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MOLECULAR MARKER ANALYSIS AS A GUIDE TO THE SOURCES OF FINE ORGANIC AEROSOLS

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ABSTRACT

The molecular composition of fine particulate ($D_p \geq 2 \mu\text{m}$) organic aerosol emissions from the most important sources in the Los Angeles area has been determined. Likewise, ambient concentration patterns for more than 80 single organic compounds have been measured at four urban sites (West Los Angeles, Downtown Los Angeles, Pasadena, and Rubidoux) and at one remote offshore site (San Nicolas Island). It has been found that cholesterol serves as a marker compound for emissions from charbroilers and other meat cooking operations. Vehicular exhaust being emitted from diesel and gasoline powered engines can be traced in the Los Angeles atmosphere using fossil petroleum marker compounds such as steranes and pentacyclic triterpanes (e.g., hopanes). Biogenic fine particle emission sources such as plant fragments abraded from leaf surfaces by wind and weather can be traced in the urban atmosphere. Using distinct and specific source organic tracers or assemblages of organic compounds characteristic for the sources considered it is possible to estimate the influence of different source types at any urban site where atmospheric data are available.

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INTRODUCTION

Carbonaceous compounds constitute the largest contributor to the fine particulate matter in the atmosphere of highly industrialized and urbanized areas. Organic aerosol comprises 25% to 30% of total fine aerosol mass in the greater Los Angeles area.^{1,2} Fine particulate matter ($d_p \leq 2.0 \mu\text{m}$) is known to be easily inhalable and has been considered responsible, together with gaseous pollutants, for the possible health effects connected with air pollutants. Elevated concentrations of organic compounds in fine respirable particles measured in urbanized areas are of considerable concern because many of the organics present in the atmosphere are known mutagens and carcinogens. In order to design an advanced strategy for the control of fine primary organic particulate emissions, more knowledge is necessary regarding source/receptor relationships.

The purpose of this research is to provide a molecular characterization of the primary organic particulate matter emitted from urban pollution sources, to provide parallel data on the concentration of these compounds found in ambient air, and to use these data to devise and test new methods for relating emissions to air quality for many organic compounds. A dilution source sampling system was employed to collect primary fine aerosol emissions from 18 major urban source types that contribute close to 80% of the fine organic aerosol emitted in the Los Angeles area.^{3,4} Ambient fine particle samples were collected for one entire year at four urban locations and at one remote offshore sampling site.^{1,2} The identification and quantification of organic compounds present in these samples has been conducted by high resolution GC- and GC/MS- techniques. The identification of organic marker compounds that are characteristic of particular source types has been emphasized. These marker compounds then can be used along with source/receptor modeling techniques to quantify the presence of the effluent from particular source types within ambient aerosol samples. From the 18 major primary organic aerosol sources investigated, the following 10 sources will be characterized and their molecular source signatures discussed: charbroiling and frying of meat, noncatalyst and catalyst equipped automobiles, diesel trucks, paved road dust, brake lining dust, tire wear debris, and vegetative detritus derived from the green and dead leaves of urban plants.^{5,6,7,8}

EXPERIMENTAL METHODS

Ambient and Source Sampling Programs. The source and ambient sampling programs have been documented elsewhere^{1,2,4,5,6,7,8} and are also summarized by Cass et al.⁹ earlier in this conference proceedings.

Sample Extraction. An extraction protocol has been followed which has been described in detail elsewhere.^{2,9,5,10,11} Here, only a short overview will be given. All source and ambient samples were exposed to an extraction scheme that employed successive application of hexane (twice), followed by benzene/2-propanol(2:1) (three times). Each of the five extraction steps was conducted for a 10 min. period and supported by mild ultrasonic agitation. After sample volume reduction, one aliquot of each sample extract was derivatized by adding freshly produced diazomethane to convert organic acids to their methyl ester analogues.

Sample Analysis, Compound Quantification and Quality Assurance. Extract analyses were accomplished using a Finnigan 4000 quadrupole mass spectrometer (GC/MS) interfaced with an INCOS data system. The GC/MS analyses were conducted in the electron impact mode. For compound separation a 30-m fused-silica DB-1701 column was used (J&W Scientific, Rancho Cordova, CA). For parallel analysis a Varian 4600 high-resolution gas chromatograph (HRGC) operated with a FID detector system was employed.^{10,11} Compound identification was performed with the help of the NIST mass spectral library accessed by the data system and, where available, by comparison with the retention times and fragmentation patterns of authentic standards. Peak quantification was accomplished using the HRGC- and GC/MS-systems and was based on the combined use of deuterated tetracosane ($n\text{-C}_{24}\text{D}_{50}$) as internal standard and 1-phenyldodecane as coinjection standard. The peak masses were corrected for the relative response (relative to 1-phenyldodecane) of prepared sets of standard compounds. A quality assurance program was followed which included solvent testing, procedural blanks, and recovery monitoring etc.^{5,10,11,12}

RESULTS AND DISCUSSION

In the following discussion of the composition of the primary organic aerosol sources investigated, the specific source testing procedures will be omitted as far as possible in order to provide space for a more comprehensive discussion of the findings. The interested reader is referred to the journal articles cited.^{5,6,7,8} Likewise, most of the data on the ambient fine organic particle composition used here to trace the primary source emissions can be found elsewhere.¹¹

Charbroilers and Meat Cooking. Meat cooking operations account for about 21% of all primary fine organic particulate matter (as OC) released into the urban atmosphere within an 80 × 80 km area defined over central Los Angeles and Orange Counties, CA.^{1,5} To investigate the source signature of fine organic aerosols released during meat cooking, hamburger meat with 21% fat (regular) and 10% fat (extralean) was cooked both over a commercial natural gas charbroiler and by frying. The four sets of cooking experiments resulted in appreciable differences in the emission rate of fine particulate matter released per kg of meat cooked. Charbroiling produced in general much higher emissions than frying, and emissions were more pronounced when meat with a higher fat content was cooked.

More than 75 organic compounds were identified in the meat cooking aerosol including *n*-alkanes, *n*-alkanoic acids, *n*-alkenoic acids, dicarboxylic acids, *n*-alkanals, *n*-alkanols, *n*-alkanones, furans, lactones, amides, nitriles, PAH, pesticides, cholesterol, and others. Most

of these compound classes also were identified in the atmospheric samples taken by Gray et al.² and analyzed by Rogge et al.¹¹ Cholesterol was examined to determine if it could serve as a marker compound for meat cooking in the urban atmosphere. Because cholesterol is biosynthesized by higher animals (and to a smaller degree by plant life and is not present in fossil fuel) it seems to be a promising candidate. To test this hypothesis, daily cholesterol emission rates have been determined to be 25.6 - 30.4 kg day⁻¹ using the meat consumption data for the greater Los Angeles area and the experimental results.⁵ Using our source inventory of fine particulate organic compound mass (OC) emitted per day in that area⁴, it was found that cholesterol accounts for about 0.07 - 0.08% of that fine particulate organic matter emitted. The fine aerosol organic carbon concentration in the West Los Angeles atmosphere was measured to be 9.1 μg m⁻³ during October 1982^{1,2}, a month with a very clear cholesterol peak in the ambient aerosol sample examined. If 0.08% of that organic compound mass were present as cholesterol, than its ambient concentration would reach about 7.3 ng m⁻³. In fact, 14.6 ng m⁻³ of cholesterol was found in the ambient fine particle samples collected in October 1982. Although roughly twice as high as estimated from the basin wide emission inventory, the cholesterol concentration found at West Los Angeles could indeed be contributed by meat cooking operations. Other possible biogenic sources have been recently investigated including dead and green leaf surface detritus and cigarette smoke. Of this group of sources, only cigarette smoke contains detectable amounts of cholesterol. From daily cigarette consumption data and our experimental data on cigarette smoke composition, a contribution of roughly 0.4 ng m⁻³ to the ambient cholesterol level was determined for West Los Angeles in October 1982. This shows that none of the other sources examined to date significantly interfere with the use of cholesterol to trace meat cooking operations in the urban atmosphere.

Noncatalyst and Catalyst-Equipped Automobiles and Heavy-Duty Diesel Trucks. Internal combustion engines (stationary and mobile) burning gasoline and diesel fuel contribute more than 21% of the primary fine particulate organic carbon (OC) to the Los Angeles atmosphere.^{1,4} The organic chemical composition of fine particulate ($d_p \leq 2.0\mu\text{m}$) exhaust emissions from six noncatalyst autos, seven catalyst-equipped autos, and two heavy-duty diesel trucks was investigated by gas chromatography/mass spectrometry. More than 100 organic compounds have been quantified, including *n*-alkanes, *n*-alkanoic acids, one *n*-alkenoic acid, substituted benzaldehydes, polycyclic aromatic hydrocarbons and their oxygenated homologues, steranes, pentacyclic triterpanes, azanaphthalenes, and others.

Because steranes and pentacyclic triterpanes are common constituents of crude oil and consequently also of some higher boiling petroleum products e.g. lubricant oils, it seems promising to use such fossil petroleum marker compounds to trace vehicular emissions in the heavily urbanized atmosphere. In order to use steranes and pentacyclic triterpanes as molecular markers to trace the presence of particulate exhaust emissions from internal combustion engines in the urban atmosphere, the ambient concentrations of such compounds must be dominated by that source category. To determine if this indeed is the case, the emission inventory for Los Angeles during 1982 was used⁴ in connection with source testing experiments to determine the daily emission rates of these fossil petroleum markers from motor vehicle exhaust, tire wear particles, road dust, oil burning industrial and commercial boilers, and roofing tar pots. For minor sources that have not been tested including surface coating processes, organic chemical processes, asphalt roof manufacturing, and miscellaneous petroleum industry emissions, the fractional fossil marker content of the organic aerosol emissions was assumed to be as found for roofing tar pot emissions.

Balancing the total emissions for the fossil petroleum markers investigated, it was

shown that roughly 85% of these compounds emitted to the Los Angeles area atmosphere are contributed by internal combustion engine exhaust. For the year 1982, average annual ambient concentrations of the steranes and triterpanes were measured and found to be 6.5 ng m^{-3} at West Los Angeles, 17.1 ng m^{-3} at downtown Los Angeles, and 7.3 ng m^{-3} at Pasadena.

These ambient concentrations of the fossil petroleum markers released from internal combustion engines were used to check the consistency of our emission inventory by a method similar to that described earlier for charbroiling and meat cooking operations. It was found that the marker concentrations estimated from the vehicular share of the emission inventory agreed well with measured fossil petroleum marker concentrations at West Los Angeles and Pasadena, whereas the measured concentrations at downtown Los Angeles were higher by a factor of three compared to the predictions. Because the estimated ambient fossil petroleum marker concentrations were based on an equally distributed basin-wide mixture of emission sources, areas with unusually high traffic densities such as downtown Los Angeles would be expected to be underestimated. Working the other direction from the ambient tracer concentrations found at downtown Los Angeles and the tracer content of vehicle exhaust, the vehicle exhaust contribution to primary organic aerosol levels at downtown Los Angeles can be estimated directly.

Paved Road Dust, Tire Debris, and Organometallic Brake Lining Abrasion Products. In order to evaluate the complex interaction of traffic related sources within an urban area, emissions other than vehicular exhaust such as paved road dust, brake lining wear, and tire abrasion products also have to be investigated. Here, fine particulate ($d_p \leq 2.0 \mu\text{m}$) road dust, fine particulate brake lining wear, and total particle tire tread debris extracts were analyzed using gas chromatography/mass spectrometry. More than 100 organic compounds are quantified in each of the individual samples including *n*-alkanes, *n*-alkanoic acids, *n*-alkenoic acids, *n*-alkanals, *n*-alkanols, benzoic acids, substituted benzaldehydes, polyalkylene glycol esters, benzothiazole, PAH, oxy-PAH, steranes, hopanes, natural resins, pesticides and other compound types.

Pierson and Brachaczek¹² used SBR (styrene butadiene rubber) detected by infrared absorption spectroscopy to trace airborne particulate tire tread debris. Kim et al.¹³ utilized as a tracer benzothiazole generated by pyrolysis of vulcanization accelerators which are common constituents in the tire stock. In this work, we have sought to determine whether or not there exist solvent-soluble compounds in tire wear debris that could serve as tracers. The distribution of the sequence of the higher molecular weight *n*-alkanes $> \text{C}_{34}$ that can be measured in tire wear debris might well be used as tire debris marker compounds. Although such *n*-alkanes can be found in road dust samples that might contain tire debris, our ambient samples do not show measurable amounts of these higher molecular weight *n*-alkanes, indicating that more fine particulate matter has to be collected to reduce the detection limit. Benzothiazole, derived from vulcanization accelerators known as thiazoles and sulphenamides also has been quantified in our tire debris particle extracts. Because benzothiazole is semi-volatile it could become adsorbed onto fine particulate matter from the gas phase during sampling. Using solvent extraction techniques, a benzothiazole signal from ambient particle samples could reflect both rubber particle-bound material as well as particle-adsorbed benzothiazole that was originally in the gas phase. Further research on the occurrence of benzothiazole in the atmosphere will be needed before it can be concluded whether or not it is a useful tracer for airborne tire debris.

Organometallic brake lining wear particles do not contain many unusual extractable organic compounds except for polyalkylene glycol ethers which also have been identified in the ambient samples but not in the fine particulate road dust samples investigated here (There are, however, unusual elements in this type of source sample). Polyalkylene glycol ethers are mainly used as hydraulic fluids (e.g. brake fluids) and to a minor extent as

solvents in protective coatings, printing inks, and other chemical specialties.⁷

The organic carbon content of fine paved road dust released to the Los Angeles urban atmosphere contributes nearly 16% of the total fine organic matter (OC) released to that area, and thus is one of the largest single sources.⁴ Therefore, it is important to characterize road dust emissions. The organic chemical composition of the fine particulate road dust closely resembles ambient fine particulate matter collected in the Los Angeles area. Paved road dust is an agglomerate of many direct and indirect (via ambient deposition) fine particulate source emissions and the partial contributions of major sources to the road dust itself can be estimated by molecular marker methods. It is seen that road dust contains major contributions from vehicle exhaust aerosol and from plant debris or garden soil. In order to model the turnover and the re-entrainment of road dust to the ambient atmosphere, the organic chemical characterization on a molecular level provided by the present work can be combined with the concentration of crustal elements such as Al, Si that are contributed by the soil material present in road dust. Using a combination of organic and inorganic compounds it should be possible to monitor the organic compound fluxes from the road surfaces to the ambient air.

Particulate Abrasion Products from Leaf Surfaces of Urban Plants. In order to model and predict the chemical composition and concentration levels of airborne fine particulate organic matter, it is necessary to characterize the source profiles of the major anthropogenic and biogenic sources. It has been observed that appreciable amounts of the carbonaceous aerosol consists of contemporary (non-fossil) carbon in the Los Angeles atmosphere which is due to both anthropogenic and biogenic sources. In order to evaluate the contributions of leaf surface waxes to the urban atmosphere, a representative sample from the dominant plant species was investigated. Green and dead leaves from 62 different plant species that are characteristic of the Los Angeles area were harvested and composited according to the actual leaf mass distribution for that area. The leaf composites were gently agitated in clean Teflon bags while a purified air stream was diverted through the bags in order to simulate leaf surface abrasion by the wind. Organic compounds including *n*-alkanes, *n*-alkanoic and *n*-alkenoic acids, *n*-alkanols, *n*-alkanals, terpenoid compounds, and trace amounts of PAH were identified and quantified. Pronounced differences were observed between the composition of dead and green leaf abrasion particles. By comparing the results from the present study with that of other biogenic source samples and ambient fine particle samples it was found that higher molecular weight *n*-alkanes (C₂₇ - C₃₃) with their pronounced odd/even carbon number predominance provide a suitable marker compound assemblage that can be used to trace vegetative detritus in the urban atmosphere.

CONCLUSIONS

The work in progress provides the necessary input data to model the interaction of anthropogenic and biogenic primary fine particle emission sources with the urban atmosphere. Here, 10 primary sources have been characterized and their molecular signatures determined. The identification and quantification scheme was aimed not only to determine many organic compounds but also to test and verify the possibility that marker compounds characteristic of particular sources can be used to trace primary source emissions in the urban atmosphere.

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