analysis:

Mass spectrometric analysis was performed using a Finnigan 4000 quadrupole gas chromatograph/mass spectrometer (GC/MS) interfaced with an INCOS data acquisition system. Ionization was produced by electron impact with an electron energy of 70 eV. The scanning frequency was set at 0.5 sec^{-1} , ranging from 50 to 550 Daltons (Rogge et al. 1993b). 1-phenyldodecane was used as a coinjection standard. The chromatographic column used was a 30-m fused-silica DB-1701 column (bonded 86% dimethyl 14% cyanopropylphenyl polysiloxane, 0.25 μm film thickness, 0.32 mm i.d., J&W Scientific, Rancho Cordova, CA). Temperature programming consisted of injection at 65°C, isothermal hold at 65°C for 10 min, temperature increase of 10°C for 21 min, followed by an isothermal hold at 275°C for another 49 minutes.

High-Resolution Gas Chromatography:

Supplementary analyses were 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). The chromatographic column and temperature program used for HRGC analysis was identical to that described previously for the GC/MS system.

Compound Identification:

Compounds were identified and confirmed by a sequential process. First, compound identification was conducted by comparison of the unknown compound mass fragmentation pattern to the National Institute of Standards and Technology (NIST) mass spectral reference library, contained in the Finnigan 4000 GC/MS INCOS data system. Further comparison was made to: (1) an updated version of the NIST-library (IBM-AT, version 3), which provided additional search options; and to (2) the BNL DAS/ECD mass spectral data base which is a unique compilation of mass spectrometric fragmentation data and chromatographic factors (e.g., retention times, response factors, key fragmentations) for standard compounds and for molecular tracers obtained from unique source studies of particulate carbon emissions to the atmosphere (includes standards relevant to Grand Canyon vegetation, soil dust, and wood smoke aerosol data). Second, the preliminary identification of compounds is confirmed by comparison of their mass fragmentation patterns and elution times to that of authentic standards which are injected

onto the GC/MS system used here. For the Grand Canyon project, over 150 authentic standard compounds were analyzed to be used for quantitation by GC/MS analysis. Compound identification was judged: (a) positive, when the sample spectrum, standard spectrum and NIST-library spectrum were identical and also the retention time of the authentic standard and the sample compound were comparable; (b) probable, same as above, except no authentic standard was available, but the NIST-library spectrum and the DAS/ECD-library spectrum agreed very well with the sample spectrum; (c) possible, same as above, except that the sample mass fragmentation pattern contained additional ions from other compounds having minor peak coelution; and (d) tentative, when the sample spectrum revealed additional mass fragments from one or more coeluting compounds (noise) with substantial overlap.

Source Sampling:

Likely sources of particulate matter emissions to the Grand Canyon area atmosphere were examined. These sources sampled included plant fragments shed from the surface of local vegetation, smoke from campfire-like combustion of local wood, soil dust from Hopi Point, soil dust from Indian Gardens, and smoke from combustion of live and dead local vegetation.

To simulate the creation of particles that are shed from plant surfaces as leaves are brushed together by the wind, a composite sample of local vegetation was agitated in a clean Teflon bag. This vegetation composite consisted of Utah Juniper (118.0g), Banana Yucca (84.6g), Pinyon Pine (71.3g), Ponderosa Pine (36.6g), native grasses (15.2g) and sagebush (3.8g). Air that had been purified by passage through a HEPA filter, an activated carbon bed and a second particle filter was blown into the Teflon bag and air samples containing the source aerosol were simultaneously withdrawn from the bag. Samples of fine particle vegetative detritus and total aerosol vegetative detritus were collected on 47mm diameter quartz fiber and Teflon filter substrates as was described earlier for the ambient samples. System blank samples were taken before the first of these source tests by drawing purified air through the clean Teflon bag followed by filtration as described earlier.

Fine particle soil dust samples were prepared in an analogous manner. Bulk soil dust was placed in a clean Teflon bag and agitated as purified air was blown through the bag. Source samples were withdrawn at a total flow rate of 30 lpm through an AIHL-

design cyclone separator, to remove coarse particles, followed by division of the sample flow between several parallel 47mm diameter filter holders containing Teflon and pre-baked quartz fiber filters.

Wood smoke samples were generated by burning seasoned pine wood bought at a store located near the south rim of the Grand Canyon. The wood was burned outdoors in a metal tray lined with clean aluminum foil. Smoke from the fire was collected using the dilution sampler described by Hildemann et al. (1991) for their roofing tar pot experiments. The woodsmoke was diluted by 20 fold with purified dilution air in order to cause low vapor pressure organic vapors to condense onto the smoke particles as they would while the smoke plume cools in the atmosphere. Fine wood smoke particles were collected downstream of an AIHL-design cyclone separator by filtration onto 47mm diameter pre-fired quartz and Teflon filters, as before.

Smoke also can be produced by wildfires and forest fires that consume green or recently dead whole vegetation rather than just seasoned wood. In an attempt to examine such a source, two vegetation composites were created from mixed plant debris gathered at the Grand Canyon. Both a dead vegetation and a live vegetation composite were created. Each of these composites was burned separately on-site at the Grand Canyon under the supervision of Park personnel. The ambient aerosol samplers described earlier were used to sample within the ambient plume from these fires. Thus both fine particle and total aerosol samples were collected on pre-fired quartz fiber and Teflon filter substrates as in Figure 2.

Bulk chemical analysis of the source samples for trace elements by X-ray fluorescence, ionic species by ion chromatography, NH_4^+ by a colorimetric method, Na and Mg by AA, and EC, OC and carbonate carbon by thermal evolution and combustion analysis proceeded by the same methods as described earlier for the ambient samples. The organic compounds present in the source samples also were examined by GC/MS techniques, as described for the ambient samples.

Results

Aerosol Chemical Composition:

The average bulk chemical composition of the monthly average of each aerosol composite is shown in Figures 4-7, while the details of individual samples can be examined in Figures 8-11. At both Indian Gardens, and at 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 24.5% and 7.5% of the fine aerosol, respectively, nearly equaled by the 29.9% of the sample composed of organic compounds and 1% contributed by elemental carbon. Mineral dust is present as a minority contributor to the Indian Gardens fine aerosol, with calcium carbonate equal to 5% of that sample composite and other crustal oxides accounting for 13.1%. 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 vs. 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 14.6% of fine mass at Indian Gardens to 33.7% at Hopi Point. A portion of this unidentified mass usually is due to aerosol water present in the samples despite desiccation that cannot be measured by the methods employed here. Although the Grand Canyon is surrounded by desert, it in fact rained on several days during this experiment. The total aerosol samples shown in Figures 5 and 7 differ from the fine 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 must be structured to distinguish carbonate carbon from organic carbon, as was done in the present work.

Approximate airmass trajectories arriving at the Grand Canyon during August 1989 were computed at Brookhaven National Laboratory. Trajectories of 48 hours duration ending at 0400 hours and at 1600 hours PST daily were prepared by interpolation of 850 mb winds. In Table I, the origin of these trajectories is summarized. Graphs showing the airmass trajectories are reproduced in Appendix A.

Indian Gardens Fine Mean Concentrations

Figure 4.

Indian Gardens Total Mean Concentrations

Figure 5.

Hopi Pt. Fine Mean Concentrations

Figure 6.

Hopi Pt. Total Mean Concentrations

Figure 7.

INDIAN GARDENS FINE - AUG. 1989

Figure 8. Concentration and chemical composition of fine aerosol samples collected at Indian Gardens during August, 1989.

INDIAN GARDENS TOTAL - AUG. 1989

DATE

Figure 9. Concentration and chemical composition of total airborne particulate matter collected at Indian Gardens during August, 1989.

HOPI POINT FINE - AUGUST 1989

Figure 10. Concentration and chemical composition of fine aerosol samples collected at Hopi Point during August, 1989.

HOPI POINT TOTAL - AUGUST 1989

DATE

Figure 11. Concentration and chemical composition of total airborne particulate matter collected at Hopi Point, August 1989.

TABLE 1**Approximate Sources (48 hours earlier) of Air Masses Arriving at
The Grand Canyon During August, 1989**

<u>Date</u>	<u>Source of Air Mass</u>
August 2	Ocean/San Diego/Los Angeles
August 3	Ocean/San Diego/Baja California
August 4	Central Arizona
August 5	Baja California
August 6	Baja California
August 7	Central Arizona
August 8	New Mexico/Southern Arizona
August 9	Central Arizona/California Desert
August 10	Central Arizona
August 11	Ocean/Baja California
August 12	Mexico/California Desert
August 13	Nevada-Arizona Border
August 14	Sierras
August 15	California Desert
August 16	Central Arizona/Baja California
August 17	California Desert
August 18	Central/Southern Arizona
August 19	Baja California/Ocean
August 20	Ocean/Baja California
August 21	Ocean/Baja California/San Diego
August 22	Ocean/Baja California/San Diego
August 23	Baja California/San Diego/Ocean
August 24	Ocean/San Diego/Los Angeles/Nevada
August 25	Nevada/Ocean/San Diego
August 26	Southeastern California/Ocean/San Diego/Baja California
August 27	Ocean/San Diego

Fluctuations in the concentrations of each of the chemical components analyzed can be associated with changes in the wind trajectories as follows: (1) Sodium, magnesium, and chloride seem to fluctuate (for the most part) with changes in wind direction that involve the ocean as a source with the highest concentrations on days when air resided over the Pacific Ocean within the preceding 48 hours (particularly August 2-3 and August 19-24). This is not surprising since sea salt is primarily composed of these elements. (2) Nitrate and sulfate concentrations are shown in time series in Figures 12 - 13. Many of the highest nitrate levels recorded correspond to days when the prevailing wind trajectories passed near west coast major cities such as Los Angeles, San Diego or Tijuana on their way to the Grand Canyon. This is also not surprising since nitrogen oxides can be found in high concentrations in urban smog. Lower than average nitrate levels over the period August 9-18 are generally associated with transport over land from the south. Sulfur oxides are a major product of the combustion of sulfur-bearing fuels, and are also emitted from smelter operations. The largest sulfate values occur as the wind trajectories point to the south as a source (particularly August 9-10 and August 16) suggesting that the sources most responsible for large increases in sulfate levels during August 1989 may lie in this direction. 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, thus a more local source may also be important. (3) Fluctuations in ammonium ion levels correspond almost exactly to similar fluctuations in sulfate levels suggesting that they travel together as one unit. (4) Elemental and organic carbon concentrations are shown in time series in Figures 14 - 15. Elemental carbon levels are present at near their detection limit so apparent fluctuations in those values are not reliable enough to identify the wind direction from which this component might be transported. The ratio of elemental carbon to organic carbon 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) indicating that the Grand Canyon aerosol is enriched in organics from sources other than primary urban aerosol. (5) The organics levels fluctuate and do not appear to peak 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 Appendix A for the day of 8/6 and the early morning of 8/7). These organics may be coming primarily from local sources which would make directional inferences drawn from wind trajectory data for the Southwestern United States irrelevant. Detailed chemical analysis of the organic compounds present will be used to shed more light on the origin of the organics.

HOPI POINT FINE SULFATE/NITRATE - AUGUST 1989

Figure 12.

INDIAN GARDENS FINE SULFATE/NITRATE - AUGUST 1989

Figure 13.

HOPI POINT FINE EC/OC - AUGUST 1989

Figure 14. Organic carbon and elemental carbon concentrations at Hopi Point, August, 1989.

INDIAN GARDENS FINE EC/OC - AUGUST 1989

DATE

Figure 15. Organic carbon and elemental carbon concentrations at Indian Gardens, August, 1989.

Chemical Composition of Source Samples:

A material balance on the bulk chemical composition of those sources tested using the source test procedures of Hildemann et al. (1991) are shown in Figure 16.

Hopi Point and Indian Gardens fine particle soil dust samples contain only about 2% organic carbon by mass. Instead those soil dust samples are composed of roughly 85-90% mineral oxides plus calcium carbonate. Calcium carbonate is more abundant relative to other minerals in resuspended soil dust samples than in the actual ambient aerosol. This mismatch suggests that fine particle soil dust may be transported from distances greater than the immediate surroundings of the monitoring sites where the soil dust source samples were taken.

The pine woodsmoke sample shown in Figure 16 is composed almost entirely of organic carbon plus elemental carbon. The ratio of elemental carbon to organic carbon from this campfire - like combustion source test using local wood is quite high, approximately 2 parts EC to 1 part OC. Since elemental carbon is present in only minor amounts in the August 1989 ambient aerosol, it follows that campfire - like combustion of wood cannot be a major contributor to the organics in those ambient aerosol samples. Fireplace combustion of soft wood apparently produces better combustion conditions and a lesser relative amount of elemental carbon (Hildemann et al., 1991), indicating that the contribution of significant amounts of organics to the ambient aerosol from other modes of wood combustion cannot yet be ruled out.

The composition of the aerosol generated from the surfaces of vegetation as it is agitated as if by the wind is shown in the two bars at the right of Figure 16. Roughly half of the fine aerosol and the total aerosol from this source consists of organic compounds accompanied by negligible amounts of elemental carbon and thus shows a composition potentially compatible with that of the atmospheric organic aerosol. The next largest component of the vegetative detritus source is deposited mineral matter resuspended from the surfaces of the vegetation.

Analysis of the samples of burning green and dead mixed vegetation shows qualitatively that these sources emit almost entirely organic compounds plus elemental carbon. The elemental carbon is mostly in the fine particle fraction. Such dense smoke

Grand Canyon Source Samples

Figure 16. The Chemical composition of particles emitted from Hopi Point fine soil dust, Indian Gardens fine soil dust, campfire - like combustion of seasoned pine (wood fire), fine particle vegetative detritus, and total aerosol vegetative detritus

was produced by these fires that the source samples taken were overloaded relative to the measurement limits of the EC/OC method used for bulk chemical analysis and thus a detailed quantitative material balance on these source samples cannot be constructed.

Origin of Organic Compounds:

The monthly average ambient aerosol composites collected at Hopi Point and at Indian Gardens were extracted and examined by gas chromatography/mass spectrometry. Each sample was searched for the more than 500 compounds listed in Table II. It is just as important to note those compounds that were not detected as it is to indicate those found because the absence of certain compounds that are characteristic of a major possible source type indicates that the contribution from that potential source is negligible.

The major organic compounds found in the Grand Canyon ambient aerosol during August 1989 include: (1) surface waxes (n-alkanes, n-alkanoic acids and n-alkanol homologous series) derived from local vegetation; (2) terpenes (C₁₀ and C₂₀ compounds) that can be correlated to the live and dead vegetation source samples collected from the dominant plant taxa present at Hopi Point and Indian Gardens; (3) partially oxidized terpenes; and (4) highly oxidized lower molecular weight organic acids (<10 carbon atoms). Categories (1) - (3) above can be correlated to the live and dead vegetation aerosol source samples produced by agitating composites of live and dead vegetation collected from the dominant plant taxa present at Hopi Point and Indian Gardens, as described in Appendix B to this report. The highly oxidized lower molecular weight organic acids described in category (4) above correspond to compounds commonly associated with secondary organic aerosols formed from the atmospheric reaction of gas phase precursors (Grosjean, 1977).

The four ambient aerosol composites of Table II showed only small amounts of the woodsmoke marker compounds that were collected from local sources of seasoned pine wood smoke and from combustion of vegetation from Hopi Point. In particular the woodsmoke marker compound retene is not found in these ambient samples collected in August 1989, even though we have found such compounds in samples taken in prior years when burning was known to have occurred in the area (Mazurek et al., 1991).

Table II

Organic Compounds Evaluated by GC/MS Analysis for Grand Canyon Ambient Aerosol Samples

	COMPOUND IDENTIFICATION:			
	a=positive; b=probable; c=possible; d=tentative nd=not detected; ns=not searched; tr=trace			
	F7204 Hopi Pt. FINE Composite	F7209 Hopi Pt. TOTAL Composite	F7203 Indian Gds FINE Composite	F7208 Indian Gds TOTAL Composite
HOMOLOGOUS COMPOUND SERIES				
n-Alkanes				
n-Decane	nd	nd	nd	nd
n-Dodecane	nd	nd	nd	nd
n-Tridecane	nd	nd	nd	nd
n-Tetradecane	nd	nd	nd	nd
n-Pentadecane	nd	nd	nd	nd
n-Hexadecane	nd	nd	nd	nd
n-Heptadecane	nd	nd	nd	nd
n-Octadecane	nd	a,tr	nd	nd
n-Nonadecane	nd	nd	nd	nd
n-Cosane	nd	a,tr	nd	a,tr
n-Heneicosane	nd	b	b	b
n-Docosane	nd	a	a	a
n-Tricosane	b, tr	b	b	b
n-Tetracosane	a,tr	a	a	a
n-Pentacosane	b	b	b	b
n-Hexacosane	a	a	a	a
n-Heptacosane	b	b	b	b
n-Octacosane	a	a	a	a
n-Nonacosane	b	b	b	b
n-Triacontane	a	a	a	a
n-Hentriacontane	b	b	b	b
n-Dotriacontane	a	a	a	a,tr
n-Tritriacontane	b	b	b	b,tr
n-Tetatriacontane	a	a	a	a,tr
n-Pentatriacontane	nd	nd	b,tr	nd
n-Hexatriacontane	nd	nd	a,tr	nd

Table II

COMPOUND IDENTIFICATION:					a=positive; b=probable; c=possible; d=tentative nd=not detected; ns=not searched; tr=trace		
F7204 Hopi Pt. FINE Composite	F7209 Hopi Pt. TOTAL Composite	F7203 Indian Gds FINE Composite	F7208 Indian Gds TOTAL Composite				
n-Alkanoic Acids (as methyl esters)							
n-Hexanoic acid, methyl ester	a, tr	a	a	a			a
n-Heptanoic acid, methyl ester	nd	nd	b	b, tr			
n-Octanoic acid, methyl ester	a	a	a	a			a
n-Nonanoic acid, methyl ester	a	a	a	a			a
n-Decanoic acid, methyl ester	a	a	a	a			a
n-Undecanoic acid, methyl ester	a	a	a	a			a
n-Dodecanoic acid, methyl ester	a	a	a	a			a
n-Tridecanoic acid, methyl ester	a	a	a	a			a
n-Tetradecanoic acid, methyl ester	a	a	a	a			a
n-Pentadecanoic acid, methyl ester	a	a	a	a			a
n-Hexadecanoic acid, methyl ester	a	a	a	a			a
n-Heptadecanoic acid, methyl ester	a	a	a	a			a
n-Octadecanoic acid, methyl ester	a	a	a	a			a
n-Nonadecanoic acid, methyl ester	a	a	a, tr	a			a
n-Eicosanoic acid, methyl ester	a	a	a, tr	a			a
n-Heneicosanoic acid, methyl ester	a	a	a, tr	a			a
n-Docosanoic acid, methyl ester	a	a	a	a, tr			a
n-Tricosanoic acid, methyl ester	a	a	a	a			a
n-Tetracosanoic acid, methyl ester	a	a	a, tr	a, tr			a
n-Pentacosanoic acid, methyl ester	a	a	a, tr	a, tr			a
n-Hexacosanoic acid, methyl ester	a	a	a, tr	a, tr			a
n-Heptacosanoic acid, methyl ester	a	a	a, tr	a, tr			a
n-Octacosanoic acid, methyl ester	a	a	a, tr	a			a
n-Nonacosanoic acid, methyl ester	nd	nd	nd	nd			nd
n-Triacontanoic acid, methyl ester	a	a	a, tr	a, tr			a
n-Dotriacontanoic acid, methyl ester	b	b, tr	b, tr	b, tr			b, tr
n-Tetracontanoic acid, methyl ester	nd	nd	nd	nd			nd
n-Alkanols							
3-Hexanol, 3,5-dimethyl	nd	nd	c	nd			nd
1-Decanol	nd	nd	nd	nd			nd

Table II

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	F7204 Hopl Pt. FINE Composite	F7209 Hopl Pt. TOTAL Composite	F7203 Indian Gds FINE Composite	F7208 Indian Gds TOTAL Composite
1-Tetradecanol	nd	nd	nd	nd
1-Heptadecanol	nd	nd	nd	nd
1-Octadecanol	nd	nd	nd	nd
1-Nonadecanol	nd	nd	nd	nd
1-Eicosanol	nd	nd	nd	nd
1-Docosanol	nd	nd	nd	nd
1-Tetracosanol	nd	nd	nd	nd
1-Pentacosanol	nd	nd	nd	nd
1-Hexacosanol	nd	nd	nd	nd
1-Octacosanol	nd	nd	nd	nd
1-Triacontanol	a	a	nd	a
1-Dotriacontanol	a,tr	a	nd	nd
	nd	nd	nd	nd
Wax Components -- Series 1				
Wax component scan 976	nd	nd	nd	nd
Wax component scan 1046	nd	nd	nd	nd
Wax component scan 1051	nd	nd	nd	nd
Wax component scan 1055	nd	nd	nd	nd
Wax component scan 1157	nd	nd	nd	nd
Wax component scan 1163	nd	nd	nd	nd
Wax component scan 1217	nd	nd	nd	nd
Wax component scan 1246	nd	nd	nd	nd
Wax component scan 1320	nd	nd	nd	nd
Wax component scan 1329	nd	nd	nd	nd
Wax component scan 1568	nd	nd	nd	nd
Wax component scan 1581	nd	nd	nd	nd
Wax component scan 1585	nd	nd	nd	nd
Wax Components -- Series 2				
Wax component scan 1027	nd	nd	nd	nd
Wax component scan 1040	nd	nd	nd	nd
Wax component scan 1123	nd	nd	nd	nd

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	F7204 Hopl Pt. FINE Composite	F7209 Hopl Pt. TOTAL Composite	F7203 Indian Gds FINE Composite	F7208 Indian Gds TOTAL Composite
Wax component scan 1154	nd	nd	nd	nd
Wax component scan 1175	nd	nd	nd	nd
Wax component scan 1187	nd	nd	nd	nd
Wax component scan 1211	nd	nd	nd	nd
Wax component scan 1272	nd	nd	nd	nd
Wax component scan 1277	nd	nd	nd	nd
Wax component scan 1281	nd	nd	nd	nd
Wax component scan 1301	nd	nd	nd	nd
Wax component scan 1348	nd	nd	nd	nd
Wax component scan 1369	nd	nd	nd	nd
Wax component scan 1387	nd	nd	nd	nd
Wax component scan 1495	nd	nd	nd	nd
Wax component scan 1540	nd	nd	nd	nd
n-Alkan-2-ones				
2-Alkanone scan 630	nd	nd	nd	nd
2-Pentadecanone, 6,10,14-trimethyl-	c	d	c	c
2-Alkanone scan 756	nd	nd	nd	nd
2-Nonacosanone	nd	d, tr	nd	nd
2-Triacontanone	nd	nd	nd	nd
2-Hentriacontanone	nd	nd	nd	nd
2-Tritriacontanone	nd	nd	nd	nd
2-Alkanone scan 1529	nd	nd	nd	nd
n-Aldehydes				
n-Aldehyde scan 976	nd	nd	nd	nd
Hexacosanal	nd	nd	nd	nd
Octacosanal	nd	nd	nd	nd
2-Octadecenal	c	c	nd	nd
Triacontanal	nd	nd	nd	nd
Dotriacontanal	nd	nd	nd	nd
Tetracontanal	nd	nd	nd	nd

Table II

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	F7204 Hopi Pt. FINE Composite	F7209 Hopi Pt. TOTAL Composite	F7203 Indian Gds FINE Composite	F7208 Indian Gds TOTAL Composite
TERPENES				
Monoterpenoids (C10 Compounds)				
Cineole (Eucalyptol; cajeputol)	nd	nd	nd	nd
Linalool oxide	nd	nd	nd	nd
Camphor	a	a, tr	a	a, tr
4-Terpineol (p-Menth-1-en-4-ol, (R)-, (-); 3-cyclohexen-1-ol, 4-methyl-1-(1-met	nd	nd	nd	nd
Monoterpenoid scan 456	d	nd	nd	nd
Borneol	nd	nd	nd	nd
alpha-Terpineol (3-Cyclohexene-1-methanol, alpha, alpha4-trimethyl-)	nd	nd	nd	nd
Monoterpenoid scan 491	nd	nd	nd	nd
Bornyl acetate	d	d, tr	d, tr	nd
Monoterpenoid scan 515	nd	nd	nd	nd
Verbenone (Bicyclo[3.1.1]hept-3-en-2-one, 4,6,6-trimethyl-)	d	c, tr	d	nd
Menthol (Cyclohexanol, 5-methyl-2-(1-methylethyl)-, (1alpha-2beta-S)-)	nd	nd	nd	nd
2-Norpinanone, 3,6,6-trimethyl- (Bicyclo[3.1.1]heptan-2-one, 3,6,6-trimethyl-	c	c	c	d
Monoterpenoid acid scan 575	nd	nd	d	d
Monoterpenoid acid scan 584	c	nd	d	d
Monoterpenoid scan 599	d	d	nd	nd
Monoterpenoid scan 601	d	d	d	d
Monoterpenoid scan 634	nd	nd	nd	nd
Camphorsulfonic acid	nd	nd	nd	nd
Sesquiterpenoids (C15 Compounds)				
Cadina-1(10),6,8-triene (5,6,7,8-Tetrahydrocadalene)	nd	nd	nd	nd
Sesquiterpenoid scan 594	nd	nd	nd	nd
beta- or delta-Cadinene (Naphthalene, 1,2,3,5,6,8a-hexahydro-4,7-dimethyl-1-(	nd	nd	nd	nd
Calamenene (Naphthalene, 1,2,3,4-tetrahydro-1,6,7-trimethyl-)	nd	nd	nd	nd
Farnesol (2,6,10-Dodecatrien-1-ol, 3,7,11-trimethyl-	nd	nd	nd	nd
Nerolidol (1,6,10-Dodecantrien-3-ol, 3,7,11-trimethyl-)	nd	nd	nd	nd

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	F7204 Hopi Pt. FINE Composite	F7209 Hopi Pt. TOTAL Composite	F7203 Indian Gds FINE Composite	F7208 Indian Gds TOTAL Composite			
Guaiol	nd	nd	nd	nd	nd		nd
Sesquiterpenoid scan 657	nd	nd	nd	nd	nd		nd
Sesquiterpenoid scan 658	nd	nd	nd	nd	nd		nd
Caryophyllene (VAN)	nd	nd	nd	nd	nd		nd
Sesquiterpenol scan 660	nd	nd	nd	nd	nd		nd
beta- or delta-Cadinol (1-Naphthalenol, 1,2,3,4,4A,7,8,8A-octahydro-1,6-dimeth	nd	nd	nd	nd	nd		nd
Sesquiterpenoid scan 679	nd	nd	nd	nd	nd		nd
Sesquiterpenoid scan 683	nd	nd	nd	nd	nd		nd
Ylangene	nd	nd	nd	nd	nd		nd
Cedreanol	nd	nd	nd	nd	nd		nd
1H-3a,7-Methanoazulen-5-ol, octahydro3,8,8-trimethyl-6-methylene- (Cedren	nd	nd	nd	nd	nd		nd
Sesquiterpenoid scan 670	nd	nd	nd	nd	nd		nd
Sesquiterpenoid scan 674	nd	nd	nd	nd	nd		nd
Sesquiterpenoid scan 705	nd	nd	nd	nd	nd		nd
Eudesmol (2-Naphthalenemethanol, decahydro-, alpha,alpha,4A-trimethyl-8-m	nd	nd	nd	nd	nd		nd
Cadinol/Cedrol?	nd	nd	nd	nd	nd		nd
Santalol	nd	nd	nd	nd	nd		nd
Copaene	nd	nd	nd	nd	nd		nd
Longifolene [1S-(1alpha,3betabeta,4alpha,8betabeta)]-decahydro-4,8,8-trimeth	nd	nd	nd	nd	nd		nd
Sesquiterpenol scan 660	nd	nd	nd	nd	nd		nd
(+)-Longifolane	nd	nd	nd	nd	nd		nd
2H-Cyclopropa[A]naphthalen-2-one	nd	nd	nd	nd	nd		nd
Sesquiterpenol scan 741	nd	nd	nd	nd	nd		nd
Eudesmol isomer (2-Naphthalenemethanol, decahydro-, alpha, alpha..)	nd	nd	nd	nd	nd		nd
Thujopsene	nd	nd	nd	nd	nd		nd
Diterpenoids (C20 Compounds)							
Manoyl oxide or epimanoyl oxide (1H-Naphtho[2,1b]pyran, 3-ethenyldodecahy	c	c	c		c		d,tr
Diterpenoid scan 1004	nd	nd	nd		nd		nd
Labdane (Labdene)	nd	nd	nd		nd		nd
Labdatiene	nd	nd	nd		nd		nd
Triterpenoids (C30 Compounds)							

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	F7204 Hopi Pt. FINE Composite	F7209 Hopi Pt. TOTAL Composite	F7203 Indian Gds FINE Composite	F7208 Indian Gds TOTAL Composite			
3beta-Lupeol-TMS ether	ns	ns	ns	ns		ns	ns
Erythrodiol-TMS ether	ns	ns	ns	ns		ns	ns
Friedelin	nd	nd	nd	nd		nd	nd
Oleanolic acid	nd	nd	nd	nd		nd	nd
(3beta)-Olean-12-ene-3,28-diol (Erythrodiol)	nd	nd	nd	nd		nd	nd
17beta(H),21alpha(H)-Bishomohpan-32-ol-TMS ether	ns	ns	ns	ns		ns	ns
9-Ferrene	nd	nd	nd	nd		nd	nd
Allobetulin-TMS ether	ns	ns	ns	ns		ns	ns
Betulin	nd	nd	nd	nd		nd	nd
Betulin-TMS ether	ns	ns	ns	ns		ns	ns
Friedelin-3beta-ol-TMS ether	ns	ns	ns	ns		ns	ns
Friedelin-5alpha-ol-TMS ether	ns	ns	ns	ns		ns	ns
Glycyrhethinic acid-di-TMS ether	ns	ns	ns	ns		ns	ns
Lup-20(30)-ene	nd	nd	nd	nd		nd	nd
Lupeol	nd	nd	nd	nd		nd	nd
Methyl 3beta-hydroxyolean-12-en-28-oate	nd	nd	nd	nd		nd	nd
Methyl betulinate-TMS ether	ns	ns	ns	ns		ns	ns
Methyl morolate-TMS ether (Morolic acid)	ns	ns	ns	ns		ns	ns
Methyl oleanate-TMS ether	ns	ns	ns	ns		ns	ns
Methyl ursolate-TMS ether	ns	ns	ns	ns		ns	ns
Moradiol-TMS ether	ns	ns	ns	ns		ns	ns
Ursolic acid	nd	nd	nd	nd		nd	nd
alpha-Amyrin	nd	nd	nd	nd		nd	nd
alpha-Amyrin-TMS ether	ns	ns	ns	ns		ns	ns
beta-Amyrin	nd	nd	nd	nd		nd	nd
beta-Amyrin-TMS ether	ns	ns	ns	ns		ns	ns
WOOD SMOKE MARKERS							
Resin Compounds							
Phenanthrene, 7-ethenyl-1,2,3,4,4a,4b,5,6,7,8,10,10a-dodecahydro...	nd	nd	nd	nd		nd	nd

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	F7204 Hopi Pt. FINE Composite	F7209 Hopi Pt. TOTAL Composite	F7203 Indian Gds FINE Composite	F7208 Indian Gds TOTAL Composite			
1-Phenanthrenecarboxaldehyde, 1,2,3,4,4A,9,10,10A-octahydro-1,4-...	nd	nd	nd	nd	nd	nd	nd
1-Phenanthrenecarboxaldehyde...	nd	nd	nd	nd	nd	nd	nd
Dehydroabietane (Phenanthrene, 1,2,3,4,4a,9,10,10a-octahydro-1,1,4a-trimeth	nd	nd	nd	nd	nd	nd	nd
Simonellite	nd	nd	nd	nd	nd	nd	nd
Podocarpa-8,11,13-trien-15-oic acid, methyl ester (R- and S-isomers)	a, tr	a	nd	nd	nd	nd	nd
8,15-Pimaradien-18-oic acid, methyl ester	nd	nd	nd	nd	nd	nd	nd
1-Phenanthrenecarboxaldehyde, 7-ethenyl-1,2,3,4,4A,4B,5,6,7,9,...	nd	nd	nd	nd	nd	nd	nd
8,15-Isopimaradien-18-oic acid, methyl ester	nd	nd	nd	nd	nd	nd	nd
1-Pimaric acid, methyl ester	nd	nd	nd	nd	nd	nd	nd
Methyl 16,17-bisnorhydroabietate	nd	nd	nd	nd	nd	nd	nd
Sandaracopimaric acid, methyl ester	nd	nd	nd	nd	nd	nd	nd
Retene	nd	nd	nd	nd	nd	nd	nd
Isopimaric acid, methyl ester	nd	nd	nd	nd	nd	nd	nd
1-Phenanthrenecarboxylic acid, 1,2,3,4,4A,4B,5,6,7,9,10,10A-Dodecahydro...	nd	nd	nd	nd	nd	nd	nd
Dehydroabietic acid, methyl ester	a	a	a	a	a	a	a
13-Isopropyl-5a-podocarpa-6,8,11,13-tetraen-16-oic acid, methyl ester (R-isom	b, tr	b, tr	b, tr	b, tr	b, tr	b, tr	b, tr
1-Phenanthrenecarboxylic acid, 7-ethenyl-...	nd	nd	nd	nd	nd	nd	nd
Abietic acid, methyl ester	nd	nd	nd	nd	nd	nd	nd
13-Isopropyl-5a-podocarpa-6,8,11,13-tetraen-16-oic acid, methyl ester (S-isom	nd	d	d	nd	nd	nd	nd
1-Phenanthrenecarboxylic acid, 7-ethenyl-1,2,3,4,4A...	nd	nd	nd	nd	nd	nd	nd
1-Phenanthrenecarboxylic acid, 7-ethenyl, 1,2,3,4,4A,...	nd	nd	nd	nd	nd	nd	nd
1-Phenanthrenecarboxaldehyde, 1,2,3,4,4A...	nd	nd	nd	nd	nd	nd	nd
7-Oxodehydroabietic acid, methyl ester (7-Ketodehydroabietic acid, methyl est	a, tr	a	a, tr	a, tr	a, tr	a	a
Bisnorsimonellite	nd	nd	nd	nd	nd	nd	nd
Norsimonellite (1,2,3,4-Tetrahydroretene)	nd	nd	nd	nd	nd	nd	nd
Dehydro-1-epiabietate (Callitrisic acid, methyl ester)	nd	nd	nd	nd	nd	nd	nd
Podocarpic acid, 12-methoxy, methyl ester, (Methyl o-Methylpodocarpate)	nd	nd	nd	nd	nd	nd	nd
2,10-Phenanthrenediol, 4B,5,6,7,8,8A,9,10-octahydro-4B,8,8-trimethyl...	c, tr	c, tr	c, tr	d, tr	d, tr	d, tr	d, tr
Wood Lignan/Lignin Components							
Methoxybenzene (Anisole)	b	b	b	b	b	b	b
Phenol, 4-methoxy- (p-guaiacol)	nd	nd	nd	nd	nd	nd	nd
Phenol, 2-methoxy-4-methyl- (4-Methylguaiacol)	nd	nd	nd	nd	nd	nd	nd

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	F7204 Hopi Pt. FINE Composite	F7209 Hopi Pt. TOTAL Composite	F7203 Indian Gds FINE Composite	F7208 Indian Gds TOTAL Composite		
Benzene, 1,4-dimethoxy-2-methyl-	nd	nd	nd	nd	nd	nd
Benzene, 3,4-dimethoxy-1-methyl	nd	nd	nd	nd	nd	nd
Phenol, 2-methoxy-4-propyl- (1-Guaiacylpropane)	nd	nd	nd	nd	nd	nd
1,2-Benzenediol (Pyrocatechol, Catechol)	nd	nd	nd	nd	nd	nd
Phenol, 2,6-dimethyl- (Xylenol)	nd	nd	nd	nd	nd	nd
Phenol, 2-methoxy-4-(2-propenyl)- (Eugenol)	nd	nd	nd	nd	nd	nd
Phenol, 2-methoxy-4-(1-propenyl)- (Isoeugenol)	nd	nd	nd	nd	nd	nd
Phenol, (E)-2-methoxy-5-(1-propenyl)- (trans-m-propenyl guaiacol)	nd	nd	nd	nd	nd	nd
Benzaldehyde, 4-hydroxy-3-methoxy- (Vanillin)	nd	nd	nd	nd	nd	nd
Benzaldehyde, 3,4-dimethoxy- (Vanillin, methyl ester; Veratraldehyde)	nd	nd	nd	nd	nd	nd
Benzoic acid, 3,4-dimethoxy-, methyl ester (Vanillic acid, methyl ester; Veratric	nd	nd	nd	nd	nd	nd
2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)- (Guaiacylacetone; acetonyl guaia	nd	nd	nd	nd	nd	nd
Benzaldehyde, 3,4,5-trimethoxy- (Syringaldehyde methyl ether)	nd	nd	nd	nd	nd	nd
Benzeneacetic acid, 3,4-dimethoxy-, methyl ester (Homovanillic acid, methyl e	nd	nd	nd	nd	nd	nd
Phenol, 4-(3-hydroxy-1-propenyl)-2-methoxy- (Coniferyl alcohol)	nd	nd	nd	nd	nd	nd
Ethanone, 1-(2-naphthalenyl)-	nd	nd	nd	nd	nd	nd
Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)	nd	nd	nd	nd	nd	nd
Benzeneacetic acid, 4-hydroxy-3-methoxy-, methyl ester	nd	nd	nd	nd	nd	nd
Benzeneacetic acid, 4-hydroxy-3-methoxy- (Homovanillic acid; 4-carboxymeth	nd	nd	nd	nd	nd	nd
Benzaldehyde, 4-hydroxy-3,5-dimethoxy- (Syringaldehyde)	nd	nd	nd	nd	nd	nd
2-Propanone, 1-(3,4,5-trimethoxyphenyl)- (1-Syringylethanone methyl ether)	nd	nd	nd	nd	nd	nd
Ethanone, 1-(4-Hydroxy-3,5-dimethoxyphenyl)- (4-Acetylsyringol)	nd	nd	nd	nd	nd	nd
2-Propanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)- (1-Syringylethanone; acetone	nd	nd	nd	nd	nd	nd
Methane, bis(3,4-dimethoxyphenyl)-	nd	nd	nd	nd	nd	nd
Benzene, 1,1'-(1,2-ethanediyl)bis[3-hydroxy-4-methoxy-]- (Divanillyl)	nd	nd	nd	nd	nd	nd
Divanillylmethane	nd	nd	nd	nd	nd	nd
Tetrahydro-3,4-diveratrylfuran ((+)-3,4-diveratryltetrahydrofuran)	nd	nd	nd	nd	nd	nd
Tetrahydro-3-vanillyl-4-veratrylfuran	nd	nd	nd	nd	nd	nd
Tetrahydro-3,4-divanillylfuran	nd	nd	nd	nd	nd	nd
19-Norabieta-4(18),8,11,13-tetraene	nd	nd	nd	nd	nd	nd
Furanone, dihydro-3,4-diveratryl-2(3H)-	nd	nd	nd	nd	nd	nd
Furanone, dihydro-3-(2',3',4'-trimethoxyphenyl)-4-veratryl-2(3H)- (and isomers)	nd	nd	nd	nd	nd	nd
Furanone, dihydro-3,4-bis[(4-hydroxy-3-methoxyphenyl)methyl]- (3R-trans)-2(3	nd	nd	nd	nd	nd	nd
1,2-Divanillylethane	nd	nd	nd	nd	nd	nd

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F7204 Hopi Pt. FINE Composite	F7209 Hopi Pt. TOTAL Composite	F7203 Indian Gds FINE Composite	F7208 Indian Gds TOTAL Composite		
13-Methylpodocarpa-8,11,13-triene	nd	nd	nd		nd
19-Norabieta-4,8,11,13-tetraene	nd	nd	nd		nd
19-Norabieta-8,11,13-triene	nd	nd	nd		nd
2-Propanone, 1-(3,4-dimethoxyphenyl)- (Guaiacacetone methyl ether)	nd	nd	nd		nd
Abieta-7,13-diene	nd	nd	nd		nd
Benzene, 1,1'-(1,2-ethanediyl)bis[4-methoxy-]- (Dianisyl)	nd	nd	nd		nd
Benzeneacetic acid, 4-methoxy- (Homoanisic acid)	nd	nd	nd		nd
Benzeneacetic acid, 4-methoxy-, methyl ester (Homoanisic acid, methyl ester)	nd	nd	nd		nd
Benzoic acid, 3,4,5-trimethoxy-, methyl ester (Syringic acid, methyl ester)	nd	nd	nd		nd
Benzoic acid, 2,4-dimethoxy- (Veratric acid)	nd	nd	nd		nd
Benzoic acid, 4-hydroxy-3,5-dimethoxy- (Syringic acid)	nd	nd	nd		nd
Benzoic acid, 4-hydroxy-3-methoxy- (Vanillic acid)	nd	nd	nd		nd
Bisguaiacylsyringyl	nd	nd	nd		nd
Dehydroabietin	nd	nd	nd		nd
Disyringyl	nd	nd	nd		nd
Disyratryl	nd	nd	nd		nd
Ethane, bis(3,4,5-trimethoxyphenyl)-	nd	nd	nd		nd
Furanone, dihydrovanillylsyringyl-2(3H)- (and isomers)	nd	nd	nd		nd
Phenol, 2-methoxy (Guaiacol)	nd	nd	nd		nd
Phenol, 2-methyl (o-Cresol)	nd	nd	nd		nd
Phenol, 3-methyl (m-Cresol)	nd	nd	nd		nd
Phenol, 4-methyl (p-Cresol)	nd	nd	nd		nd
AROMATIC HYDROCARBONS					
Aromatic Hydrocarbons (unsubstituted)					
Benzene, 1,2-dimethyl- (o-Xylene)	nd	nd	nd		nd
Benzene, 1-methylethyl- (Isopropylbenzene)	nd	nd	nd		nd
1H-Indene, 2,3-dihydro- (Indan)	nd	nd	nd		nd
Benzene, 2,2-dimethylpropyl- (Neopentylbenzene)	nd	nd	nd		nd
Benzene, 1,2,3,4-Tetramethyl-	nd	nd	nd		nd
Naphthalene	nd	nd	nd		nd

Table II

COMPOUND IDENTIFICATION:					a=positive; b=probable; c=possible; d=tentative nd=not detected; ns=not searched; tr=trace		
	F7204 Hopi Pt. FINE Composite	F7209 Hopi Pt. TOTAL Composite	F7203 Indian Gds FINE Composite	F7208 Indian Gds TOTAL Composite			
Benzene, 1,3,4-Tris(1-methylethyl)- (1,3,5-Triisopropylbenzene)	nd	nd	nd	nd			nd
Naphthalene, 2-methyl-	nd	nd	nd	nd			nd
Naphthalene, 1-methyl-	nd	nd	nd	nd			nd
Naphthalene, 2,6-dimethyl-	nd	nd	nd	nd			nd
Benzene, hexamethyl-	nd	nd	nd	nd			nd
Acenaphthene	nd	nd	nd	nd			nd
Naphthalene, 2,3,5-trimethyl-	nd	nd	nd	nd			nd
Fluorene	nd	nd	nd	nd			nd
Fluorene, 2-methyl-	nd	nd	nd	nd			nd
Phenanthrene	nd	nd	nd	nd			nd
Anthracene	nd	nd	nd	nd			nd
Methyl phenanthrene	nd	nd	nd	nd			nd
4H-Cyclopenta[def]phenanthrene	nd	nd	nd	nd			nd
Methyl phenanthrene	nd	nd	nd	nd			nd
Methyl phenanthrene	nd	nd	nd	nd			nd
Naphthalene, 2-phenyl-	nd	nd	nd	nd			nd
C2 Phenanthrene	nd	nd	nd	nd			nd
Fluoranthene	nd	nd	nd	nd			nd
Pyrene	nd	nd	nd	nd			nd
Acphenanthrylene	nd	nd	nd	nd			nd
C3 Phenanthrene	nd	nd	nd	nd			nd
Benzo[c]fluorene	nd	nd	nd	nd			nd
2,3-Benzofluorene (11H-Benzo[b]fluorene)/1,2-Benzofluorene (11H-Benzo[a]fluorene)	nd	nd	nd	nd			nd
1,1'-Binaphthalene	nd	nd	nd	nd			nd
Benzo[c]phenanthrene	nd	nd	nd	nd			nd
Benzo[ghi]fluoranthene	nd	nd	nd	nd			nd
Dimethyl anthracene/phenanthrene	nd	nd	nd	nd			nd
Cyclopenta(cd)pyrene	nd	nd	nd	nd			nd
Benz[a]anthracene	nd	nd	nd	nd			nd
Chrysene/triphenylene (coelute)	nd	nd	nd	nd			nd
Triphenylene/chrysene (coelute)	nd	nd	nd	nd			nd
Benzo[k]fluoranthene	nd	nd	nd	nd			nd
Benzo[b]fluoranthene (Benz[e]acephenanthrylene)	nd	nd	nd	nd			nd
Benzo[j]fluoranthene	nd	nd	nd	nd			nd

Table II

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	F7204 Hopi Pt. FINE Composite	F7209 Hopi Pt. TOTAL Composite	F7203 Indian Gds FINE Composite	F7208 Indian Gds TOTAL Composite			
Benzo[e]pyrene	nd	nd	nd	nd	nd	nd	nd
Benzo[a]pyrene	nd	nd	nd	nd	nd	nd	nd
Perylene	nd	nd	nd	nd	nd	nd	nd
Aromatic MW=266	nd	nd	nd	nd	nd	nd	nd
Anthracene, 9,10-diphenyl-	nd	nd	nd	nd	nd	nd	nd
Aromatic MW=266	nd	nd	nd	nd	nd	nd	nd
Aromatic MW=278	nd	nd	nd	nd	nd	nd	nd
Aromatic MW=266	nd	nd	nd	nd	nd	nd	nd
Aromatic MW=278	nd	nd	nd	nd	nd	nd	nd
Aromatic MW=278	nd	nd	nd	nd	nd	nd	nd
Aromatic MW=276	nd	nd	nd	nd	nd	nd	nd
Aromatic MW=276	nd	nd	nd	nd	nd	nd	nd
Aromatic MW=276	nd	nd	nd	nd	nd	nd	nd
Indeno[1,2,3-cd]fluoranthene	nd	nd	nd	nd	nd	nd	nd
Benzo[b]triphenylene	nd	nd	nd	nd	nd	nd	nd
Indeno[1,2,3-cd]pyrene	nd	nd	nd	nd	nd	nd	nd
Dibenz[a,h]anthracene	nd	nd	nd	nd	nd	nd	nd
Methyl dibenz[a,h]anthracene/benzo[b]triphenylene/benzo[b]chrysene	nd	nd	nd	nd	nd	nd	nd
Benzo[g,h,i]perylene	nd	nd	nd	nd	nd	nd	nd
Dibenzo[def,mno]chrysene (Anthanthrene)	nd	nd	nd	nd	nd	nd	nd
Aromatic MW=276	nd	nd	nd	nd	nd	nd	nd
Aromatic MW=300	nd	nd	nd	nd	nd	nd	nd
Coronene	nd	nd	nd	nd	nd	nd	nd
1,2,4,5-Dibenzopyrene (Naphtho[1,2,3,4-def]chrysene)	nd	nd	nd	nd	nd	nd	nd
Phenanthrene, tetradecahydro- (Perhydrophenanthrene)	nd	nd	nd	nd	nd	nd	nd
Aromatic Carboxylic Acids							
Methyl 2-furoate (2-furancarboxylic acid, methyl ester)	nd	nd	nd	nd	nd	nd	nd
Benzoic acid, methyl ester	nd	nd	nd	nd	nd	nd	nd
Benzoic acid, 4-methyl- methyl ester	nd	nd	nd	nd	nd	nd	nd
Benzoic acid, 3-methyl-, methyl ester	nd	nd	nd	nd	nd	nd	nd
Benzoic acid, 3-methoxy-, methyl ester (m-Anisic acid, methyl ester)	nd	nd	nd	nd	nd	nd	nd
Benzoic acid, 4-methoxy-, methyl ester (Anisic acid, methyl ester)	nd	nd	nd	nd	nd	nd	nd

Table II

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	F7204 Hopi Pt. FINE Composite	F7209 Hopi Pt. TOTAL Composite	F7203 Indian Gds FINE Composite	F7208 Indian Gds TOTAL Composite
1,4-Benzenedicarboxylic acid, dimethyl ester (Dimethyl terephthalate)	a, tr	a	a	a, tr
Benzoic acid, 2,4,5-trimethyl-	nd	nd	nd	nd
1,2-Benzenedicarboxylic acid, dimethyl ester (Dimethyl phthalate)	a	a	a	a
1,3-Benzenedicarboxylic acid, dimethyl ester (Dimethyl phthalate)	nd	nd	nd	a, tr
Benzoic acid, 4-hydroxy-3-methoxy-, methyl ester	nd	nd	nd	nd
Benzenecetic acid, alpha-hydroxy-3-methoxy-, methyl ester	nd	nd	nd	nd
Benzenepropanoic acid, 4-hydroxy-, methyl ester	nd	nd	nd	nd
Benzoic acid, 2-hydroxy-4,5-dimethoxy-, methyl ester	nd	nd	nd	nd
Benzoic acid, 4-methoxy- (Anisic acid)	nd	nd	nd	nd
Aromatic Aldehydes				
Benzaldehyde, 3-methoxy-	nd	nd	nd	nd
Benzaldehyde, 4-methoxy- (Anisaldehyde)	nd	nd	nd	nd
Benzaldehyde, 3-hydroxy-	nd	nd	nd	nd
Benzaldehyde, 3,4-dihydroxy-	nd	nd	nd	nd
2-Furancarboxaldehyde (2-Furaldehyde)	nd	nd	nd	nd
2-Furancarboxaldehyde, 5-(hydroxymethyl)- (5-(Hydroxymethyl)-2-furaldehyde)	nd	nd	nd	nd
2-Furancarboxaldehyde, 5-methyl- (5-Methyl-2-furaldehyde)	nd	nd	nd	nd
Benzaldehyde, 4-hydroxy- (p-Hydroxybenzaldehyde)	nd	nd	nd	nd
Aromatic Ketones				
2-Pyrrolidinone, 1-methyl-	nd	nd	nd	nd
2-Cyclopenten-1-one, 3,4,5-trimethyl-	nd	nd	nd	nd
2,5-Pyrrolidinedione, 1-methyl-	nd	nd	nd	nd
2,5-Cyclohexadiene-1,4-dione, 2-methyl-5-(1-methylethyl)-	nd	nd	nd	nd
Elhanone, 1-(2-hydroxy-5-methoxyphenyl)-	nd	nd	nd	nd
1H-Inden-1-one, 2,3-dihydro-	nd	nd	nd	nd
Elhanone, 1-(4-methoxyphenyl)-	nd	nd	nd	nd
Elhanone, 1-(2-hydroxy-5-methylphenyl)-	d	nd	nd	nd
1(2H)-Naphthalenone, 3,4-dihydro	nd	nd	nd	nd
1-Propanone, 1-(4-methoxyphenyl)-	nd	nd	nd	nd
1,2-Naphthalenedione, 5-hydroxy- (Juglone)	nd	nd	nd	nd

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	F7204 Hopi Pt. FINE Composite	F7209 Hopi Pt. TOTAL Composite	F7203 Indian Gds FINE Composite	F7208 Indian Gds TOTAL Composite			
Acetone, 3,4-dimethoxyphenyl-	nd	nd	nd	nd	nd		nd
Ethanone, 1-(3,4-dimethoxyphenyl)-	nd	nd	nd	nd	nd		nd
Benzophenone	nd	nd	nd	nd	nd		nd
2-Butanone, 4-(4-hydroxy-3-methoxyphenyl)- (Vanillyl acetone)	nd	nd	nd	nd	nd		nd
Ethanone, 1-(4-hydroxy-3-methoxyphenyl)- (4-Acetylguaiaicol; acetovanillone)	nd	nd	nd	nd	nd		nd
1-Propanone, 1-(2,4-dimethoxyphenyl)-	nd	nd	nd	nd	nd		nd
Ethanone, 1-(3,4,5-trimethoxyphenyl)-	nd	nd	nd	nd	nd		nd
Methanone, (4-methylphenyl)phenyl- (Phenyl p-tolyl ketone)	nd	nd	nd	nd	nd		nd
9H-Fluoren-9-one	nd	nd	nd	nd	nd		nd
4H-1-Benzopyran-4-one, 5,7-dihydroxy-2-methyl-	nd	nd	nd	nd	nd		nd
9H-Xanthen-9-one	nd	nd	nd	nd	nd		nd
9(10H)-Anthracenone (Anthrone)	nd	nd	nd	nd	nd		nd
9,10-Phenanthrenedione	nd	nd	nd	nd	nd		nd
1H-Phenalen-1-one	nd	nd	nd	nd	nd		nd
9,10-Anthracenedione	a,tr	nd	nd	nd	nd		nd
7H-Benz[de]anthracen-7-one	nd	nd	nd	nd	nd		nd
4H-1-Benzopyran-4-one, 2,3-dihydro-7-2-(3-hydroxyphenyl...)-	nd	nd	nd	nd	nd		nd
1,2-Cyclopentanedione, 3-methyl-	nd	nd	nd	nd	nd		nd
2(3H)-Furanone	nd	nd	nd	nd	nd		nd
2-Cyclopenten-1-one	nd	nd	nd	nd	nd		nd
2-Cyclopenten-1-one, 2-methyl-	nd	nd	nd	nd	nd		nd
Ethanone, 1-(3,4-dihydroxy-5-methoxyphenyl)-	nd	nd	nd	nd	nd		nd
2(4H)-Benzofuranone, 5,6,7,7A-tetrahydro-4,4,7A-trimethyl-	c	d	c	d	d		d
Aromatic Alcohols							
Benzenemethanol (Benzyl alcohol)	c,tr	b	b,tr	c	c		c
Phenol, 3-methoxy- (m-Guaiacol)	nd	nd	nd	nd	nd		nd
Phenol, 2,6-dimethoxy- (Syringol)	nd	nd	nd	nd	nd		nd
1,4-Benzenediol, 2-methyl	nd	nd	nd	nd	nd		nd
Benzyl alcohol, 4-hydroxy-3-methoxy- (Vanillyl alcohol)	nd	nd	nd	nd	nd		nd
1,3-Benzenediol, 4-ethyl	nd	nd	nd	nd	nd		nd
1-Naphthol, 6,7-dimethyl-	nd	nd	nd	nd	nd		nd
Phenol, 2,6-dimethoxy-4-(2-propenyl)- (Methoxyeugenol)	nd	nd	nd	nd	nd		nd

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	F7204 Hopi Pt. FINE Composite	F7209 Hopi Pt. TOTAL Composite	F7203 Indian Gds FINE Composite	F7208 Indian Gds TOTAL Composite
Benzyl alcohol, alpha-isobutyl-2,4,6-trimethyl	nd	nd	nd	nd
1-Naphthalenol, 3-methyl	nd	nd	nd	nd
2-Phenanthrenol, 4B,5,6,7,8,8A,9,10-octahydro-4B,8,8-trimethyl...	nd	nd	nd	nd
Ethane, 1,2-bis[4-hydroxy-3-methoxyphenyl]- (1,2-Diguaiacylethane)	nd	nd	nd	nd
1,2-Benzenediol, 4-methyl- (4-Methylcatechol)	nd	nd	nd	nd
Ethane, 1,2-bis(4-hydroxy-3,5-dimethoxyphenyl)- (1,2-Disyringylethane)	nd	nd	nd	nd
Ethane, 1-(4-hydroxy-3,5-dimethoxyphenyl)-2-(4-hydroxy-3-methoxyphenyl)- (1	nd	nd	nd	nd
Phenol, 2,6-dimethoxy-4-methyl- (4-Methylsyringol)	nd	nd	nd	nd
Phenol, 2,6-dimethoxy-4-propyl- (4-Propylsyringol)	nd	nd	nd	nd
Phenol, 4-ethyl-2,6-dimethoxy- (4-Ethylsyringol)	nd	nd	nd	nd
Phenol, 4-ethyl-2-methoxy- (4-Ethylguaiacol)	nd	nd	nd	nd
Aromatic Ethers				
Benzene, 1,4-dimethoxy-	nd	nd	nd	nd
Benzene, 1,3-dimethoxy-	nd	nd	nd	nd
Benzene, 1,2-dimethoxy- (Veratrole)	nd	nd	nd	nd
Benzene, 1,4-dimethoxy-2-methyl-	nd	nd	nd	nd
Benzene, 1,2,3-trimethoxy- (Methyl syringol)	nd	nd	nd	nd
Benzene, 1,2-dimethoxy-4-ethenyl-	nd	nd	nd	nd
Anthracene, 1,4-dimethoxy	nd	nd	nd	nd
Benzene, 1,3-dimethoxy-2-(2-propenyloxy)- (Allylsyringol)	nd	nd	nd	nd
Benzene, 2,3-dimethoxypropyl-	nd	nd	nd	nd
Propane, 1-(4-methoxyphenyl)-	nd	nd	nd	nd
Aromatic Heterocyclic Compounds				
Naphtho[2,1-B]furan	nd	nd	nd	nd
Dibenzofuran	nd	nd	nd	nd
Dibenzofuran, 2-methoxy-	nd	nd	nd	nd
Furan, 2-methyl-	nd	nd	nd	nd
Pyridine, 2-methoxy-	nd	nd	nd	nd
1H-Isoindole-1,3(2H)dione, 2-methyl-	b	d	b	b

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	F7204 Hopi Pt. FINE Composite	F7209 Hopi F.I. TOTAL Composite	F7203 Indian Gds FINE Composite	F7208 Indian Gds TOTAL Composite			
Nicotine (Pyridine, 3-(1-methyl-2-pyrrolidinyl)-, (S)-)							
1-Nitronaphthalene	nd	nd	nd	nd	nd	nd	nd
2-Nitronaphthalene	nd	nd	nd	nd	nd	nd	nd
2-Nitrobiphenyl	nd	nd	nd	nd	nd	nd	nd
Benzo[H]quinoline	nd	nd	nd	nd	nd	nd	nd
Phenanthridine	nd	nd	nd	nd	nd	nd	nd
3-Nitrobiphenyl	nd	nd	nd	nd	nd	nd	nd
4-Nitrobiphenyl	nd	nd	nd	nd	nd	nd	nd
2-Nitrofluorene	nd	nd	nd	nd	nd	nd	nd
9-Nitroanthracene	nd	nd	nd	nd	nd	nd	nd
2-Nitrofluoranthene	nd	nd	nd	nd	nd	nd	nd
1-Nitropyrene	nd	nd	nd	nd	nd	nd	nd
Difalene isomer	nd	nd	nd	nd	nd	nd	nd
Difalene	nd	nd	nd	nd	nd	nd	nd
Benzothiazole	nd	nd	nd	nd	nd	nd	nd
Thiophene, 2-propyl-	nd	nd	nd	nd	nd	nd	nd
Dibenzothiophene	nd	nd	nd	nd	nd	nd	nd
Thioxanthone	nd	nd	nd	nd	nd	nd	nd
STEROLS							
Phytosterols (and derivatives)							
(3beta)-Stigmast-5-en-3-ol (beta-Sitosterol)	nd	nd	nd	nd	nd	nd	nd
Stigmasta-3,5-dien-7-one	nd	nd	nd	nd	nd	nd	nd
Stigmast-4-en-3-one	nd	nd	nd	nd	nd	nd	nd
Ergosta-4,22-dien-3-one (Brassicasterone)	nd	nd	nd	nd	nd	nd	nd
Neohop-13(18)-ene	nd	nd	nd	nd	nd	nd	nd
Taraxasterol	nd	nd	nd	nd	nd	nd	nd
psi-Taraxasterol-TMS ether	ns	ns	ns	ns	ns	ns	ns
Cholesterol (and derivatives)							

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	F7204 Hopi Pt. FINE Composite	F7209 Hopi Pt. TOTAL Composite	F7203 Indian Gds FINE Composite	F7208 Indian Gds TOTAL Composite			
Cholesta-1,4-dien-3-one	nd	nd	nd	nd	nd	nd	nd
Cholestan-3-one	nd	nd	nd	nd	nd	nd	nd
MISC. ACYCLIC COMPOUNDS							
Hydroxy and Oxo Acids (as methyl esters)							
Propanoic acid, 2-methyl-, 3-hydroxy-2,4,4-trimethyl pentyl ester	c	nd	b	c	c		
2-Butenoic acid, 2-methoxy-3-methyl-, methyl ester	nd	nd	nd	nd	nd		
Pentanoic acid, 3-hydroxy-, methyl ester	nd	d	d	c	c		
3-Oxo-butanoic acid, 1,1-dimethylethyl ester	c	nd	c	d, tr	nd		
4-Oxo-pentanoic acid, methyl ester	b	b	b	nd	nd		
4-Oxo-hexanoic acid, methyl ester	c	b	c	b	b		
4-Oxo-hexanoic acid, 5-methyl-, methyl ester	c	c	c	d	d		
5-Oxo-hexanoic acid, methyl ester	b	b	c, tr	c	c		
4-Oxo-nonanoic acid, methyl ester	c	c	c	c	c		
Branched and Unsaturated Acids							
Butanoic acid, 3- or 2-methyl, 2-methyl propyl ester	nd	d	nd	nd	nd		
2-Butenoic acid, 3-methyl-, methyl ester	nd	nd	c	nd	nd		
n-Heptenoic acid, methyl ester	nd	nd	nd	nd	nd		
Hexadecanoic acid, 15-methyl-, methyl ester	nd	nd	nd	nd	nd		
(Z)-9-Octadecenoic acid (Oleic acid)	nd	nd	nd	nd	nd		
(Z,Z)-9,12-Octadecadienoic acid (Linoleic acid)	nd	nd	nd	nd	nd		
(Z)-9-Octadecenoic acid, methyl ester (Oleic acid, methyl ester)	nd	nd	nd	nd	nd		
(Z,Z)-9,12-Octadecadienoic acid, methyl ester (Linoleic acid, methyl ester)	nd	nd	nd	nd	nd		
2-Propenoic acid, methyl ester (Methyl acrylate)	nd	nd	nd	nd	nd		
Dicarboxylic and Tricarboxylic Acids (as methyl esters)							
Propanedioic acid, dimethyl ester (Dimethyl malonate)	nd	nd	nd	nd	nd		
Butanedioic acid, dimethyl ester (Dimethyl succinate)	nd	nd	nd	nd	nd		
2-Butenedioic acid, dimethyl ester (Dimethyl fumarate)	nd	nd	nd	nd	nd		

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	F7204 Hopi Pt. FINE Composite	F7209 Hopi Pt. TOTAL Composite	F7203 Indian Gds FINE Composite	F7208 Indian Gds TOTAL Composite
Propanedioic acid, methyl-, dimethyl ester (Dimethyl methyl malonate)	a	a	a	a
Butanedioic acid, methyl-, dimethyl ester (Dimethyl methyl succinate)	nd	nd	nd	nd
Succinaldehydic acid, 2-methyl-, methyl ester, 4-(dimethyl acetal)-	b	b	b	c, tr
Propanedioic acid, methoxy-, dimethyl ester (Dimethyl methoxy malonate)	nd	nd	nd	nd
Pentanedioic acid, dimethyl ester (Dimethyl glutarate)	a	a	a	a
Pentanedioic acid, 2-methyl-, dimethyl ester	d	c	c	c
Hexanedioic acid, dimethyl ester (Dimethyl adipate)	a	a	a	a
Hexanedioic acid, 3-methyl-, dimethyl ester	d	c	c	c
Heptanedioic acid, dimethyl ester (Dimethyl pimelate)	nd	nd	nd	nd
2-Pentenedioic acid, 2-methoxy-, dimethyl ester	nd	nd	nd	nd
Heptanedioic acid, 3-methyl-, dimethyl ester	nd	nd	nd	nd
Octanedioic acid, dimethyl ester (Dimethyl suberate)	nd	nd	nd	nd
Nonanedioic acid, dimethyl ester	c	c	c	c
Decanedioic acid, dimethyl ester (Dimethyl sebacate)	nd	nd	nd	nd
1,2,3-Propanetricarboxylic acid, 1-hydroxy-, trimethyl ester	d	d	d	d
Lactones				
Oxacyclotetradecane-2,11-dione, 13-methyl- scan 705	c	c	d	nd
Oxacycloheptadecan-2-one scan 770	c	c	d	c
2(3H)-Furanone, dihydro-4,4-dimethyl-	c	nd	c	d
Ketones				
10-Nonadecano...	nd	nd	nd	nd
PETROLEUM MARKERS				
Steranes				
20R-5alpha(H), 14beta(H), 17beta(H)-Cholestane	nd	nd	nd	nd
20S-5alpha(H), 14beta(H), 17beta(H)-Cholestane	nd	nd	nd	nd
20R-5alpha(H), 14alpha(H), 17alpha(H)-Cholestane	nd	nd	nd	nd
20R-5alpha(H), 14beta(H), 17beta(H)-Ergostane	nd	nd	nd	nd

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		F7204 Hopi Pt. FINE Composite	F7209 Hopi Pt. TOTAL Composite	F7203 Indian Gds FINE Composite	F7208 Indian Gds TOTAL Composite
20S-5alpha(H), 14beta(H), 17beta(H)-Ergostane		nd	nd	nd	nd
20R-5alpha(H), 14beta(H), 17beta(H)-Sitostane		nd	nd	nd	nd
20S-5alpha(H), 14beta(H), 17beta(H)-Sitostane		nd	nd	nd	nd
Pentacyclic Triterpanes					
22,29,30-Trisnorneohopane		nd	nd	nd	nd
17alpha(H), 21beta(H)-29-Norhopane		nd	nd	nd	nd
17alpha(H), 21beta(H)-Hopane		nd	nd	nd	nd
22S-17alpha(H), 21beta(H)-30-Homohopane		nd	nd	nd	nd
22R-17alpha(H), 21beta(H)-30-Homohopane		nd	nd	nd	nd
22S-17alpha(H), 21beta(H)-30-Bishomohopane		nd	nd	nd	nd
22R-17alpha(H), 21beta(H)-30-Bishomohopane		nd	nd	nd	nd
HETERO COMPOUNDS					
Formamide, N-(1-methylpropyl)- scan 151		c	nd	d	d
Formamide, N,N-dibutyl scan 565		b	nd	a	a
2-Propanol, 1,3-dichloro-, phosphate (3:1) (Fyrol FR-2)		nd	d, tr	b	b

A similar analysis of soil dust samples collected separately from Hopi Point and from Indian Gardens also showed no chemical similarity to the ambient aerosol samples. This indicates that the organics content of soil dust is a minor contributor to the overall organics loading in the Grand Canyon atmosphere.

Rogge et al. (1993a) have shown that fossil petroleum markers such as pentacyclic triterpanes (hopanes) and steranes can be used to trace the presence of motor vehicle exhaust in the atmosphere. An analysis of these molecular tracers that are found in the exhaust from automobiles and diesel trucks was conducted also for the Grand Canyon ambient aerosol composites, and no detectable input from this vehicular source was found. Likewise, tire dust tracers (e.g. benzothiazole; high molecular weight n-alkanes $\geq C_{35}$) and meat cooking smoke markers (e.g. cholesterol) are not found in detectable quantities.

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. That summertime organic aerosol is contributed largely from local vegetation plus secondary organic aerosol formed from the low vapor pressure products of atmospheric chemical reactions. Although woodsmoke markers such as retene have been observed in previous summers at the Grand Canyon when fires were known to be burning in the area, wood smoke was not a major contributor to the aerosol during August 1989. No detectable amounts of the fossil petroleum markers found in motor vehicle exhaust are present in the Grand Canyon aerosol samples analyzed here, indicating that no more than a minor input of vehicle exhaust primary aerosol is possible at the time studied.

Acknowledgments

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Appendix A

48 Hour Airmass Trajectories Arriving At The Grand Canyon During August, 1989

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/2/89 0400 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/2/89 1600 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/3/89 0400 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/3/89 1600 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/4/89 0400 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/4/89 1600 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/5/89 0400 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/5/89 1600 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/6/89 0400 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/6/89 1600 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/7/89 0400 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/7/89 1600 PST

WIND TRAJECTORIES OVER GRAND CANYON

36 HOUR BACK TRAJECTORY ENDING 8/8/89 0400 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/8/89 1600 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/9/89 0400 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/9/89 1600 FST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/10/89 0400 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/10/89 1600 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/11/89 0400 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/11/89 1600 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/12/89 0400 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/12/89 1600 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/13/89 0400 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/13/89 1600 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/14/89 0400 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/14/89 1600 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/15/89 0400 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/15/89 1600 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/16/89 0400 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/16/89 1600 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/17/89 0400 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/17/89 1600 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/18/89 0400 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/18/89 1600 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/19/89 0400 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/19/89 1600 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/20/89 0400 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/20/89 1600 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/21/89 0400 PST

WIND TRAJECTORIES OVER GRAND CANYON
12 HOUR SEGMENTS ENDING 8/21/89 1600 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/22/89 0400 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/22/89 1600 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/23/89 0400 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/23/89 1600 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/24/89 0400 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/24/89 1600 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/25/89 0400 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/25/89 1600 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/26/89 0400 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/26/89 1600 PST

WIND TRAJECTORIES OVER GRAND CANYON

12 HOUR SEGMENTS ENDING 8/27/89 0400 PST

WIND TRAJECTORIES OVER GRAND CANYON
12 HOUR SEGMENTS ENDING 8/27/89 1600 PST

Appendix B

CARBONACEOUS AEROSOL PARTICLES FROM COMMON VEGETATION
IN THE GRAND CANYON

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Abstract

The problem of visibility reduction in the Grand Canyon due to fine organic aerosol particles in the atmosphere has become an area of increased environmental concern. Aerosol particles can be derived from many emission sources. In this report, we focus on identifying organic aerosols derived from common vegetation in the Grand Canyon. These aerosols are expected to be significant contributors to the total atmospheric organic aerosol content.

Aerosol samples from living vegetation were collected by resuspension of surface wax and resin components liberated from the leaves of vegetation common to areas of the Grand Canyon. The samples were analyzed using high-resolution gas chromatography/mass spectrometry (GC/MS). Probable identification of compounds was made by comparison of sample spectra with National Institute of Standards and Technology (NIST) mass spectral references and positive identification of compounds was made when possible by comparison with authentic standards as well as NIST references. Using these references, we have been able to positively identify the presence of n-alkane and n-alkanoic acid homolog series in the surface waxes of the vegetation sampled. Several monoterpenes, sesquiterpenes, and diterpenes were identified also as possible biogenic aerosols which may contribute to the total organic aerosol abundance leading to visibility reduction in the Grand Canyon.

Carbonaceous Aerosol Particles from Common Vegetation in the Grand Canyon

Introduction

Aerosol particles in desert regions has become an area of increasing environmental research. One desert region which has been affected by the presence of aerosol particles is the Grand Canyon. The scenic view of the canyon is at times obscured greatly due to the haze produced by the presence of fine particulate matter suspended in the troposphere. The visibility reduction results from the ability of these particles to both scatter and absorb solar radiation. [1]

Aerosol particles are released into the atmosphere by many sources both natural and anthropogenic. Recent studies have shown that carbonaceous aerosol is the largest contributor to the total fine particulate mass at many desert sites. [2-6] In this report, we focus on identifying carbonaceous aerosols from live vegetation sampled at Hopi Point, AZ (southern rim of the Grand Canyon). These fine particle aerosols (size $< 2.0 \mu\text{m}$) are derived from epicuticular plant waxes, resinous exudates, and the lipid fraction of airborne microorganisms. [7] Samples of dead vegetation were also collected at Hopi Point as well as live and dead vegetation from Indian Gardens, AZ. However, extensive data reduction has not been performed for these samples as of yet.

Experimental Section

Sample Collection. A grab sampling technique was used to collect samples of live vegetation common to Hopi Point, AZ. These samples included vegetation from the Ponderosa Pine Forest and Pinyon-Juniper Woodlands on the southern rim of the Grand Canyon. Elevational belts, called life zones, have been established in which the dominant vegetation of the area reflects ecosystem ecology as a function of elevation. The Pinyon-Juniper Woodland is part of the Upper Sonoran Zone having an elevation of approximately

3500 to 7000 feet and the Ponderosa Pine Forest is part of the Transition Zone having an elevation of approximately 7000 to 8250 feet. [8] Figure 1 gives a pictorial summary of the life zones and plant communities of the Grand Canyon and Table 1 represents the vegetation collected for sampling.

To simulate the abrasion of leaf surfaces by wind, the leaves of the vegetation collected were placed in a clean Teflon bag and agitated to liberate and suspend surface waxes and resins. The contents of the Teflon bag was withdrawn through 2 μ m size cut cyclon separators and collected on quartz fiber filters. (9)

Each filter was spiked with a known amount of perdeuterated tetracosane (n-C₂₄D₅₀) to serve as an internal recovery standard in GC/MS analysis. (10-12) Samples were extracted from the quartz fiber filters by the addition of three 15 ml portions of hexane, followed by three 15 ml portions of a 2:1 mixture of benzene/isopropanol. (13) Details of the extraction procedure and volume reduction procedure have been outlined in an earlier report (13). Once sample volume reduction was completed, the concentrated extract was divided into two aliquots. One aliquot was reacted with diazomethane to convert organic acids to their methyl esters and acidic hydroxy compounds to their methoxy analogues. (13)

GC/MS Analysis. Samples were analyzed using a Varian 4600 high-resolution gas chromatograph (HRGC). A Grob injector was used and the injector temperature was kept at 300°C. A 30 meter fused silica column was employed for compound separation. The gas chromatograph was connected to a flame ionization detector, operating at a sensitivity of 10⁻¹² mV. Mass spectrometric analysis was performed using a Finnigan 4000 quadrupole gas chromatograph/mass spectrometer interfaced with an INCOS data acquisition system. Ionization was produced by electron impact with an electron energy of 70eV. The scanning frequency was set at 0.5 sec⁻¹, ranging from 50 to 550 Daltons. (13) 1-phenyldodecane was used as a coinjection standard.

Results and Discussion

Compounds were identified by comparison of their mass fragmentation patterns to the NIST mass spectral reference library contained in the Finnigan INCOS data system. Additional searching was performed using the IBM-AT, version 3, 1990, NIST library.

Table 1. Dominant Vegetation Collected at Hopi Point, AZ.

Life Zone	Community	Vegetation Common Name	Vegetation Scientific Name	Plant Family
Transition	Ponderosa Pine Forest	Native grass		
Transition	Ponderosa Pine Forest	Ponderosa Pine	Pinus ponderosa	Pinaceae
Transition Upper Sonoran	Ponderosa Pine Forest Pinyon-Juniper Woodland	Sagebrush	Artemisia tridentata	Compositae
Upper Sonoran	Pinyon-Juniper Woodland	Utah Juniper	Juniperus osteosperma	Cupressaceae
Upper Sonoran	Pinyon-Juniper Woodland	Banana Yucca	Yucca baccata	Liliaceae
Upper Sonoran	Pinyon-Juniper Woodland	Pinyon	Pinus edulis	Pinaceae

Figure 1. Life zones and plant communities of the Grand Canyon. Approximate location of sampling sites, Indian Gardens and Hopi Point, are indicated.

Source: S. Whitney, 1982. [8].

When standards were available, compound identification was confirmed by comparison of mass fragmentation patterns and retention times of the sample with authentic standards analyzed using the same GC/MS system.(13)

The following key was used to denote the accuracy of compound identification: (a) positive, when the sample spectrum, standard spectrum, and NIST library spectrum were identical and also the retention time of the authentic standard and the sample were comparable; (b) probable, same as above except no authentic standard was available, but the NIST library spectrum agreed well with the sample spectrum; (c) possible, same as above, except that the sample mass fragmentation pattern contained additional ions from other compounds having minor peak coelution; (d) tentative, when the sample spectrum revealed additional mass fragments from one or more coeluting compounds with substantial overlap.

Figure 2 shows a typical gas chromatograph for vegetation samples. This chromatograph is for the live vegetation component collected as fine aerosol at Hopi Point, AZ. Compound identification for this sample is listed in Table 2.

Members of the n-alkane homolog series, n-C₁₆ to n-C₃₆, have been identified in this sample with C₂₃ to C₃₆ being the most prevalent range. The n-alkanes exhibit very similar mass fragmentation patterns. The key fragment ions displayed in the mass spectra of n-alkanes include masses 57, 71, 85, 99, 113, 129 etc.(7) Because the fragmentation patterns of n-alkanes are so similar, identification was based on the molecular ion and comparison of retention times with authentic standards. A typical mass fragmentation pattern for n-alkanes is shown in Figure 3.

High molecular weight n-alkanes (C₁₂ to C₄₀) are produced by biosynthetic processes which occur in vegetation.(14-16) These n-alkanes are derived from epicuticular plant waxes.(17-22) The n-alkane homologs show strong odd carbon number predominance providing evidence that n-alkanes having an odd number of carbon atoms are more abundant in plant waxes.(13) A selected ion plot of mass m/z 57 for the isolation of n-alkane homologs is shown in Figure 4. This figure clearly demonstrates the existence of odd carbon number predominance. Table 3 lists the n-alkane homologs identified in the selected ion plot.

Figure 2. GC/MS plot of reconstructed ion current [RIC] vs. scan time for fine aerosol sample, F7217, derived from live vegetation common to Hopi Point, AZ.

Table 2.

GC/MS Injection F7217 -- Live Vegetation, Hopi Point, Fine Aerosol

Peak Number	File Scan Number	Compound Name	Formula	Compound Identification*
<u>Standard Compounds</u>				
31	F7217.0735	1-Phenyldodecane	C18H30	a
42	F7217.0851	Perdeutero tetracosane	C24D50	a
<u>n-Alkanes</u>				
	F7217.	n-Decane	C10H22	nd
	F7217.	n-Dodecane	C12H26	nd
	F7217.	n-Tridecane	C13H28	nd
	F7217.	n-Tetradecane	C14H30	nd
	F7217.	n-Pentadecane	C15H32	nd
	F7217.0618	n-Hexadecane	C16H34	a
	F7217.	n-Heptadecane	C17H36	nd
	F7217.	n-Octadecane	C18H38	nd
30	F7217.0721	n-Nonadecane	C19H40	b
33	F7217.0750	n-Cosane	C20H42	a
	F7217.	n-Heneicosane	C21H44	nd
40	F7217.	n-Docosane	C22H46	nd
	F7217.0836	n-Tricosane	C23H48	b
	F7217.	n-Tetracosane	C24H50	nd
45	F7217.0887	n-Pentacosane	C25H52	b
	F7217.	n-Hexacosane	C26H54	nd
49	F7217.0934	n-Heptacosane	C27H56	b
	F7217.	n-Octacosane	C28H58	nd
53	F7217.0987	n-Nonacosane	C29H60	b
55	F7217.1020	n-Triacontane	C30H62	a
57	F7217.1062	n-Heneltriacontane	C31H64	b
	F7217.	n-Dotriacontane	C32H66	nd
62	F7217.1172	n-Tritriacontane	C33H68	b
63	F7217.1247	n-Tetratriacontane	C34H70	a
66	F7217.1358	n-Pentatriacontane	C35H72	b
67	F7217.1454	n-Hexatriacontane	C36H74	a

Table 2 (continued)

GC/MS Injection F7217 -- Live Vegetation, Hopi Point, Fine Aerosol

Peak Number	File Scan Number	Compound Name	Formula	Compound Identification*
<u>n-Alkanolic Acids (as methyl esters)</u>				
1	F7217.0161	n-Hexanoic acid methyl ester	C7H14O2 (C6 FA)	a
3	F7217.0281	n-Heptanoic acid methyl ester	C8H16O2 (C7 FA)	b
5	F7217.0405	n-Octanoic acid methyl ester	C9H18O2 (C8 FA)	a
10	F7217.0476	n-Nonanoic acid methyl ester	C10H20O2 (C9 FA)	a
13	F7217.0530	n-Decanoic acid methyl ester	C11H22O2 (C10 FA)	a
15	F7217.0575	n-Undecanoic acid methyl ester	C12H24O2 (C11 FA)	a
19	F7217.0616	n-Dodecanoic acid methyl ester	C13H26O2 (C12 FA)	a
22	F7217.0653	n-Tridecanoic acid methyl ester	C14H28O2 (C13 FA)	a
28	F7217.0688	n-Tetradecanoic acid methyl ester	C15H30O2 (C14 FA)	a
30	F7217.0721	n-Pentadecanoic acid methyl ester	C16H32O2 (C15 FA)	a
34	F7217.0752	n-Hexadecanoic acid methyl ester	C17H34O2 (C16 FA)	a
	F7217.0782	n-Heptadecanoic acid methyl ester	C18H36O2 (C17 FA)	a
39	F7217.0811	n-Octadecanoic acid methyl ester	C19H38O2 (C18 FA)	a
41	F7217.0839	n-Nonadecanoic acid methyl ester	C20H40O2 (C19 FA)	a
44	F7217.0864	n-Eicosanoic acid methyl ester	C21H42O2 (C20 FA)	a
	F7217.0889	n-Heneicosanoic acid methyl ester	C22H44O2 (C21 FA)	a
	F7217.0913	n-Docosanoic acid methyl ester	C23H46O2 (C22 FA)	a
52	F7217.0937	n-Tricosanoic acid methyl ester	C24H48O2 (C23 FA)	a
	F7217.0963	n-Tetradocosanoic acid methyl ester	C25H50O2 (C24 FA)	a
	F7217.0993	n-Pentadocosanoic acid methyl ester	C26H52O2 (C25 FA)	a
56	F7217.1028	n-Hexacosanoic acid methyl ester	C27H54O2 (C26 FA)	a
	F7217.1071	n-Heptacosanoic acid methyl ester	C28H56O2 (C27 FA)	a
59	F7217.1123	n-Octacosanoic acid methyl ester	C29H58O2 (C28 FA)	a
	F7217.	n-Nonacosanoic acid methyl ester	C30H60O2 (C29 FA)	nd
64	F7217.1268	n-Triacontanoic acid methyl ester	C31H62O2 (C30 FA)	a

Table 2 (continued)

GC/MS Injection F7217 -- Live Vegetation, Hopi Point, Fine Aerosol

Peak Number	File Scan Number	Compound Name	Formula	Compound Identification*
<u>n-Alkanols</u>				
58	F7217.1113	1-Octacosanol	C ₂₈ H ₅₈ O	a
<u>n-Alkan-2-ones</u>				
20	F7217.0630	nd	nd	d
61	F7217.1138	nd	nd	d
65	F7217.1292	nd	nd	d
<u>Monoterpenoids (C₁₀ compounds)</u>				
4	F7217.0368	Linalool oxide	C ₁₀ H ₁₈ O ₂	d
7	F7217.0450	Camphor	C ₁₀ H ₁₆ O	d
8	F7217.0458	4-Terpineol	C ₁₀ H ₁₈ O	d
9	F7217.0471	Borneol	C ₁₀ H ₁₈ O	d
11	F7217.0480	α -Terpineol	C ₁₀ H ₁₈ O	d
12	F7217.0516	Bornyl acetate	C ₁₂ H ₂₀ O ₂	d
16	F7217.0585	Monoterpenoid acid	C ₁₂ H ₂₄ O ₃	d
29	F7217.703	Camphorsulfonic acid	C ₁₀ H ₁₆ O ₄ S	d
<u>Sesquiterpenoids (C₁₅ compounds)</u>				
17	F7217.0603	δ -Cadinene	C ₁₅ H ₂₄	d
18	F7217.0612	Calamenene	C ₁₅ H ₂₂	d
21	F7217.0641	Nerolidol or Farnesol	C ₁₅ H ₂₆ O	d
23	F7217.0660	Sesquiterpenol	C ₁₅ H ₂₄ O	d
24	F7217.0666	Ylangene or thujopsene	C ₁₅ H ₂₄	d
25	F7217.0670	Sesquiterpenol	C ₁₅ H ₂₄ O	d
26	F7217.0676	Cadinol	C ₁₅ H ₂₆ O	d
27	F7217.0679	Cedreanol	C ₁₅ H ₂₆ O	d
32	F7217.0741	Sesquiterpenol	C ₁₅ H ₂₆ O	d

Table 2 (continued)

GC/MS Injection F7217 -- Live Vegetation, Hopi Point, Fine Aerosol

Peak Number	File Scan Number	Compound Name	Formula	Compound Identification*
35	F7217.0756	Sesquiterpenol	C15H22O	d
36	F7217.0771	Sesquiterpenol	C15H26O	d
<u>Diterpenoids (C20 compounds)</u>				
37	F7217.0779	Manoyl oxide or epimanoyl oxide	C20H34O	d
54	F7217.1004	Diterpenoid	nd	d
<u>Aromatic Hydrocarbons</u>				
2	F7217.0168	Methoxybenzene	C7H8O	c
6	F7217.0431	Phenol	C6H6O	b
14	F7217.0572	1,1'-Biphenyl	C12H10	b
<u>Contaminants -- Phthalate Esters</u>				
38	F7217.0799	1,2-Benzenedicarboxylic acid, butyl 2-methylpropyl ester	C16H22O4	b
48	F7217.0916	Benzyl butyl phthalate	C19H20O4	b
50	F7217.0943	1,2-Benzenedicarboxylic acid, diisooctyl ester	C24H38O4	b
<u>Contaminants -- Organosilanes</u>				
43	F7217.0856	Organosilane	nd	d
47	F7217.0909	Organosilane	nd	d
51	F7217.0960	Organosilane	nd	d
56	F7217.1028	Organosilane	nd	d
60	F7217.1128	Organosilane	nd	d

Table 2 (continued)*

GC/MS Injection F7217 -- Live Vegetation, Hopi Point, Fine Aerosol

Peak Number	File Scan Number	Compound Name	Formula	Compound Identification*
<u>ResIn Components</u>				
46	F7217.0858	Retene	C18H18	a
	F7217.(ca 878)	Methyl l-pimarate	C21H32O2	a
	F7217.0876	Methyl isopimarate	C21H32O2	b
	F7217.0890	Methyl dehydroabietate	C21H30O2	a
	F7217.0891	Methyl 13-isopropyl-5a-podocarpa-	C21H28O2	b
	F7217.(ca 893)	Methyl o-methylpodocarpate	C19H26O3	a
	F7217.(ca 900)	Methyl abietate	C21H32O2	b
	F7217.(ca 951)	Methyl 13-isopropyl-5a-podocarpa- isomer	C21H28O2	c
	F7217.0982	Methyl 7-ketodehydroabietate	C21H28O3	a

* a = positive, when the sample spectrum, standard spectrum and NIST-library spectrum were identical and also the retention time of the authentic standard and the sample compound were comparable

b = probable, same as above, except no authentic standard was available, but the NIST-library spectrum agreed very well with the sample spectrum and retention time of the standard

c = possible, same as above, except that the sample mass fragmentation pattern contained additional ions from other compounds having minor peak coelution

d = tentative, when the sample spectrum revealed additional mass fragments from one or more coeluting compounds (noise) with substantial overlap

nd = not detected

Figure 3. Plot of mass fragmentation pattern vs. relative ion intensity for scan 1062 from live vegetation, fine aerosol sample (F7217). This mass spectrometric plot is for the n-alkane homolog, n-C₃₁H₆₄, and shows a very small molecular ion at m/z 436.

Figure 4. Selected ion plot of mass m/z 57 vs. scan time for isolation of n-alkane homologs (n-C₁₉ to -C₃₆) from live vegetation, Hopi Point, fine aerosol sample (F7217).

Table 3.

GC/MS Injection F7217 -- Live Vegetation, Hopi Point, Fine Aerosol
 Selected Ion Plot of Mass m/z 57 vs. Scan Time for Isolation of n-Alkane Homologs (n-C19 to -C36).

Peak Number	File, Scan, Number	Compound Name	Formula
<u>n-Alkanes</u>			
1	F7217.0721	n-Nonadecane	C19H40
2	F7217.0750	n-Cosane	C20H42
3	F7217.0809	n-Heneicosane	C21H44
4	F7217.0836	n-Tricosane	C23H48
5	F7217.0862	n-Tetracosane	C24H50
6	F7217.0887	n-Pentacosane	C25H52
7	F7217.0911	n-Hexacosane	C26H54
8	F7217.0934	n-Heptacosane	C27H56
9	F7217.0958	n-Octacosane	C28H58
10	F7217.0987	n-Nonacosane	C29H60
11	F7217.1021	n-Triacontane	C30H62
12	F7217.1062	n-Henitriacontane	C31H64
13	F7217.1172	n-Triatriacontane	C33H68
14	F7217.1247	n-Tetraatriacontane	C34H70
15	F7217.1358	n-Pentatriacontane	C35H72
16	F7217.1454	n-Hexatriacontane	C36H74

Along with the n-alkanes, the n-alkanoic acids prove to be major contributors to the organic aerosol content from the vegetation sampled. With the exception of C₂₉, the n-alkanoic acids, C₆ to C₃₀, have been identified successfully in the Hopi Point, live vegetation sample. The n-fatty acids are derived from epicuticular plant waxes and microbial lipid deposits on leaf surfaces.(7,15,23-33) The n-alkanes have a characteristic fragment of mass 74.(7) Figure 5 shows a selected ion plot of mass m/z 74 and Table 4 lists the n-alkanoic acid homologs identified in the selected ion plot. Unlike the n-alkanes, the n-alkanoic acids display strong even carbon number predominance.(27,32,34)

1-Octacosanol and the n-alkan-2-ones are derived from the same sources as the n-alkanes and n-alkanoic acids. The n-alkan-2-ones were classified as such due to their fragmentation patterns, however, compound names could not be specified.

Several monoterpenoids (C₁₀), sesquiterpenoids (C₁₅), and diterpenoids (C₂₀) have been tentatively identified as aerosols derived from the vegetation sampled. These compounds are constituents of resins from the conifer vegetation.(35) Although the identification of these compounds is only tentative, they are logical possibilities due to the type of vegetation sampled, i.e. Ponderosa pine, pinyon, and juniper. Several unknown sesquiterpenoids and diterpenoids have been classified as such due to their fragmentation patterns and molecular formulas.

The phthalate esters and organosilanes detected are sample contaminants derived from the silicone greases, plastics, and rubber components which are contributed from the sampling equipment and analytical procedures. (7) Several aromatic hydrocarbons (e.g. 1,1'-biphenyl) are also contaminants and originate from the organic extraction solvents.

Conclusions

The n-alkanes and n-alkanoic acid series appear to be prominent contributors to the total organic aerosol particulate matter traceable to plant waxes and resins. Identification of terpenoids emitted directly into the environment by vegetation provides insight into the possible terpenoid chemical compounds which undergo photochemical reactions in the atmosphere.

Although the concentrations of these aerosols have not yet been determined, the identification of the aerosols produced by vegetation is an important first step towards

Figure 5. Selected ion plot of mass m/z 74 vs. scan time for isolation of n-alkanolic acids (as methyl esters) from live vegetation, Hopi Point, fine aerosol sample (F7217).

Table 4.

GC/MS Injection F7217 -- Live Vegetation, Hopi Point, Fine Aerosol
 Selected Ion Plot of Mass m/z 74 vs. Scan Time for Isolation of n-Alkanoic Acids (as methyl esters)

Peak Number	File Scan Number	Compound Name	Formula
1	F7217.0161	n-Hexanoic acid methyl ester	C7H14O2 (C6 FA)
2	F7217.0281	n-Heptanoic acid methyl ester	C8H16O2 (C7 FA)
3	F7217.0405	n-Octanoic acid methyl ester	C9H18O2 (C8 FA)
4	F7217.0476	n-Nonanoic acid methyl ester	C10H20O2 (C9 FA)
5	F7217.0530	n-Decanoic acid methyl ester	C11H22O2 (C10 FA)
6	F7217.0575	n-Undecanoic acid methyl ester	C12H24O2 (C11 FA)
7	F7217.0616	n-Dodecanoic acid methyl ester	C13H26O2 (C12 FA)
8	F7217.0653	n-Tridecanoic acid methyl ester	C14H28O2 (C13 FA)
9	F7217.0688	n-Tetradecanoic acid methyl ester	C15H30O2 (C14 FA)
10	F7217.0721	n-Pentadecanoic acid methyl ester	C16H32O2 (C15 FA)
11	F7217.0752	n-Hexadecanoic acid methyl ester	C17H34O2 (C16 FA)
12	F7217.0782	n-Heptadecanoic acid methyl ester	C18H36O2 (C17 FA)
13	F7217.0811	n-Octadecanoic acid methyl ester	C19H38O2 (C18 FA)
14	F7217.0839	n-Nonadecanoic acid methyl ester	C20H40O2 (C19 FA)
15	F7217.0864	n-Eicosanoic acid methyl ester	C21H42O2 (C20 FA)
16	F7217.0889	n-Heneicosanoic acid methyl ester	C22H44O2 (C21 FA)
17	F7217.0909	n-Docosanoic acid methyl ester	C23H46O2 (C22 FA)
18	F7217.0937	n-Tricosanoic acid methyl ester	C24H48O2 (C23 FA)
19	F7217.0963	n-Tetracosanoic acid methyl ester	C25H50O2 (C24 FA)
20	F7217.0993	n-Pentacosanoic acid methyl ester	C26H52O2 (C25 FA)
21	F7217.1028	n-Hexacosanoic acid methyl ester	C27H54O2 (C26 FA)
22	F7217.1071	n-Heptacosanoic acid methyl ester	C28H56O2 (C27 FA)
23	F7217.1123	n-Octacosanoic acid methyl ester	C29H58O2 (C28 FA)
24	F7217.1187	n-Nonacosanoic acid methyl ester	C30H60O2 (C29 FA)
25	F7217.1266	n-Triacontanoic acid methyl ester	C31H62O2 (C30 FA)

understanding the organic aerosol composition which contributes to visibility reduction in the Grand Canyon. Knowing the types of organic compounds present as aerosols and their origins helps in determining a natural background for the total organic aerosol content.

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