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Table of Contents

Chapter 1

Chapter 2

Chapter 4

Chapter 5

Chapter 7

Organic Compounds in Cigarette Smoke 197

Chapter 8

Organic Compounds from Industrial Spray Painting Operations 226

Chapter 9

List of Figures

List of Tables

Abstract

A dilution source sampling system is used to quantify the air pollutant emissions from major urban air pollution sources. The emissions from catalyst-equipped gasoline-powered motor vehicles, noncatalyst gasoline-powered motor vehicles, diesel trucks, meat charbroiling, the cooking of vegetables with seed oils, fireplace combustion of softwood and hardwood, cigarette combustion, and paint spray coating operations are characterized. Semi-volatile and particle-phase organic compounds in the diluted source emissions are collected simultaneously by both a traditional filter/PUF (polyurethane foam) sampling train and by an advanced organic compound-based denuder/filter/PUF sampling train to provide information on the gas/particle phase distribution of the semi-volatile organic compounds. Emission rates of hundreds of organic compounds, spanning carbon numbers from C_1 to C_{29} are determined by gas chromatography/mass spectrometry and gas chromatography with flame ionization detection. Fine particle mass emission rates and fine particle elemental chemical composition are measured as well.

Executive Summary

Gas-phase volatile organic compounds, semi-volatile organic compounds and high molecular weight particle-phase organic compounds have been simultaneously quantified on a single compound basis in the emissions from major sources of urban air pollutants. These sources include catalyst-equipped gasoline-powered motor vehicles, noncatalyst gasoline-powered motor vehicles, medium duty diesel trucks, meat charbroiling, cooking operations that use seed oils, cigarette combustion, and spray coating operations. A dilution source sampling system was employed to dilute hot exhaust emissions with activated carbon-filtered and HEPA-filtered air which in the presence of sufficient residence time causes those organic vapors that will form particulate matter upon cooling in the atmosphere instead to condense onto pre-existing particles in the source exhaust within the dilution sampler itself. The emissions thus can be sampled at near atmospheric temperature and pressure in order to obtain data on the partitioning of organic compounds between the gas and particle phases. Advanced sampling techniques were used to characterize the gas/particle phase distribution of semi-volatile organic compounds in the diluted and cooled exhaust emissions.

The organic compound emissions profiles developed during the source testing program were used in receptor-based air pollution models to determine the primary source contributions to volatile organic gases, semi-volatile organic

gases, fine particle organic compounds, fine particle mass and individual organic compound concentrations in the urban atmosphere. The model results also can be used to place an upper limit on the contribution of secondary organic aerosol to atmospheric fine particle concentrations. The model was used to help understand the source contributions to atmospheric pollutants under summer photochemical smog conditions in California's South Coast Air Basin.

Meat Charbroiling

Emission rates of 120 organic compounds, spanning carbon numbers from C_1 to C_{29} were quantified in the exhaust from meat charbroiling including n-alkanoic acids, n-alkenoic acids, carbonyls, lactones, alkanes, aromatics, polycyclic aromatic hydrocarbons, alkenes, and steroids. Ethylene, formaldehyde, and acetaldehyde were found to be the predominant light gas-phase organic compounds emitted from the charbroiling operations. n-Alkanoic acids, n-alkenoic acids, and carbonyls made up a significant fraction of the quantified semi-volatile and particle-phase organic compound emissions. Meat charbroiling is one of the few sources identified to date that contributes to the high molecular weight aldehydes measured in the urban atmosphere. Semi-volatile and particle-phase organic compounds were collected for quantification by two simultaneous sampling protocols: (1) quartz fiber filters followed by polyurethane foam (PUF) cartridges, and (2) XAD-coated annular denuders followed by quartz fiber filters and PUF cartridges. Good agreement was observed for the total mass emissions collected by the two different sampling procedures; however, the partitioning of the semi-volatile organic compounds between the gas phase and particle phase, as measured by the two sampling procedures, showed significant differences for n-alkanoic acids, indicating that significant artifact adsorption of these compounds occurs to the filter in the filter/PUF sampling system.

Cooking Vegetables in Seed Oil

Two cooking methods and three types of seed oils were examined: vegetables stir fried in soybean oil, vegetables stir fried in canola oil, and potatoes deep fried in hydrogenated soybean oil. The emission rates of 99 organic compounds were quantified, including n-alkanes, branched alkanes, alkenes, n-alkanoic acids, n-alkenoic acids, carbonyls, aromatics, polycyclic aromatic hydrocarbons (PAH), and lactones. Carbonyls and fatty acids (n-alkanoic and n-alkenoic acids) made up a significant portion of the organic compounds emitted from all three seed oil cooking procedures. The compositional differences in the organic compound emissions between the different cooking operations were consistent with the differences in the organic composition of the various cooking oils used. The distribution of the n-alkanoic acids between the gas and particle phases was found to be in good agreement with gas/particle partitioning theory. The relative importance of emissions from commercial cooking operations that employ seed oils to the total emissions of

C_{16} and C_{18} n-alkanoic acids in the Los Angeles urban area was estimated, and showed that cooking with seed oils accounted for approximately 12% of the total primary emissions of these acids. Estimates indicated that cooking with seed oils may make up a significant fraction of the emissions of the n-alkanoic acids in the molecular weight range of nonanoic acid.

Diesel Trucks

Emissions from late-model medium-duty diesel trucks were quantified using a two-stage dilution source sampling system. The diesel trucks were driven through the hot-start Federal Test Procedure (FTP) urban driving cycle on a transient chassis dynamometer. Emission rates of 52 gas-phase volatile hydrocarbons, 67 semi-volatile and 28 particle-phase organic compounds, and 26 carbonyls, were quantified along with fine particle mass and chemical composition. It was found that all C_1-C_{13} carbonyls combined account for 63% of the gas-phase organic compound mass emitted from medium duty-diesel trucks. Fine particulate matter emission rates and chemical composition were quantified simultaneously by two methods: a denuder/filter/PUF sampler and a traditional filter sampler. Both sampling techniques yielded the same elemental carbon emission rate of 56 mg per km driven, but the particulate organic carbon emission rate determined by the denuder-based sampling technique was found to be 35% lower than the organic carbon mass collected by the traditional filter-based sampling technique due to a positive vapor-phase sorption artifact that affects the traditional filter sampling technique. The distribution of organic compounds in the diesel fuel used in this study was compared to the distribution of these compounds in the vehicle exhaust. Significant enrichment in the ratio of unsubstituted polycyclic aromatic hydrocarbons (PAH) to their methyl and dimethyl substituted homologues was observed in the tailpipe emissions relative to the fuel. Isoprenoids and tricyclic terpanes were quantified in the semi-volatile organics emitted from diesel vehicles. When used in conjunction with data on the light gas-phase hydrocarbons and elemental carbon emitted, the isoprenoids and the tricyclic terpanes may help trace the presence of diesel exhaust in atmospheric samples.

Gasoline-Powered Motor Vehicles

Organic compounds present in the tailpipe emissions from an in-use fleet of gasoline-powered automobiles and light-duty trucks were quantified using a two stage dilution source sampling system. The vehicles were driven through the cold-start Federal Test Procedure (FTP) urban driving cycle on a transient dynamometer. Emission rates of gas-phase volatile hydrocarbons, semi-volatile and particle-phase organic compounds, carbonyls, and fine particle mass and chemical composition were quantified. Six isoprenoids and two tricyclic terpanes, which were quantified using new source sampling techniques for semi-volatile organic compounds, have been identified as potential tracers for gasoline-powered motor vehicle effluent emissions. A composite sample of the commercially-distributed California Phase II Reformulated Gasoline used in these tests was analyzed by several analytical methods to quantify the organic compound distribution in the gasoline including some organic compounds that are found in the atmosphere as semi-volatile and particle-phase species. These results allowed a direct comparison of the semi-volatile and particle-phase organic compound emissions from gasoline-powered motor vehicles to the gasoline burned by these vehicles. The distribution of n-alkanes and isoprenoids emitted from the catalyst-equipped gasoline-powered vehicles was found to be the same as the distribution of these compounds in the gasoline used. In contrast, the distribution of polycyclic aromatic hydrocarbons (PAH) present in the gasoline was significantly different from the distribution of the PAH in the tailpipe emissions.

Fireplace Combustion of Wood

The emissions rates of volatile organic compounds (VOC), gas-phase semi-volatile organic compounds, and particle-phase organic compounds from residential fireplace combustion of wood were measured. Firewood from a conifer tree (pine) and from two deciduous trees (oak and eucalyptus) were burned to determine organic compound emissions profiles for each wood type including the distribution of the alkanes, alkenes, aromatics, polycyclic aromatic hydrocarbons (PAH), phenol and substituted phenols, guaiacol and substituted guaiacols, syringol and substituted syringols, carbonyls, alkanoic acids, resin

acids, and levoglucosan. Levoglucosan was the major constituent in the fine particulate emissions from all three wood types, contributing 18 to 30 percent of the fine particulate organic compound emissions. Guaiacol (2-methoxyphenol), guaiacols with additional substituents at position 4 on the molecule, and resin acids were found to be emitted in significant quantities from pine wood combustion. Syringol (2,6-dimethoxyphenol) and syringols with additional substituents at position 4 on the molecule were emitted in large amounts from oak and eucalyptus firewood combustion but these compounds were not detected in the emissions from pine wood combustion. Syringol and most of the substituted syringols are found to be semi-volatile compounds that are present in both the gas and particle phases, but two substituted syringols which have not been previously quantified in wood smoke emissions, propionylsyringol and butyrlsyringol, were found exclusively in the particle-phase and can be used to help trace wood smoke particles in the atmosphere. Benzene, ethene, and acetylene are often used as tracers for motor vehicle exhaust in the urban atmosphere. Our measurements showed that the contribution of wood smoke to the ambient concentration of benzene, ethene, and acetylene is large enough in areas with substantial wood combustion that use of these compounds as if they were vehicle tracers could lead to an overestimate of the contribution of motor vehicle tailpipe exhaust to atmospheric VOC concentrations.

Cigarette Smoke

One hundred and thirty-seven gas-phase, semi-volatile, and particle-phase organic compounds including alkanes, olefins, aromatics, polycyclic aromatic hydrocarbons (PAH), fatty acids, carbonyls, nicotine and other nitrogen-containing organic compounds were quantified in the emissions from cigarette smoking. Six different brands of commercially-available cigarettes, representing four cigarette manufacturers, were smoked by a cigarette customer to obtain an average cigarette smoke emissions profile that combined both sidestream and exhaled mainstream smoke. Gas-phase emissions were found to have significant alkanes, olefins, aromatics, carbonyls and nicotine content. Quantified particle-phase emissions also contain nicotine accompanied by noticeable contributions from alkanes, phenols, and fatty acids. Nicotine was emitted at the highest rate of all of the individual non-methane organic compounds quantified in the emissions from cigarette smoke followed by isoprene and acetaldehyde. Olefins and carbonyls were the largest contributors to low molecular weight volatile gas-phase organic compound emissions followed next by alkanes and aromatic hydrocarbons. The distribution of light gas-phase hydrocarbons and carbonyls emitted from cigarette smoking was compared to the distribution of these compounds in wood smoke and meat charbroiling emissions. The quantitative differences in these emission profiles provide one basis for distinguishing the contributions from different sources to air pollutant levels in environments that contain cigarette smoke that is mixed with the emissions from other domestic or commercial activities. In addition, the gas/particle phase-distribution and emission rates of semi-volatile organic compounds emitted in cigarette smoke, including nicotine, triacetin, menthol and neophytadiene, have been quantified. Carbonyls, cotinine, nicotinic acid and N-oxynicotine are identified as supplemental particle-phase tracers for cigarette smoke, which could be used along with the high molecular weight iso- and anteiso-alkanes to track cigarette smoke contributions to air pollutant concentrations.

Spray Coating Operations

Gas-phase and particle-phase emissions from industrial-scale spray painting operations were measured. A water-based paint and an oil-based paint were examined, representing a subset of the spray paints used in southern Califronia. The emissions rates of 35 organic compounds that included alkanes, aromatics, aldehydes, ketones, and esters were quantified, along with the fine particle mass emission rate and fine particle elemental composition. Total non-methane organic gas emissions from water-based spray coating operations were dominated by the emission of acetone and butanone. Total non-methane organic gas emissions from oil-based spray coating operations were found to contain alkanes, cycloalkanes, aromatics, and aliphatic ketones. Fine particle and semi-volatile organic compound mass emissions from the use of both paint types were much lower than the mass emissions of gas-phase organic compounds. Texanol (2,2,4-trimethyl-1,3-pentanediol monoisobutyrate), a semi-volatile organic compound emitted from spray coating operations using water-based paints that can be measured by standard GC/MS techniques, was identified as a potentially useful tracer for the emissions from water-based spray coating operations. Organic carbon and titanium (presumably present as titanium dioxide) were the largest contributors to the fine particle mass emitted from both types of paint tested in the present study.

A Comprehensive Source Apportionment Model for Organic Compounds

A comprehensive organic compound-based receptor model was developed to simultaneously apportion the source contributions to atmospheric gas-phase organic compounds, semi-volatile organic compounds, fine particle organic compounds, and fine particle mass concentrations. The model was applied to ambient data collected at four sites in the south coast region of California during a severe summertime photochemical smog episode, where the model was able to determine the direct primary contributions to atmospheric pollutant concentrations from ten distinct air pollution source types. The ten sources included in the model were gasoline-powered motor vehicle exhaust, diesel engine exhaust, whole gasoline vapors, gasoline headspace vapors, whole diesel fuel vapors, paved road dust, tire wear debris, meat cooking exhaust, natural gas leakage, and vegetative detritus. Gasoline engine exhaust plus gasoline vapors are the predominant sources of volatile organic gases, while gasoline and diesel engine exhaust plus diesel fuel vapors dominate the

emissions of semi-volatile organic compounds from these sources during the episode studied at all four sites. Fine particle organic compound mass on this occasion was made up of noticeable contributions from both gasoline-powered motor vehicles, diesel engines, meat cooking and paved road dust with smaller but quantifiable contributions from vegetative detritus and tire wear debris. In addition, secondary organic aerosol, which is formed from the low-vapor pressure products of gas-phase organic compound reactions, was found to be a major source of fine particle organic compound mass. The upper limit to the concentrations of secondary organic aerosol calculated both in the present study and in a previous study were shown to correlate fairly well with the concentrations of 1,2-benzenedicarboxylic acid in the atmospheric fine particle mass, indicating that this aromatic acid may be useful in tracing the presence of certain sources of secondary organic aerosol in the atmosphere.

Chapter 1

Introduction

1.1 Motivation

Organic compounds play an important role in urban air pollution. Low molecular weight gas-phase organic compounds, often called volatile organic compounds (VOCs), react with oxides of nitrogen to form ozone in photochemical smog. Emissions of these compounds from specific sources, such gasoline-powered motor vehicles (1-3), have been extensively characterized. In addition, air pollution transport and receptor models have been used to understand the chemistry, transport, and origin of the VOCs in the urban atmosphere (4-7). As these gas-phase air pollution models continue to advance, they are limited by the quality and quantity of the emissions data available to drive the models. For example, very little speciated emissions data exist for the highly reactive carbonyls, which have been shown to make up a significant portion of the chemical reactivity of the urban atmosphere (8).

In addition to the VOCs, the urban atmosphere also contains higher molecular weight organic compounds that are present in the particle phase in the atmosphere, and semi-volatile organic compounds which are present simultaneously in both the gas-phase and the particle-phase. Recent studies have begun the process of characterizing non-volatile and semi-volatile organic compounds that are present in the particle-phase in the urban atmosphere and in the emissions from air pollution sources (9-18). This information has been used in conjunction with atmospheric dispersion models (19, 20) to predict air pollutant source contributions to ambient fine particulate organic compound concentrations, but such data have not previously been incorporated into receptor-based air pollution models that use chemical substances in the source emissions as tracers to compute the relationship between the direct primary emissions of organic compounds and their concentrations in atmospheric fine particles.

In contrast to the VOC's and the heavy particle-phase organic compounds, very little is known about the emissions of semi-volatile organic compounds from air pollution sources. This is mainly due to the difficulty of collecting semi-volatile organic compounds, which are too volatile to be effectively collected on particle filters and are not volatile enough to be sampled using gas canisters. The previously collected data on the emissions of semi-volatile organic compounds from air pollution sources have been limited to specific classes of compounds such as methoxyphenols in wood smoke (21, 22) and polycyclic aromatic hydrocarbons (PAH) emitted from diesel trucks (23).

Historically, the gas-phase air pollution models and the particle-phase air pollution models have been developed in parallel with very little interaction.

These models, however, are being merged into comprehensive air pollution models that can simultaneously track the transport and chemical reaction of gas- and particle-phase organic compounds in the atmosphere. These developments have laid the foundation to study aspects of air pollution that could not be addressed in the past, including (1) the role of semi-volatile organic compounds in gas-phase chemistry and ozone formation and (2) secondary aerosol formation from VOCs and semi-volatile organic compounds. However, these modeling efforts are limited by the availability of comprehensive emissions data that simultaneously describe volatile organic gases, semi-volatile organic compounds, and particle-phase organic compounds. Further progress in the study of this aspect of air pollution, therefore, requires that measurements of these compounds from air pollution sources be made in a manner that is consistent with the atmospheric measurements against which the air pollution model results will be compared. In addition, once such emissions data have been acquired, it will be possible to explore the design of new receptor-based air quality models that use organic compounds as tracers for the effluent from specific emissions sources in order to better understand the relationship between direct primary emissions from air pollution sources and ambient pollutant concentrations.

1.2 Research Objectives

The principal objectives of this research are to quantify the emissions of volatile gas-phase, semi-volatile, and particle-phase organic compounds from air pollution sources and to develop receptor-based air pollution models which use these emissions data to quantify the primary contributions of air pollution sources to atmospheric pollutant concentrations.

Air pollutant emissions data are sought which are collected and analyzed by sampling techniques which are the same as those used for the quantification of individual organic compounds in the ambient atmosphere. This requires the use of a dilution source sampler which can dilute hot exhaust emissions from combustion sources to near ambient temperatures and pressure prior to sampling, such that the organic compounds in the cooled diluted exhaust are present at near their atmospheric equilibrium distribution between the gas- and particle-phases. In addition, the sampler must be specifically configured for the simultaneous collection and quantification of gas-phase, semi-volatile and particle-phase organic compounds, a development which has not been reported previously. Sampling and analytical techniques for the collection and quantification of a broad range of semi-volatile organic compounds are needed, and a desired characteristic of the sampling technique is that it should achieve an accurate determination of the particle/gas phase partitioning of the semi-volatile organic compounds present in the diluted source emissions.

In this work, the major sources of organic compounds emissions to the urban atmosphere first are tested to quantify the emissions of volatile gas-phase hydrocarbons, carbonyls, semi-volatile organic compounds, and particle-phase organic compounds along with fine particle mass and elemental composition. Then receptor-based air quality models are developed that utilize these emissions source data to understand the relationship between the direct primary emissions from air pollution sources and the atmospheric concentrations of these pollutants. This is done by using unusual organic compounds that are present in the emissions from some sources but not others as tracers for the effluent from particular sources in the atmosphere. Receptor models which can elucidate the relationships between the emissions and ambient concentrations of fine organic particle mass, fine particle mass, volatile organic compound mass, semi-volatile organic compound mass, and individual organic compounds are sought.

1.3 Approach

This section provides an overview of the research presented in the following chapters. Chapters 2 through 8 describe the collection of the source emissions data and discuss the significance of the emissions from each source tested. In Chapter 2, the design of the comprehensive source sampling system for organic compounds is described, and the results of performance tests of the sampler are presented along with measurements of the emissions from meat charbroiling. Little, if any, data have existed previously that describe the emissions of gas-phase and semi-volatile carbonyls and organic acids from meat charbroiling. In addition, the distribution of n-alkanoic acids between the gas- and particle-phases in the diluted meat smoke is discussed, and it is shown that these compounds do not follow the distribution predicted by gas/particle partitioning theory, in all likelihood because semi-volatile organic compounds become trapped within solid meat-fat containing particles where they cannot easily repartition into the vapor phase.

Chapter 3 discusses the emissions from cooking with seed oils. Organic compound fingerprints that describe the emissions from these cooking operations, using different seed oils, are presented along with a discussion of the gas/particle partitioning of n-alkanoic acids in the diluted exhaust from cooking with seed oils. The n-alkanoic acids in the diluted exhaust from these sources follow gas/particle partitioning theory, which differs from the distribution of the same compounds in the diluted meat charbroiling exhaust. The emissions of n-alkanoic acids and carbonyls from cooking with seed oils are shown to be significant contributors to the urban atmospheric concentrations of these compounds.

Chapter 4 reports the emissions from medium-duty diesel trucks operated over the hot-start portion of the Federal Test Procedure (FTP) urban driving cycle on a chasis dynamometer. Gas-phase carbonyls and diesel fuel components are found in large quantities in the exhaust emissions from diesel engines. The distribution of the organic compounds present in diesel fuel is compared to the distribution of these compounds in the tailpipe emissions from the diesel trucks, showing a significant change in the ratio of alkylated-PAH to unsubstituted PAH following combustion. In addition, the distribution of specific n-alkanes, isoprenoids, and tricyclic terpanes in the emissions from diesel trucks is shown to be the same as previously reported in the Los Angeles area atmosphere, indicating that these compounds are likely to be useful to help trace diesel engine exhaust in the atmosphere.

Chapter 5 details the measurement and emissions from both gasoline-powered catalyst-equipped motor vehicles and noncatalyst gasoline-powered motor vehicles operated over the cold-start FTP dynamometer cycle. Significant differences are seen in the total mass emissions and in the distribution of organic compounds between the catalyst-equipped vehicles and the non-catalyst equipped vehicles. A comparison of the composition of the gasoline used during the source tests and emissions from the gasoline-powered motor vehicles shows a significant decrease in the ratio of alkylated-PAH to unsubstituted PAH present in the vehicle exhaust as compared to the fuel, a transformation similar to that observed for the diesel engines.

In Chapter 6, the emissions from fireplace combustion of two types of hardwood and one softwood are presented. Levoglucosan is found to be a major constituent in the fine particulate matter emitted from all three types of wood burned, and it is shown that the distribution of syringol- and guaiacol- type compounds can be used to distinguish between the emissions from hardwood and softwood combustion. Gas-phase emissions of acetylene, ethene, and benzene from wood combustion are shown to be important to the ambient concentrations of these compounds during a period of high wood burning. This result is significant since acetylene, ethene and benzene are often used by other investigators to differentiate between the contributions from whole gasoline evaporation versus gasoline-powered motor vehicle exhaust in the atmosphere; interference from the effects of wood combustion could introduce significant uncertainties into such calculations.

The emissions of organic compounds present in cigarette smoke are quantified in Chapter 7. Of particular significance is the measurement of the phase distributions of semi-volatile organic compounds which may have been used incorrectly as cigarette smoke tracers in the past while only tracking the particle-phase concentrations of these compounds.

Chapter 8 covers the emissions from spray paint coating operations using both water-based paint and oil-based paint. Texanol, a semi-volatile organic compound, is found to be emitted in significant quantities from spray coating with water-based paints.

In Chapter 9, a comprehensive receptor-based air quality model is developed that simultaneously tracks source contributions to volatile organic compounds, semi-volatile organic compounds and particle-phase organic compounds by using individual organic compounds as tracers for the relevant emissions sources. The model is applied to study the south coast region of southern California during a severe summertime air pollution episode.

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Chapter 2

Organic Compounds from Meat Charbroiling

2.1 Introduction

Atmospheric dispersion models (1, 2) and an atmospheric receptor model that uses organic compounds as tracers (3) have been used to understand the relationship between fine particulate matter emitted from meat cooking operations and atmospheric fine particle concentrations. In the Los Angeles area, meat cooking operations were found to contribute up to approximately 20% of the annual average fine organic particle concentrations in the atmosphere at four air quality monitoring sites in 1982. Although the relationship between ambient fine particle concentrations and primary particle emissions from meat cooking operations is relatively well characterized, little is known about the relationship between the emissions from meat cooking operations and other aspects of air pollution such as photochemical smog formation, secondary organic aerosol formation, and the ambient concentrations of air toxics. The lack of understanding of the effect of meat cooking emissions on these aspects of air quality is largely due to two reasons: 1) the lack of data on the emissions of gas-phase and semi-volatile organic compounds from meat cooking operations, and 2) the previous inability of air pollution models to address the role of semi-volatile organic compounds in secondary aerosol formation and photochemical smog.

Significant progress has been made in recent years toward understanding the atmospheric behavior of semi-volatile organic compounds (4, 5). In addition, air pollution models are now capable of better addressing the role of secondary organic aerosol formation from reactive organic gases (6). These two developments have laid the foundation for the development of comprehensive air pollution models which will be able to simultaneously track the gas-phase and particle-phase organic compound concentrations and the chemistry and physics of the interaction of gas-phase organic compounds with the associated particulate matter. A limiting factor in the application of these models to studying specific air pollution problems is the scarcity of emissions inventory data for the semi-volatile organic compounds covering virtually all major urban air pollution sources. To this end, a series of air pollution source tests is being conducted to obtain comprehensive emissions source profiles covering gas-phase, semi-volatile, and particle-phase organic compounds, including hydrocarbons, carbonyls, and organic acids, plus fine particle emission rates and fine particle elemental composition. The current paper addresses the measurement of such emissions from meat charbroiling operations.

2.2 Experimental Methods

2.2.1 Comprehensive Source Sampler

An advanced source sampling system has been developed which facilitates the simultaneous measurement of gas-phase, semi-volatile and particle-phase organic compound emission rates; fine particle mass emission rates and fine particle elemental composition. The portable dilution tunnel was originally developed for fine particulate measurements by Hildemann et al. (7) and has been extended with additional equipment that allows single compound quantification of gas-phase and semi-volatile organic compound emissions. In this dilution source sampler, which can operate as a single-stage dilution tunnel or a two-stage dilution tunnel, hot exhaust emissions are mixed with a 10 to 100 fold excess of activated carbon-filtered and HEPA-filtered air which in the presence of sufficient residence time causes those organic vapors that will form particulate matter upon cooling in the atmosphere instead to condense onto pre-existing particles in the source exhaust within the dilution sampler itself. The emissions thus can be sampled at near atmospheric temperature and pressure in order to obtain data on the partitioning of organic compounds between the gas and particle phases.

A diagram of the front portion of the dilution source sampler used here is shown in Figure 1 of Hildemann et al. (7). Modification of that sampler begins as the diluted mixture of particles and gases is withdrawn from the residence time chamber located at the far downstream side of the sampling system. As shown in Figure 2.1 of the present work, samples are withdrawn through AIHL-design cyclone separators (8) which are operated at a flowrate of 30 lpm such that fine particles with aerodynamic diameters smaller than 1.8 μm in diameter pass through the cyclones along with all gas-phase species. Semi-volatile organic and fine particle-phase compounds then are collected with two different sampling trains that operate in parallel. The first sampling train begins with a XAD-coated annular denuder (URG, Inc.; 400 mm long, 4 channel denuder), shown on the right side of Figure 2.1. The flow next is divided between three quartz fiber filters (47 mm diameter, Pallflex Tissuequartz 2500 QAO) operated in parallel at a flowrate of 10 lpm each. The flow out of each of the three quartz fiber filters is then combined and is passed through two polyurethane foam (PUF) cartridges (Atlas Foam; density = 0.022 g cm^{-3}, ILD = 30; 5.7 cm diameter by 7.6 cm long) operated in series. The gas-phase semi-volatile organic compounds are collected by the annular denuder while particles and particle-phase organic compounds pass through the denuder and are collected on the filters downstream of the denuder. The PUFs downstream of the filters collect any semi-volatile organics that blow off the filters.

The XAD coated annular denuders are prepared by a modified version of the procedure originally developed by Gundel et al. (9) and are operated at a

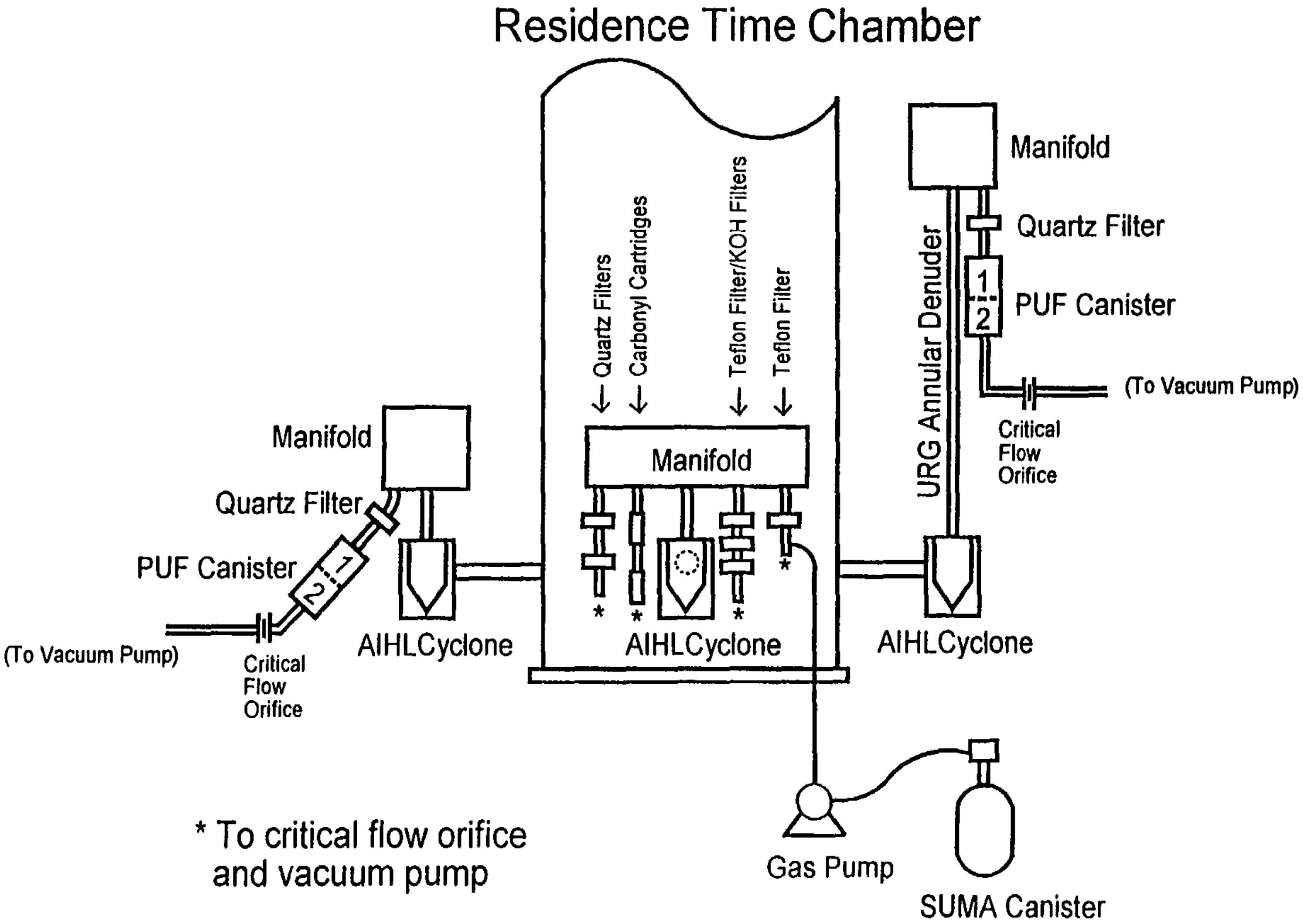

Figure 2.1. Sampling equipment connected to the comprehensive dilution source sampler for the measurement of gas-phase, semi-volatile, and particle-phase organic compounds, and fine particle mass and chemical composition.

flowrate of 30 lpm. Briefly, the XAD coated annular denuders are coated with a slurry of XAD-4 (Sigma Amberlite XAD-4). The XAD-4 is ground with a mortar and pestle to pass through a 400 mesh sieve, cleaned, then slurried into a solvent mixture of dichloromethane/acetone/hexane (2:3:5) (Fisher Optima Grade). The internal walls of the denuder are wetted with an aliquot of the XAD slurry and then rinsed with four successive batches of a clean XAD-free dichloromethane/acetone/hexane mixture (denuder solvent). The denuder is then dried with high purity nitrogen. The slurry application is repeated five more times. The XAD-4 adheres directly to the etched glass denuder walls and no adhesive is required (9). Within 12 hours prior to being used in a source test, the denuder is cleaned by four successive extractions with the denuder solvent in the presence of mild shaking of the solvent-filled denuder assembly. The denuder is then dried with high purity nitrogen. Denuders are sealed with Teflon-lined end caps from the time of preparation until use.

Particle losses in a similar URG annular denuder have been evaluated at operating conditions similar to those used in the current study, and it has been shown that electrically neutral fine particle losses are less than 5% for particles with diameters between 0.015 and 0.75 μm (10). Experimental results reported by Gundel et al. (9) and experiments conducted in the course of the present project also demonstrate low fine particle losses in the denuders. Typically only one denuder/filter/PUF sampling unit is placed in operation during a source test. A single denuder is used for a sampling time of up to approximately 30 minutes. The denuders are changed during source tests lasting longer than 30 minutes to assure that sampling is almost continuous throughout the source test cycle.

Prior to the current project, the use of XAD-coated denuder technology has only been reported for the collection of PAH (9) and nitro-PAH (11). The current research requires that the technology be applicable to many classes of organic compounds. For this reason, tests were conducted to demonstrate the ability to extract and recover a broad range of organic compounds from these denuders. A denuder was spiked with a standard suite containing over 100 compounds including series of n-alkanes, n-alkanoic acids, n-alcohols, PAH, fatty acid methyl esters, phenol, and benzaldehyde. All of these compounds were found to be quantitatively extracted from the denuders by four successive extractions with denuder solvent as described above, with no residual compounds remaining as measured by a second round of this extraction procedure. In addition, results will be presented in the current study showing good agreement between the total mass emission rates (but not necessarily phase separation) measured by the denuder/filter/PUF sampling train and a less complex filter/PUF sampling train.

A second type of semi-volatile and particle-phase organic compound sampling train is operated simultaneously in parallel with the denuder/filter/PUF system. In this second system, an AIHL-design cyclone separator operated at 30 lpm is followed by three filter/PUF units in parallel each operated continuously at a flowrate of 10 lpm throughout the source test cycle. Each of the filter/PUF units consists of a quartz fiber filter (47 mm diameter, Pallflex Tissuequartz 2500 QAO) followed by two PUF cartridges (Atlas Foam) operated in series as shown on the left side of Figure 2.1. Each PUF cartridge consists of a 5.7 cm diameter by 7.6 cm long cylinder of polyurethane foam which is sized to retain 95% of the gas-phase naphthalene entering the PUF cartridge when operated at 10 lpm over the entire source test (12). Less volatile, heavier organic compounds are collected with even higher efficiencies than seen for naphthalene. During a typical source test, one cyclone/denuder/filter/PUF sampling train and four cyclones each with 3 filter/PUF assemblies are connected to the residence time chamber of the dilution tunnel; the extra filter/PUF units are intended for collection of excess sample to be used in further method development efforts.

In addition to the above sampling trains, a third type of cyclone-based filter sampler combined with VOC canisters and cartridges is operated for the collection of fine particulate matter, carbonyls, organic acids, and gas-phase organic compounds. A schematic of this system is shown in the center of Figure 2.1, pictured with the dilution tunnel's residence time chamber located behind the cyclone. Three stacked filter units and one carbonyl sampling line are connected to the outlet of an AIHL cyclone that draws air at a flowrate of 31 lpm from the residence time chamber of the source sampler. The first stacked filter unit consists of two quartz fiber filters (47 mm diameter, Pallflex Tissuequartz 2500 QAO) in series which are used for elemental and organic carbon (EC/OC) analysis by thermal evolution and combustion analysis as described by Birch and Cary (13). The OC measured on the backup quartz fiber filter is used to help understand the adsorption of semi-volatile organic compounds onto the front filter (14, 15). The second filter stack contains three filters, a Teflon membrane filter (47 mm diameter, Gelman Teflo, 2 μm pore size) followed by two KOH impregnated quartz fiber filters in series. This Teflon membrane filter is used for gravimetric determination of the fine particle mass emissions rate and is analyzed by X-ray fluorescence for 35 trace elements (16). The tandem KOH-impregnated quartz fiber filters are used to collect vapor-phase organic acids which will be analyzed in association with other research activities and will not be reported here. The third filter holder assembly contains one Teflon membrane filter which is used for a duplicate fine particle mass emissions measurement and for inorganic ion measurements by ion chromatography (17), atomic absorption spectroscopy and colorimetry (18). Downstream of that single Teflon filter the sample flow is divided, and a small portion of the flow is used to fill a 6 liter polished stainless steel SUMA canister for the collection of non-methane volatile hydrocarbons ranging from C_2 to C_{10}. The 6 liter SUMA canister is filled continuously at a constant flowrate set to fill the canister over the entire source test cycle. Carbonyls are collected at the outlet of the AIHL cyclone separator by two C_{18} cartridges impregnated with dinitrophenylhydrazine (DNPH) that are operated in series (19). The air flowrates through the DNPH impregnated cartridges are typically in the range 0.3 to 0.5 lpm.

The flowrates through each of the sampling substrates are controlled with the use of critical orifices and are measured before and after each source test with rotameters that have been calibrated using an electronic bubble flowmeter (Gilian Instrument Corporation Model # 800268). The sample and the dilution air flowrates into the dilution tunnel are monitored throughout the source tests with a venturi meter and an orifice meter, respectively. The venturi meter and the orifice meter have been calibrated using dry gas meters. From these sample and dilution air flowrates and the analytical measurements described above, quantitative emissions rates can be determined for chemically speciated fine particulate matter, as well as for individual gas-phase, semi-volatile and particle-phase organic compounds.

Electronic particle sizing instruments and a pair of MOUDI impactors also were connected to the residence time chamber during the meat charbroiling source tests to obtain particle size distributions and particle chemical composition as a function of size. The size distributions and the results obtained from the impactors will be reported elsewhere.

2.2.2 Dilution Sampler Preparation and Evaluation

Prior to the meat charbroiling source tests, the dilution source sampler was completely disassembled and cleaned by vapor degreasing. Directly after degreasing, the sampler pieces were immediately wrapped with clean aluminum foil which had been baked at 550 °C for 12 hours. After the dilution sampler was reassembled, clean dilution air was passed through the sampler as the sampler was heated to approximately 95 °C by wrapping the stainless steel sections with electrical heating tape. The sampler was maintained at 95 °C for a minimum of four hours to remove any residual light hydrocarbons remaining after vapor degreasing. All of the small sampler pieces, including the filter holders and cyclones, were thoroughly cleaned with a detergent solution, next rinsed with deionized water, and then cleaned by sonication with hexane, methanol, and dichloromethane.

The dilution air supply to the dilution tunnel consists of ambient air that has been cleaned by passage through a HEPA filter and an activated carbon bed (7). A comprehensive blank test was conducted at the onset of the source sampling program to determine the ability of the dilution air cleaning system to remove particles, semi-volatile organic compounds, carbonyls, and VOCs. The dilution air cleaning system was found to have very high removal efficiencies for particulate matter, semi-volatile organic compounds, and all carbonyls. As expected, the lightest VOCs were not completely removed by the activated carbon bed, so a system for measuring the residual VOC's in the dilution air was added to the source sampler. Dilution air is sampled and analyzed by the same procedures as used for the diluted sample gas stream described above, and source test results are then corrected by subtraction of any VOC background concentration present in the dilution air.

Particle losses in the comprehensive dilution sampler were evaluated by extracting a section of the dilution tunnel walls immediately following the completion of a cigarette source test in our laboratory. The extract was handled by the same procedures that will soon be discussed for the sample extracts, and compounds deposited per cm^2 of dilution sampler interior wall area were quantified by GC/MS. The mass of individual organic compounds that were deposited onto the entire sampler internal surface area was calculated by scaling up the mass deposited onto the extracted area of the sampler walls to represent the entire interior surface area of the sampling system. The semi-volatile organic compounds that are predominantly present in the gas phase showed no detectable losses to the walls, while the predominately particle-phase organic compounds showed losses of approximately 7%, which is consistent with earlier particle loss experiments reported by Hildemann et al. (7). The compounds which were partitioned between both the gas-phase and the particle-phase were found to have losses in between the pure particle-phase compounds and the pure gas-phase organic compounds. These results indicate that there are no preferential losses of semi-volatile organic compounds in the comprehensive dilution source sampler and that those losses that do occur affect primarily particulate matter, accounting for approximately 7% of the fine particle mass emissions.

2.2.3 Source Testing Procedure

The meat charbroiling source tests were conducted in the field at a large institutional-scale natural gas-fired charbroiler that is in current commercial use. Emissions were sampled downstream from the filter and grease extractor that exist in the charbroiler exhaust ventilation system, which was operated at flowrate of 400 m^3 min^{-1}. The source effluents were diluted by a second stage of dilution within the dilution sampler to bring the organic vapor/particle mixture to ambient conditions at 29 °C. Two charbroiler tests were conducted using commercially distributed pre-formed hamburger patties (Kraft Premier, 114 grams of meat per patty, 20% fat); one test was conducted with defrosted hamburgers and the second test was conducted using hamburgers that were still frozen when placed on the grill as is the common practice at the facility tested. In batches of eight at one time, 80 hamburger patties were cooked over a period of 85 minutes during the test in which the frozen hamburgers were not defrosted prior to cooking. In batches of eight at one time, 112 hamburger patties were cooked over a period of 72 minutes during the test where the hamburger patties were completely defrosted prior to cooking.

2.2.4 Organic Chemical Analysis

Extraction of particle-phase organic compounds collected on quartz fiber filters during the source tests is based on the previous work by Mazurek et al. (20) and Rogge et al. (21-27) and Rogge (28). Prior to sampling, the quartz fiber filters were baked at 550 °C for a minimum of 12 hours to reduce residual carbon levels associated with new filters. Immediately after sampling, the filters were stored in a freezer at -21 °C until the samples were extracted. The filters were typically extracted within one to two weeks following sample collection. Before the quartz fiber filters were extracted, they were spiked with a mixture of seven deuterated internal recovery standards: n-decane-d_{12}, n-pentadecane-d_{32}, n-tetracosane-d_{50}, n-hexanoic acid-d_{11}, n-decanoic acid-d_{19}, phenol-d_5, benzoic acid-d_5, and benzaldehyde-d_6. The samples were extracted twice with hexane (Fisher Optima Grade), followed by three successive benzene/isopropanol (2:1) extractions (benzene: high purity lots of E&M Scientific benzene; isopropanol: Burdick & Jackson). Extracts were filtered, combined, and reduced in volume to approximately 250 ml, and were split into two separate fractions. One fraction was then derivatized with diazomethane to convert organic acids to their methyl ester analogs which are amenable to GC/MS identification and quantification.

The procedures developed for the identification and quantification of organic compounds collected on the XAD-coated annular denuders and the PUF plugs were based on the methods previously developed for the analysis of air pollution samples collected on the quartz fiber filters. The analytical methods developed for the XAD-coated annular denuders and the PUF plugs can be used to quantify vapor-phase semi-volatile organic compounds that are as heavy as particle-phase organic compounds or which are as volatile as dodecane for alkanes, heptanoic acid for n-alkanoic acids, and naphthalene for polycyclic aromatic hydrocarbons under appropriate sampling conditions.

After the completion of each source test, the denuders used for sampling were extracted within 12 hours. During sample extraction, the denuder is first spiked with the same deuterated internal standard mix used for the filter extraction, and is then extracted with the use of four aliquots of 40 ml each of denuder solvent by pouring each aliquot into the denuder and shaking the Teflon capped denuder for approximately 30 seconds per aliquot. The four aliquots are composited and reduced to a volume of approximately 250 ml and then split into two separate fractions. One fraction is derivatized with diazomethane.

Prior to source sampling, the PUF plugs are cleaned by four successive extractions with a solvent mixture of dichloromethane/acetone/hexane (2:3:5) (Fisher Optima Grade). The foam plugs are repetitively compressed during the extraction. After the cleaning procedure, the PUF cartridges are air dried in the dark in an organics clean room and are then stored in annealed borosilicate jars with solvent-washed Teflon lid liners in the freezer at -21 °C. After sampling, the PUF plugs are spiked with the same internal standard mix used for the filter and denuder extractions, and then are extracted with four successive aliquots of a mixture of dichloromethane/acetone/hexane (2:3:5). The extracts are filtered, combined, reduced in volume to approximately 250 ml and then split into two separate fractions. One fraction is derivatized with diazomethane as is done with the filter extracts and the denuder extracts.

Filter, PUF, and denuder field blanks are analyzed with each set of source samples. The field blanks are prepared, stored and handled by exactly the same procedures as used for the source samples.

Both the derivatized and underivatized sample fractions are analyzed by GC/MS on a Hewlett-Packard GC/MSD (GC Model 5890, MSD Model 5972) using a 30 meter by 0.25 mm diameter HP-1701 capillary column (Hewlett-Packard). 1-Phenyldodecane is used as a co-injection standard for all sample extracts and standard runs. The deuterated n-alkanes in the internal standard are used to determine extraction recovery for the compounds quantified in the underivatized samples. The deuterated acids are used to verify that the diazomethane reactions are driven to completion. In addition, the deuterated n-alkanoic acid recoveries are used in conjunction with the recovery of deuterated tetracosane to determine the recovery of the compounds quantified in the derivatized fraction.

Semi-volatile and particle-phase organic compounds collected during the source test program are identified and quantified by gas chromatography/mass spectrometry (GC/MS). Although not all organic compounds emitted from air pollution sources are solvent extractable nor are they all elutable from a GC column, hundreds of compounds can be identified and quantified in source emissions (21, 23-28). Hundreds of authentic standards have been prepared for the positive identification and quantification of the organic compounds found in the current source test program. When quantitative standards could not be obtained for a given compound or compound class, significant effort was made to obtain a non-quantitative secondary standard that could be used for unique identification of the organic compounds. An example of such a secondary standard is the use of petroleum candle wax as a source of *iso*-alkanes and *anteiso*-alkanes that can then be used to help identify their presence when found in cigarette smoke particulate matter. Quantification of compounds identified using secondary standards has been estimated from the response factors for compounds having similar retention times and chemical structure. When neither quantitative nor secondary standards could be obtained, compound identification is classified as either 1) *probable:* when the sample mass spectrum is identical to the library spectrum but no standard was available, and 2) *possible*: same as probable except that the spectrum contained additional information due to coelution with another compound. Compounds having probable and possible identifications are noted but their emission rates are not quantified.

Total non-methane organic gases (NMOG, EPA method TO12) and individual organic vapor-phase hydrocarbons ranging from C_1 to C_{10} were analyzed from the SUMA canisters by gas chromatography/flame ion detection (GC/FID) as described by Fraser et al. (29). Carbonyls collected by the C_{18} cartridges were analyzed by liquid chromatography/UV detection as described by Grosjean et al. (30).

2.3 Results and Discussion

2.3.1 Fine Particle Mass and Chemical Composition

Fine particle emission rates and bulk chemical composition were found to be very similar in both meat charbroiling source tests in this study with an average fine particle mass emission rate of 18.8 ± 2.0 grams per kilogram of meat cooked and an aerosol organic carbon content of 56.6 ± 3.3 percent. The average emission rate is approximately half the 39.8 grams per kilogram of meat cooked reported by Hildemann et al. (31) when cooking hamburgers on the same charbroiler at longer cooking times, 7-8 minutes per burger patty as compared to the approximate 5 minute cooking duration in the current study for comparable defrosted hamburgers. The emission rate per unit of meat charbroiled thus seems to scale approximately in proportion to cooking time on the grill, which seems logical. The fraction of organic carbon in the particle emissions in the present test is not statistically different from that measured by Hildemann et al. (31). Table 2.1 shows the average fine particle emission rate and fine particle elemental and inorganic ion composition obtained during the present meat charbroiling tests. Fine particulate matter emitted from meat charbroiling contains virtually no elemental carbon and very little inorganic matter. Potassium was measured at a level of 0.34 percent of the fine particle mass, much less than organic carbon but in a higher concentration than any of the other inorganic species which were measured. Knowledge of the potassium content of meat smoke is important because non-soil potassium has been used in the past as if it were a nearly unique tracer for woodsmoke (32). In some cases, the potassium content of meat smoke should be considered as well. Smaller quantities of nitrogen as nitrite, aluminum, silicon, phosphorus, sulfur, and chloride also were detected in meat smoke, as shown in Table 2.1.

2.3.2 Non-Methane Organic Compounds

Single compound quantification of the gas-phase, semi-volatile, and particle-phase organic compound emissions was performed only on the source test which utilized defrosted hamburgers for cooking. A material balance on gas-phase and fine particulate organic compounds measured by the comprehensive dilution source sampling system during the defrosted hamburger

Table 2.1. Average Fine Particle Emission Rate and Fine Particle Chemical Composition From Meat Charbroiling. (Values shown in boldface are greater than zero by at least two standard errors).

Fine Particle Mass Emissions Rate (AVG ± STD): **18.8 ± 2.0** g kg^{-1} of Meat Cooked			
X-ray Fluorescence (Wt % of Fine Particle Mass)			
Aluminum	**0.039 ± 0.019**	Selenium	0.00 ± 0.01
Silicon	**0.082 ± 0.018**	Bromine	0.00 ± 0.01
Phosphorus	**0.066 ± 0.018**	Rubidium	0.00 ± 0.01
Sulfur	**0.19 ± 0.012**	Strontium	0.00 ± 0.01
Chlorine	**0.16 ± 0.030**	Yttrium	0.00 ± 0.01
Potassium	**0.34 ± 0.030**	Zirconium	0.00 ± 0.01
Calcium	0.01 ± 0.03	Molybdenum	0.00 ± 0.02
Titanium	0.02 ± 0.12	Palladium	0.00 ± 0.04
Vanadium	0.00 ± 0.05	Silver	0.01 ± 0.05
Chromium	0.00 ± 0.01	Cadmium	0.00 ± 0.05
Manganese	0.00 ± 0.01	Indium	0.00 ± 0.06
Iron	0.01 ± 0.01	Tin	0.00 ± 0.08
Nickel	0.01 ± 0.01	Antimony	0.00 ± 0.09
Copper	0.00 ± 0.01	Barium	0.02 ± 0.33
Zinc	0.00 ± 0.01	Lanthanum	0.01 ± 0.44
Gallium	0.00 ± 0.01	Mercury	0.00 ± 0.01
Arsenic	0.00 ± 0.01	Lead	0.00 ± 0.02
Elemental and Organic Carbon (Wt % of Fine Particle Mass)			
Organic Carbon	**33.8 ± 2.0**	Elemental Carbon	**0.0 ± 0.5**
Ionic Species by Ion Chromatography (Wt % of Fine Particle Mass)			
Chloride	**0.17 ± 0.08**	Ammonium	0.00 ± 0.15
Nitrite	0.00 ± 0.06	Sodium	**0.37 ± 0.11**
Nitrate	**0.38 ± 0.01**	Calcium	0.00 ± 0.59
Sulfate	0.00 ± 0.10	Magnesium	0.00 ± 0.06

Notes: (a) measured by downstream of the organics denuder. Organic carbon measured on undenued filter is 56.6 percent of fine particle mass.

charbroiling test is shown in Figure 2.2. These emissions include 14.9 grams of fine particulate organic compound mass per kg of meat cooked, 8.67 g kg^{-1} of C_2-C_{10} volatile hydrocarbon gases, 1.0 g kg^{-1} of higher molecular weight vapor-phase organics collected by the XAD-coated denuders, and 5.48 g kg^{-1} of C_1-C_{10} carbonyls.

2.3.3 Volatile Organic Compounds

The emissions rate of non-methane C_1-C_{10} volatile organic compounds (VOC) from meat charbroiling was measured to be 13.6 grams per kilogram of meat cooked. Although the VOC emissions from charbroiling are relatively small on a mass basis compared to other urban sources, the emissions contain noticeable amounts of several very reactive light olefinic hydrocarbons. The VOC emissions were found to consist of 2.0 percent propene, 1.6 percent butenes, and 0.8 percent 1,3-butadiene by mass, accompanied by less reactive unsaturated organics including 10.5 percent ethylene and 2.4 percent acetylene. It is unclear if these olefinic compounds are formed from the meat that is being charbroiled or are formed directly from the natural gas combustion used in the charbroiler. Table 2.2 lists the contribution of 41 volatile organic compounds to the non-methane C_1-C_{10} VOC emissions from charbroiling. The quantified volatile hydrocarbons make up 30 percent of the VOC emissions and another 36 percent of the VOC emissions consist of C_1-C_{10} aldehydes.

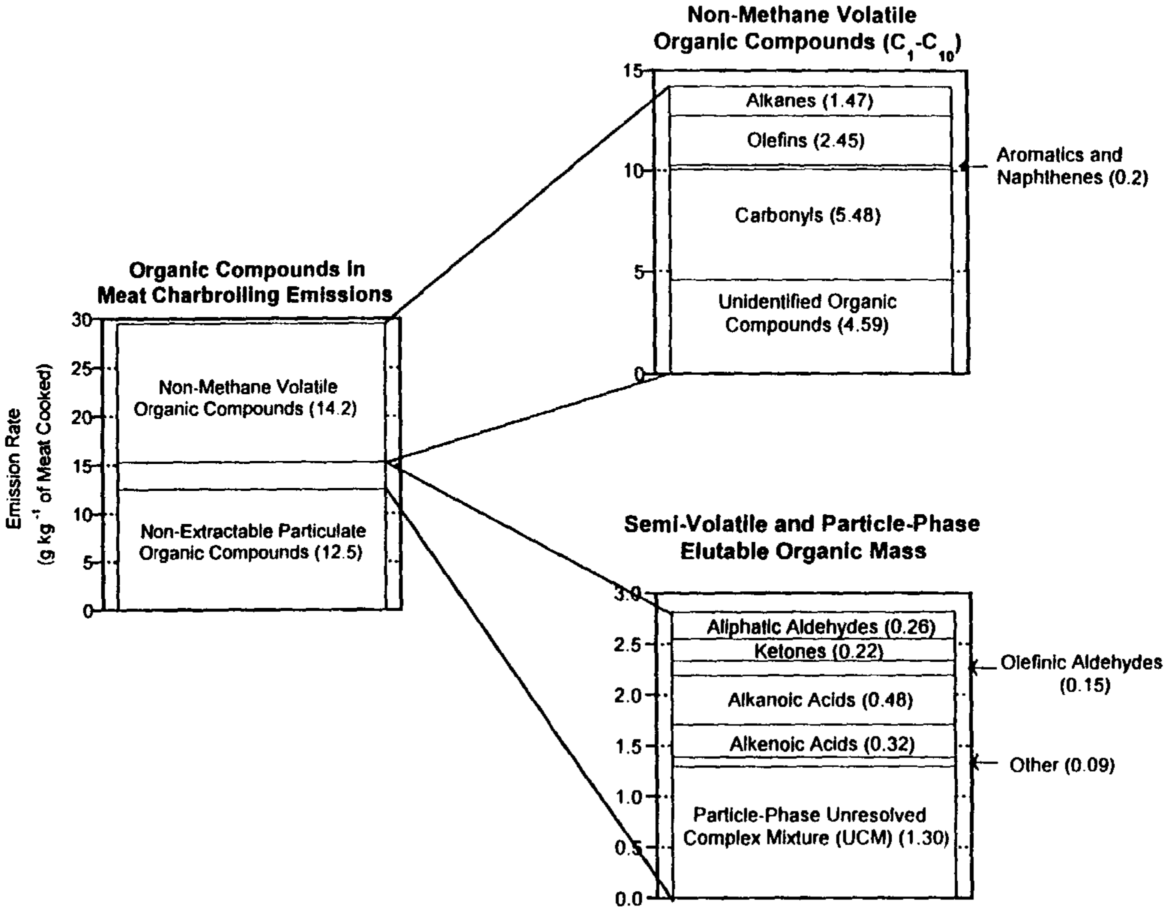

Figure 2.2. Material balance on the gas-phase, semi-volatile, and particle-phase organic compound emissions from meat charbroiling measured by the comprehensive source sampler.

Table 2.2. Organic Compound Emission Rates from Hamburger Meat Charbroiling Over a Natural Gas-Fired Grill

Compound	Gas Phase (µg kg^{-1} of meat cooked)			Fine Particle (µg kg^{-1} of meat cooked)			Total	Notes
	VOC Canister	DNPH Cartridge	XAD Denuder	Filter	PUF1	PUF2		
n-Alkanes								
Methane	18000000						18000000	a
Ethane	663000						663000	a
Propane	190000						190000	a
n-Butane	107000						107000	a
n-Pentane	87000						87000	a
n-Hexane	44000						44000	a
n-Heptane	46000						46000	a
n-Octane	38000						38000	a
n-Nonane	13000						13000	a
n-Decane							< 5000	a
n-Tridecane			3100	330			3430	b
n-Tetradecane			3110	580	1320		5000	a
n-Pentadecane			4490	520	1240		6240	b
n-Hexadecane			3110	135			3240	a
n-Heptadecane							< 400	b
n-Octadecane			1290	160			1450	a
n-Nonadecane			400		320		720	b
n-Eicosane			1020		170		1190	a
n-Heneicosane			390	130	360		880	b
n-Docosane			450	160			610	a
n-Tricosane			500	60			560	b
n-Tetracosane			430	260			690	a
n-Pentacosane			110	380	290		780	b
n-Hexacosane				260			260	a
n-Heptacosane				650			650	b
n-Octacosane				1140			1140	a
n-Nonacosane				770			770	b
Branched alkanes								
i-Butane	54000						54000	a
i-Pentane	74000						74000	a
2,3-Dimethylbutane	5000						5000	a
2-Methylpentane	22000						22000	a
2,4-Dimethylpentane	5000						5000	a
2-Methylheptane	5000						5000	a
2,2,4-Trimethylpentane	11300						11300	a
Alkenes								
Ethene	1485000						1485000	a
Propene	289000						289000	a
1-Butene	73000						73000	a

Identification notes: a) authentic quantitative standard. b) authentic quantitative standard for similar compound in series. c) secondary standard. d) probable identification. e) analyzed as a methyl ester. +) detected but not quantified. Additional Notes: † Naphthalene and nonan-2-one are too volatile for complete collection by denuder. Mass of these compounds collected on PUF is from the gas-phase. ‡ Emissions shown are for two parallel sampling techniques; total is taken from denuder/filter/PUF.

Table 2.2 (continued - page 2)

Compound	Gas Phase (µg kg^{-1} of meat cooked)			Fine Particle (µg kg^{-1} of meat cooked)			Total	Notes
	VOC Canister	DNPH Cartridge	XAD Denuder	Filter	PUF1	PUF2		
Branched alkenes								
i-Butene	159000						159000	a
Diolefins								
1,3-Butadiene	105000						105000	a
Alkynes								
Ethyne(Acetylene)	336000						336000	a
Saturated Cyclic Hydrocarbons								
Cyclopentane	5000						5000	a
Methylcyclopentane	9000						9000	a
Cyclohexane							< 5000	a
Methylcyclohexane	13000						13000	a
Biogenic hydrocarbons								
Isoprene	3000						300	a
Squalene				342			342	a
Aromatic hydrocarbons								
Benzene	83000						83000	a
Toluene	40000						40000	a
Ethylbenzene	11000						11000	a
m-Xylene + p-Xylene	12000						12000	a
Styrene							< 5000	a
o-Xylene	11000						11000	a
1,3,5-Trimethylbenzene							< 5000	a
1,2,4-Trimethylbenzene	24000						24000	a
Naphthalene †			5860		1690	1440	8990	a
Phenanthrene			1120	34	90		1220	a
Anthracene			110	51			160	a
Fluoranthene			400	120			520	a
Pyrene			570	100			670	a
Chrysene/Triphenylene			330	270			600	a
Aliphatic aldehydes								
Formaldehyde		1382000					1382000	a
Acetaldehyde		1092000					1092000	a
Propanal		504000					504000	a
Butanal/Isobutanal		373000					373000	a
Hexanal		203000					203000	a
Heptanal		125000					125000	a
Octanal		146000					146000	a
Nonanal ‡		141000	115000	32700			148000	a
Decanal ‡		70000	29500	4060			33600	a

Identification notes: a) authentic quantitative standard. b) authentic quantitative standard for similar compound in series. c) secondary standard. d) probable identification. e) analyzed as a methyl ester. +) detected but not quantified. Additional Notes: † Naphthalene and nonan-2-one are too volatile for complete collection by denuder. Mass of these compounds collected on PUF is from the gas-phase. ‡ Emissions shown are for two parallel sampling techniques; total is taken from denuder/filter/PUF.

Table 2.2 (continued - page 3)

Compound	Gas Phase (μg kg^{-1} of meat cooked)			Fine Particle (μg kg^{-1} of meat cooked)			Total	Notes
	VOC Canister	DNPH Cartridge	XAD Denuder	Filter	PUF1	PUF2		
Aliphatic aldehydes								
Undecanal ‡		35000	13600	3550			17200	a
Dodecanal ‡		38000	26200	3830			30000	a
Tridecanal			15300	2680			18000	a
Tetradecanal			14400	3580			18000	a
Pentadecanal			12850	1570			14400	b
Hexadecanal			3490				3490	b
Heptadecanal			2510				2510	b
Dicarbonyls								
Glyoxal		550000					550000	a
Methylglyoxal		334000					334000	a
Biacetyl		28000					28000	a
Ketones								
Nonan-2-one †			55700		15400	6200	77300	c
Decan-2-one			65500	10000			75500	c
Undecan-2-one			107000	3430			107000	c
Tridecan-2-one			39000	3250			42300	c
Tetradecan-2-one			61900	3400			65300	c
Pentadecan-2-one			64500	5200			69700	c
Heptadecan-2-one			21300	1680			23000	c
Unsaturated carbonyls								
Crotonaldehyde		495000					495000	a
Methacrolein		52000					52000	a
2-Decenal			98200	5950			104000	a
2-Undecenal			80600	5530			86100	a
n-Alkanoic acids								
Heptanoic acid			26000	6190			32200	a,e
Octanoic acid			29400	9290			38700	a,e
Nonanoic acid			42400	6030			48400	a,e
Decanoic acid			8890	2220			11100	a,e
Dodecanoic acid			4610	1850			6460	a,e
Tetradecanoic acid			4040	17700			21700	a,e
Pentadecanoic acid			220	5750			5970	a,e
Hexadecanoic acid			11400	163000			174000	a,e
Heptadecanoic acid				10300			10300	a,e
Octadecanoic acid			2150	96900			96100	a,e
Nonadecanoic acid				600			600	a,e
Eicosanoic acid				860			860	a,e
Docosanoic acid				350			350	a,e

Identification notes: a) authentic quantitative standard. b) authentic quantitative standard for similar compound in series. c) secondary standard. d) probable identification. e) analyzed as a methyl ester. +) detected but not quantified. Additional Notes: † Naphthalene and nonan-2-one are too volatile for complete collection by denuder. Mass of these compounds collected on PUF is from the gas-phase. ‡ Emissions shown are for two parallel sampling techniques; total is taken from denuder/filter/PUF.

Table 2.2 (continued - page 4)

Compound	Gas Phase (μg kg^{-1} of meat cooked)			Fine Particle (μg kg^{-1} of meat cooked)			Total	Notes
	VOC Canister	DNPH Cartridge	XAD Denuder	Filter	PUF1	PUF2		
n-Alkenoic acids								
9-Hexadecenoic acid				18400			18400	b,e
9-Octadecenoic acid				214000			214000	a,e
9,12-Octadecadienoic acid				32000			32000	a,e
Alkanedioic acids								
Hexanedioic acid				1990			1990	a,e
Octanedioic acid				3900			3900	a,e
Furanones (γ-Lactones)								
5-Ethyldihydro-2(3H)-furanone			6490	2850			9370	a
5-Propyldihydro-2(3H)-furanone			7020	1800			8820	b
5-Butyldihydro-2(3H)-furanone			9540	1420			11000	a
5-Pentyldihydro-2(3H)-furanone			4770	1290			6060	b
5-Hexyldihydro-2(3H)-furanone			3120	920			4040	a
5-Heptyldihydro-2(3H)-furanone				390			390	b
5-Octyldihydro-2(3H)-furanone				480			480	b
5-Nonyldihydro-2(3H)-furanone				800			800	b
5-Decyldihydro-2(3H)-furanone				1750			1750	b
5-Undecyldihydro-2(3H)-furanone				780			780	b
5-Dodecyldihydro-2(3H)-furanone				670			670	b
Other Compounds								
Cholesterol				3970			3970	a
Hexadecanamide				+				d
Octadecanamide				+				d
9-Octadecenamide				+				d
Unresolved Complex Mixture				1300000			1300000	

Identification notes: a) authentic quantitative standard. b) authentic quantitative standard for similar compound in series. c) secondary standard. d) probable identification. e) analyzed as a methyl ester. +) detected but not quantified. Additional Notes: † Naphthalene and nonan-2-one are too volatile for complete collection by denuder. Mass of these compounds collected on PUF is from the gas-phase. ‡ Emissions shown are for two parallel sampling techniques; total is taken from denuder/filter/PUF.

Formaldehyde and acetaldehyde are emitted from meat cooking operations at 1.38 and 1.09 grams per kg of meat cooked which is higher than all other emissions rates for individual VOC's except ethylene. Propanal, crotonaldehyde, and glyoxal are also emitted in significant quantities at 0.50, 0.50 and 0.55 grams kg^{-1} of meat cooked. The emissions of these carbonyls adds significantly to the reactivity of the VOCs emitted from meat cooking operations.

2.3.4 Semi-Volatile and Particle Phase Organic Compounds

Seventy-one vapor-phase semi-volatile and particle-phase organic compounds have been quantified in samples collected on the denuders, filters, and PUFs during the charbroiled meat cooking test as shown in Table 2.2. n-Alkanoic acids, n-alkenoic acids, and carbonyls make up a significant fraction of the semi-volatile and particle-phase organic compounds emitted from meat charbroiling that are extractable and elutable. 9-Octadecenoic acid (oleic acid) and n-hexadecanoic acid (palmitic acid) are emitted at by far the largest rates, with average emissions of 214,000 and 174,000 $\mu g\ kg^{-1}$ of meat cooked, respectively. n-Alkanoic acids as light as n-heptanoic acid and as heavy as n-docosanoic acid have been identified and quantified.

Significant quantities of heavy aliphatic n-aldehydes and alkan-2-ones also are found in the meat cooking exhaust, spanning the range from nonanal to heptadecanal and nonan-2-one to heptadecan-2-one. In addition, two semi-volatile olefinic aldehydes have been identified and quantified, 2-decenal and 2-undecenal. 2-Decenal and 2-undecenal have been previously identified in the head space vapor of heated peanut oil (33). Grosjean et al. (30) measured the atmospheric concentration of aliphatic aldehydes spanning the range from formaldehyde through tetradecanal in the South Coast Air Basin of California during a period of poor air quality and found noticeable quantities of the high molecular weight aliphatic aldehydes. They also showed that the chemical reactivity of the high molecular weight aldehydes taken as a group was comparable to that of formaldehyde or acetaldehyde separately. Although low molecular weight aldehydes are known to be both emitted by primary sources of air pollution as well as formed by chemical reaction in photochemical smog (34), the origin of the high molecular weight aliphatic aldehydes in the urban atmosphere has been unknown. We now know from the present study that the high molecular weight aldehydes are emitted in large quantities from meat charbroiling. Food preparation could be a significant contributor to the high molecular weight aldehydes and hence to the photochemical reactivity of the urban atmosphere. Other sources (e.g., the cooking oil fumes mentioned above) should be sought as well through further source testing. Figure 2.3 shows the distribution of emissions for semi-volatile and particle-phase fatty acids (n-alkanoic acids and alkenoic acids) and carbonyls, as well as the low molecular weight gas-phase carbonyls measured by the DNPH impregnated C_{18} cartridges.

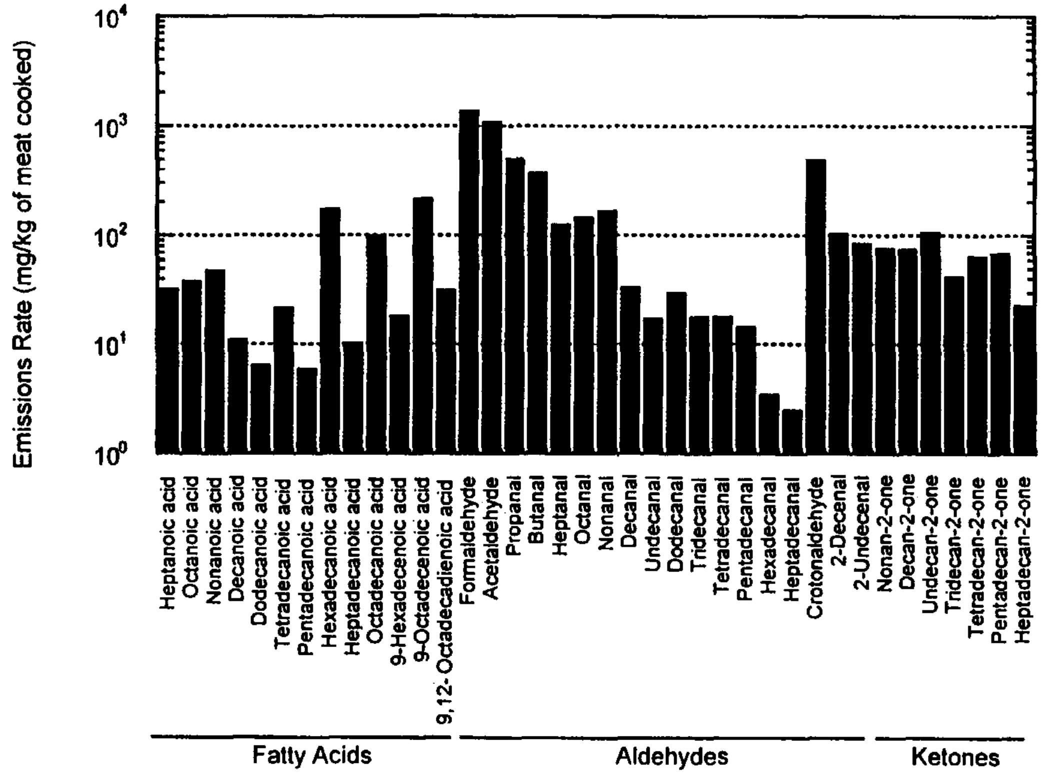

Figure 2.3. Emission rates of fatty acids and carbonyls from meat charbroiling operations.

n-Alkanes, low molecular weight PAH, and alkanedioic acids also are present in the meat charbroiling emissions. In addition, squalene and cholesterol were found at levels of approximately 342 and 3970 $\mu g\ kg^{-1}$ of meat cooked, respectively.

As previously indicated, the fine particle mass emission rate per unit of meat cooked as measured by Hildemann et al. (31) when charbroiling meat for approximately twice the cooking time used here, was reported to be approximately twice the emission rate per hamburger patty cooked in the current study. The individual organic compounds present in the particle phase during the meat charbroiling source tests conducted by Hildemann et al. (31) were reported by Rogge et al. (21). The individual organic compound emission rates normalized to fine particle organic carbon emissions for the test conducted by Hildemann et al. (31) averaged 1.12 ± 0.21 (mean ± standard deviation of the mean) times those observed in the current study. Thus the relative chemical composition of the particulate organic compounds measured in the two sets of tests are found to be quite similar. The earlier tests of Hildemann et al. (31) lack vapor phase and semi-volatile compound emissions data so no comparison is possible in these cases.

2.3.5 Comparison Between Measurement Methods for Semi-Volatile Organics

The total mass emission rate of each individual organic compound determined from the denuder/filter/PUF sampling train showed good agreement with the total mass emission rate determined from the filter/PUF sampling train. Figure 2.4 provides a comparison of the total measured emission rates obtained by the two sampling methods for individual compounds within the following compound classes: alkanoic acids, alkenoic acids, aldehydes, ketones, PAH, lactones, and alkanes.

The distribution between the gas- and particle-phase of each of the 71 organic semi-volatile and particle-phase organic compounds which were identified and quantified by the denuder/filter/PUF sampling train is given in Table 2.2. The phase distribution of the lactones, the carbonyls, and the n-alkanoic acids as measured by the denuder/filter/PUF sampling train is compared to the filter/PUF sampling train in Figure 2.5. The compounds that are quantified in Table 2.2 but not shown in Figure 2.5 are either completely in one phase or are not measured at concentrations high enough to obtain a good description of the their phase distributions by either method. For the denuder/filter/PUF sampling train the gas-phase fraction of each compound is taken as the fraction of that compound collected on the XAD-coated denuder, while the particle-phase fraction is the fraction collected on the combined filter plus PUF samples. In the case of the filter/PUF sampling train, the fraction of the

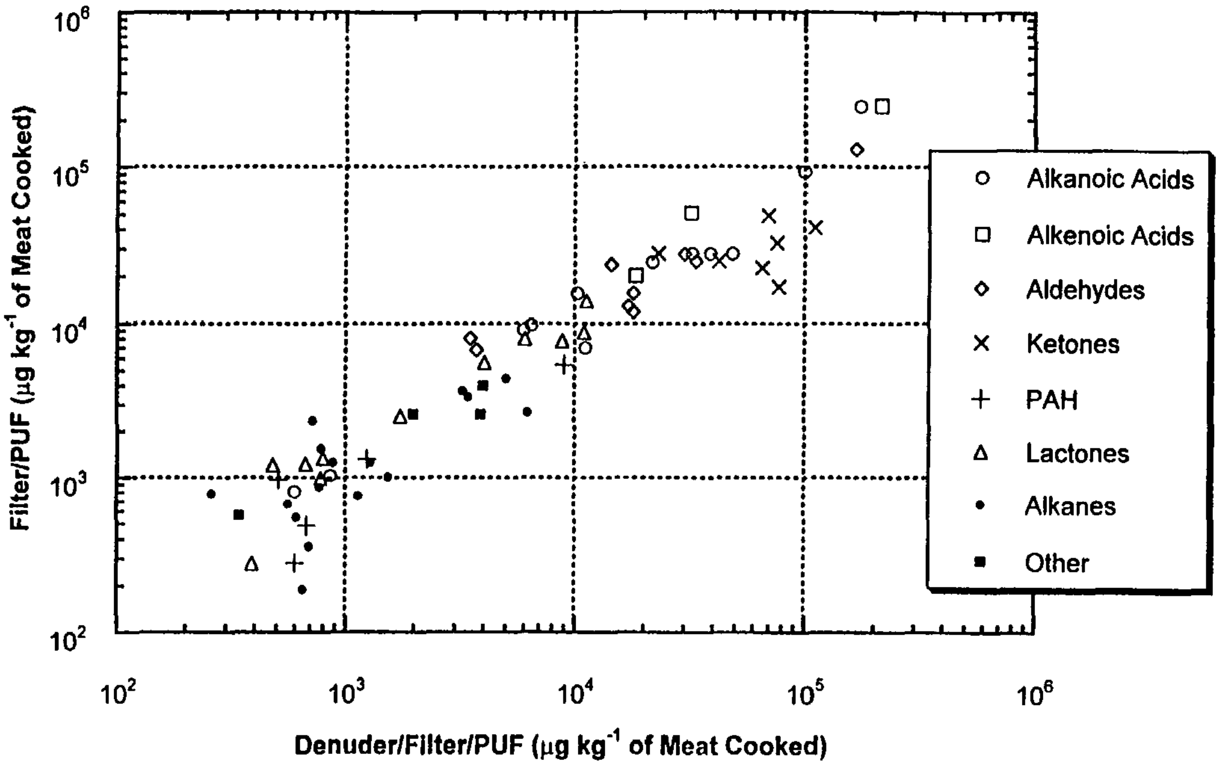

Figure 2.4. Comparison of the total mass of individual organic compounds collected by the denuder/filter/PUF and filter/PUF sampling trains during the charbroiled meat cooking source tests.

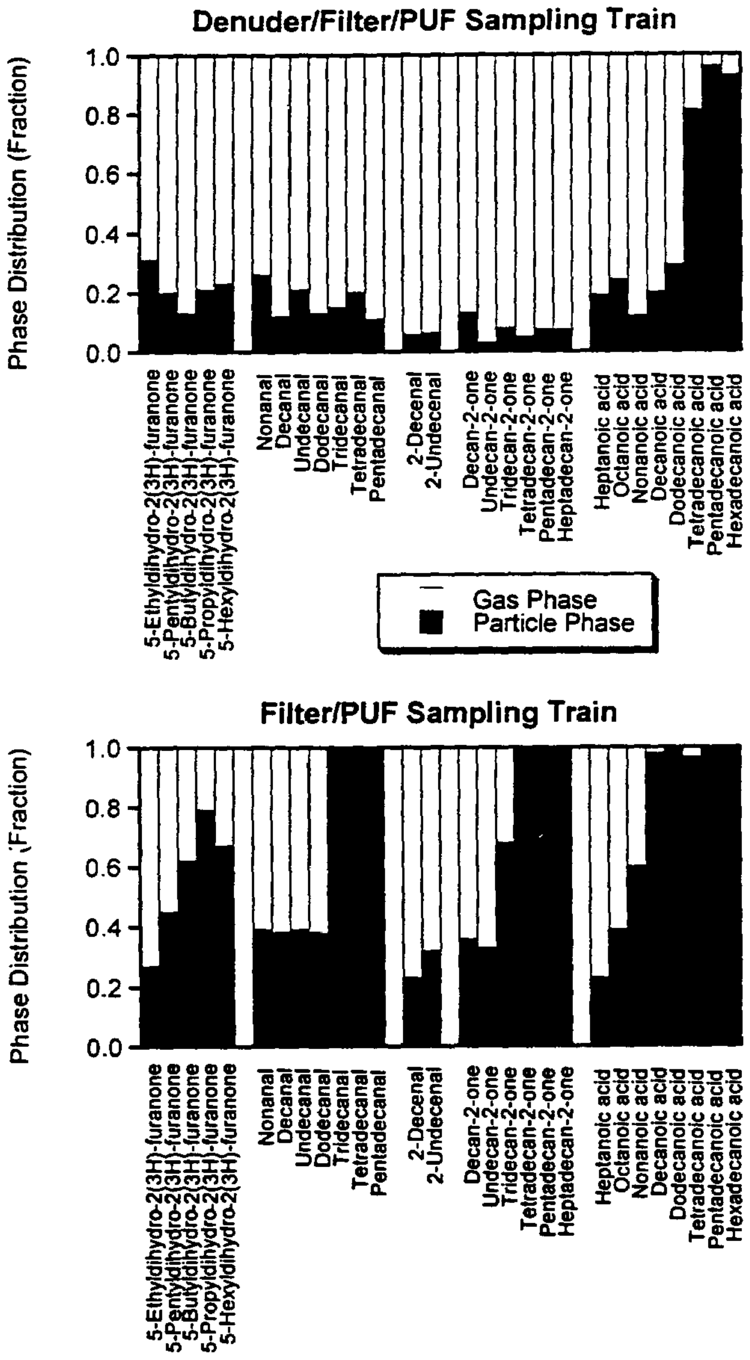

Figure 2.5. The distribution of organic compounds between the gas-phase and particle-phase in the diluted exhaust from meat charbroiling as measured by the denuder/filter/PUF and filter/PUF sampling trains.

mass collected on the filter is taken as the particle-phase portion and the gas-phase fraction is the fraction collected on the two PUFs in series located downstream of the filter.

Although the total compound masses collected by the two sampling trains show good agreement, there are significant differences in the phase distributions measured by the two sampling methods when operated simultaneously in parallel. As seen in Figure 2.5, the fraction of compound mass measured to be in the particle phase by the filter/PUF sampling system is much greater than observed by the denuder/filter/PUF sampling system for the higher molecular weight compounds in each of the compound classes. The likely explanation for this observation is that adsorption of vapor-phase semi-volatile organic compounds occurs on the filter as those vapors first pass over the filter in the filter/PUF sampling train. As seen in Figure 2.5, virtually complete sorption of the vapor-phase semi-volatile organic compounds onto the filter in the filter/PUF system occurs for the highest molecular weight species in each group. This finding has significant implications for the interpretation of the low OC loading that was found on the back-up quartz fiber filter of the tandem EC/OC filter stack. The back-up filter only contained 2.0 percent of the organic carbon found on the front filter. Traditionally, this might have been interpreted to mean that the potential for sampling artifacts was low since there was little vapor phase material collected on the back-up filter. Instead just the opposite was true: the artifact is so great that certain vapor phase species do not pass through the filter at all. This suggests that the use of the back-up filter as a measure of the adsorption to the front filter may not be applicable when taking source samples from sources similar to meat smoke exhaust.

2.3.6 Gas/Particle Partitioning: Experiment Versus Theory

Gas/particle partitioning theory (3, 35, 36) holds that the phase distribution of a semi-volatile organic compound is determined by its absorption into the particle phase matrix, and that this phase distribution can be described by a partitioning coefficient, $K_{p,opm}$, defined as:

$$K_{p,opm} = \frac{F/OPM}{A} \qquad (1)$$

where $K_{p,opm}$ is the gas/particle partitioning coefficient based on organic particulate matter as the receiving particle phase substrate in units of $m^3\ \mu g^{-1}$. F is the particle-associated mass concentration of the semi-volatile organic compound of interest in $\mu g/m^3$, OPM is the total organic particulate matter concentration into which the compound can partition in $\mu g/m^3$, and A is the gas-phase mass concentration of the compound of interest in $\mu g/m^3$. It is expected that the gas/particle partitioning coefficient, $K_{p,opm}$, will depend on the vapor pressure of the various organic compounds (36):

$$Log(K_{p,opm}) = m_{r,opm}Log(p_L^0) + b_{r,opm} \qquad (2)$$

where p_L^0 is the vapor pressure over a liquid pool of the semi-volatile organic compound of interest in torr, and $m_{r,opm}$ and $b_{r,opm}$ are coefficients that can be estimated by regressing a series of experimentally measured values of $K_{p,opm}$ on the corresponding liquid vapor pressure values, p_L^0, for the members of a given organic compound class. If the compounds have similar activity coefficients when present in the particulate organic matrix and the partitioning process has reached equilibrium, then $-m_{r,opm}$ should be close to unity. Under this condition, $b_{r,opm}$ is a constant characteristic of the partitioning for that class of compounds with the specific particle matrix.

Figure 2.6 shows the gas/particle partitioning of the alkanoic acids during these source tests as a function of the vapor pressure of each of the organic acids as measured by the filter/PUF and the denuder/filter/PUF sampling trains. The best fit curve through the denuder/filter/PUF data has a slope of -0.62, suggesting that the partitioning is not at equilibrium as described by Pankow and Bidleman (4). This suggests that the semi-volatile organic compounds have not equilibrated between the gas and particle phases either because of insufficient residence time or because the mass transfer between phases is inhibited. In similar measurements made while testing the emissions from cooking with lighter

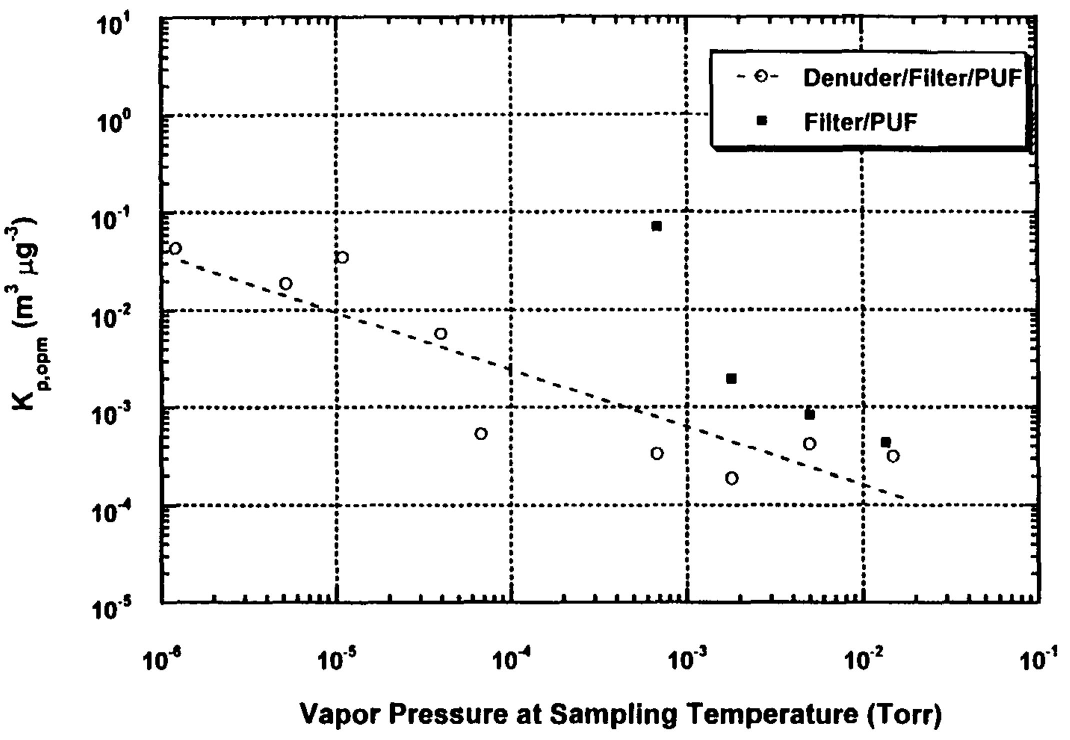

Figure 2.6. Partitioning coefficient, $K_{p,opm}$, for the n-alkanoic acids in the diluted exhaust from meat charbroiling operations as measured by the denuder/filter/PUF and filter/PUF sampling train plotted as a function of the vapor pressure of the pure compounds.

seed oils, the n-alkanoic acids were found to be partitioned as would be predicted at equilibrium (see Chapter 3). In those tests, the seed oil cooking samples had significantly less time to equilibrate than did the charbroiled meat cooking exhaust prior to sampling. For this reason it seems likely that the semi-volatile organic compounds in the charbroiled meat exhaust are inhibited from transferring to the gas phase from the particle phase or into the particle phase from the gas phase. The fact that the mass transfer to and from the meat smoke particles may be inhibited is consistent with the possibly solid character of meat fat at room temperature; meat fat is a major constituent in the diluted particle mass emissions from meat charbroiling.

The phase distribution of the n-alkanoic acids measured by the filter/PUF sampling train during the meat charbroiling test is also shown in Figure 2.6. The phase distribution measured by the filter/PUF system is significantly shifted as compared to the phase distribution measured by the denuder/filter/PUF system. All of the n-alkanoic acids have been found in much higher percentages on the filter when sampled by the filter/PUF method. In fact, all of the n-alkanoic acids with vapor pressures less than n-decanoic acid are not even detected on the PUF downstream of the particle filter in the filter/PUF system. This again suggests that a strong filter adsorption artifact exists for the n-alkanoic acids within a meat smoke matrix when sampled by the filter/PUF method.

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Chapter 3

Organic Compounds from Cooking with Seed Oils

3.1 Introduction

The C_{16} and C_{18} fatty acids (n-alkanoic acids and n-alkenoic acids) are among the most prominent single organic compounds found in the urban atmospheric fine particulate mixture (1). These particle phase acids are known to be emitted from many sources such as meat cooking operations, wood combustion, motor vehicle exhaust, and road dust (2), but air pollution modeling results for the Los Angeles Basin indicate that there must be additional as yet unquantified sources of these compounds (3, 4). Seed oils are comprised largely of esters of n-alkanoic acids (5) and fatty acids have been identified in the exhaust from heated seed oils (6). Thus, they are a likely source of the missing fatty acids emissions which could arise from food cooking operations employing seed oils. In addition, the role of the gas phase, semi-volatile and particle phase organic compounds from food frying operations in photochemical smog and secondary aerosol formation has not been evaluated largely due the lack of emissions data for sources of this type. To this end, the emissions from cooking with seed oils are investigated in the present study.

3.2 Experimental Methods

3.2.1 Comprehensive Source Sampling

The seed oil cooking emissions tests reported here were conducted using a large institutional-scale deep fryer and a large industrial-scale electric grill operated by professional chefs as they prepared commercially distributed food products. Emissions were sampled downstream from the filters and grease extractors located in the ventilation system above the appliances. The overall exhaust system was operated at an air flowrate of 400 m^3 min^{-1} and provided sufficient dilution with ambient air to bring the food cooking effluents to ambient temperature prior to collection of source samples. The diluted source effluent was withdrawn from the kitchen vent stack through AIHL-design cyclone separators (7) which were operated at flowrates such that coarse particles with aerodynamic diameters greater than 1.8 μm were trapped while fine particles and gases passed through the cyclone separator. Fine particle emissions data are emphasized in the present study, because such data are needed for use in the development of urban and regional emissions control strategies for fine particles that will be required under the newly adopted National Ambient Air Quality Standard for fine particulate matter in the United States (8).

Semi-volatile and fine particle-phase organic compounds were collected directly from the exhaust vent using both a denuder/filter/PUF sampling train and a filter/PUF sampling train. The details of these sampling configurations are described in Chapter 2. The filter/PUF samples collected during the seed oil cooking tests were not analyzed as part of this study and have been stored for use in future research projects. Fine particulate matter, carbonyls, organic acids, and gas phase hydrocarbons were also collected during these tests by the same cyclone-based unit as described in Chapter 2.

The ambient air entrained into the exhaust hood above the appliances contained low concentrations of background contaminants that must be subtracted from the source effluent. These background semi-volatile and particle phase organic compound concentrations were sampled from the ambient air in the kitchen by a filter/PUF sampling train. As discussed in Chapter 2, the total mass of each individual organic compound collected by the denuder/filter/PUF sampling train agreed well with the total mass collected by the filter/PUF sampling train. Fine particle mass, fine particle bulk elemental composition, carbonyls, organic acids, and gas phase hydrocarbons present in the background air were measured by use of a sampling train that duplicates the measurements made in the stack above the cooking appliances.

3.2.2 Source Testing Procedure

The vegetable stir frying source tests were conducted on an industrial-size electric grill using a commercially distributed mixture of precut broccoli, red and green peppers, celery, and onions (Ingardia Brothers Produce Inc., Costa Mesa, CA). Soybean oil (Vons Company Inc., Los Angeles, CA) was used for one test and canola oil (Cargill Foods, Minneapolis, MN) was used for the other vegetable stir fry source test. Both the soybean oil and the canola oil tests were conducted while stir frying 22.6 kg of vegetables using approximately 1.5 liters of seed oil and 3 kg of stir fry sauce (Chef Mate, Nestles; main ingredients: water, soy sauce, high fructose corn syrup, sherry, vegetable oil, and modified food starch) over a period of one hour. The denuder/filter/PUF sampling train was operated throughout the stir fry source tests except for the approximately 1 minute required to replace the denuder in the middle of the test. The full suite of chemical measurements described above was made during the soybean oil source test while all measurements except for gas-phase volatile hydrocarbons and fine particle trace elements and ionic species were made during the canola oil stir fry source test.

The deep fried potatoes source test was conducted using an industrial scale deep fryer at 175 °C which was filled with commercial hydrogenated soybean oil (Creamy Liquid Shortening, Kraft Food Service, Preferred). The hydrogenated soybean oil in the deep fryer during the source test had been in use for several days of cooking prior to the tests and was considered relatively fresh by the cooking staff. Sixty-eight kilograms of deep frying potatoes (Kraft 3/8 inch Grade A fancy, Frozen) were cooked in 1.13 kg batches in two parallel fryers operating simultaneously over a period of 75 minutes by placing the frozen potatoes directly in the hot cooking oil. The denuder/filter/PUF sampling train was operated for two 30-minute time periods during the cooking test, while all other sampling equipment was operated continuously throughout the test. Gas-phase volatile hydrocarbons and fine particle trace elements and ionic species measurements were not made during the deep fried potatoes cooking source test.

3.2.3 Organic Chemical Analysis

The extraction procedure employed for semi-volatile organic compounds collected on XAD-coated annular denuders and PUF cartridges, as well as particle-phase organic compounds collected on quartz fiber filters, are discussed in Chapter 2. The extracts collected on these substrates were reduced in volume to approximately 250 μl and were then split into two fractions. One fraction was derivatized with diazomethane to convert organic acids to their methyl ester analogs.

Filter, PUF, and denuder field blanks were analyzed with each set of source samples. The field blanks were prepared, stored and handled by exactly the same procedures as used for the source samples.

Both the derivatized and underivatized sample fractions are analyzed by GC/MS on a Hewlett-Packard GC/MSD (GC Model 5890, MSD Model 5972) using a 30 m by 0.25 mm diameter HP-1701 capillary column (Hewlett-Packard). 1-Phenyldodecane was used as a co-injection standard for all sample extracts and standard runs. The deuterated internal standards were used to determine extraction recovery for the compounds quantified in the underivatized samples, and the deuterated acids were used to verify that the diazomethane reactions were driven to completion. In addition, the deuterated n-alkanoic acid recoveries were used in conjunction with the recovery of deuterated tetracosane to determine the recovery of the compounds quantified in the derivatized fraction.

Hundreds of authentic standards have been prepared for the positive identification and quantification of the organic compounds found in the current source test program. When quantitative standards could not be obtained for a given compound or compound class, significant effort was made to obtain a non-quantitative secondary standard that could be used for unique identification of the organic compounds. Quantification of compounds identified using secondary standards has been estimated based on the response factors for compounds having similar retention times and chemical structures.

Total non-methane organic gases (NMOG, EPA method TO12) and individual organic vapor phase hydrocarbons ranging from C_1 to C_{10} were analyzed from the SUMA canisters by gas chromatography/flame ionization detection (GC/FID). Carbonyls collected by the C_{18} impregnated cartridges were analyzed by liquid chromatography/UV detection.

3.3 Results and Discussion

A material balance for the gas-phase and fine particle-phase organic compounds emitted from stir frying vegetables in soybean oil is shown in Figure 3.1. The total mass of organic carbon in the particle phase was measured from one of the quartz fiber filters located downstream of the XAD coated denuder. Organic compound mass was obtained by assuming a ratio of 1.4 between organic compound mass and organic carbon. Of the 15.7 mg of fine particle-phase organic compound mass emitted per kg of vegetables cooked during the soybean oil-based vegetable stir fry test, 82% of the mass is composed of free fatty acids (n-alkanoic acids and n-alkenoic acids). n-Alkanes and olefinic n-aldehydes make up smaller but noticeable portions of the mass emitted. It should be noted that virtually all of the fine particle mass can be identified at the single compound level. A similar mass balance can be constructed for the

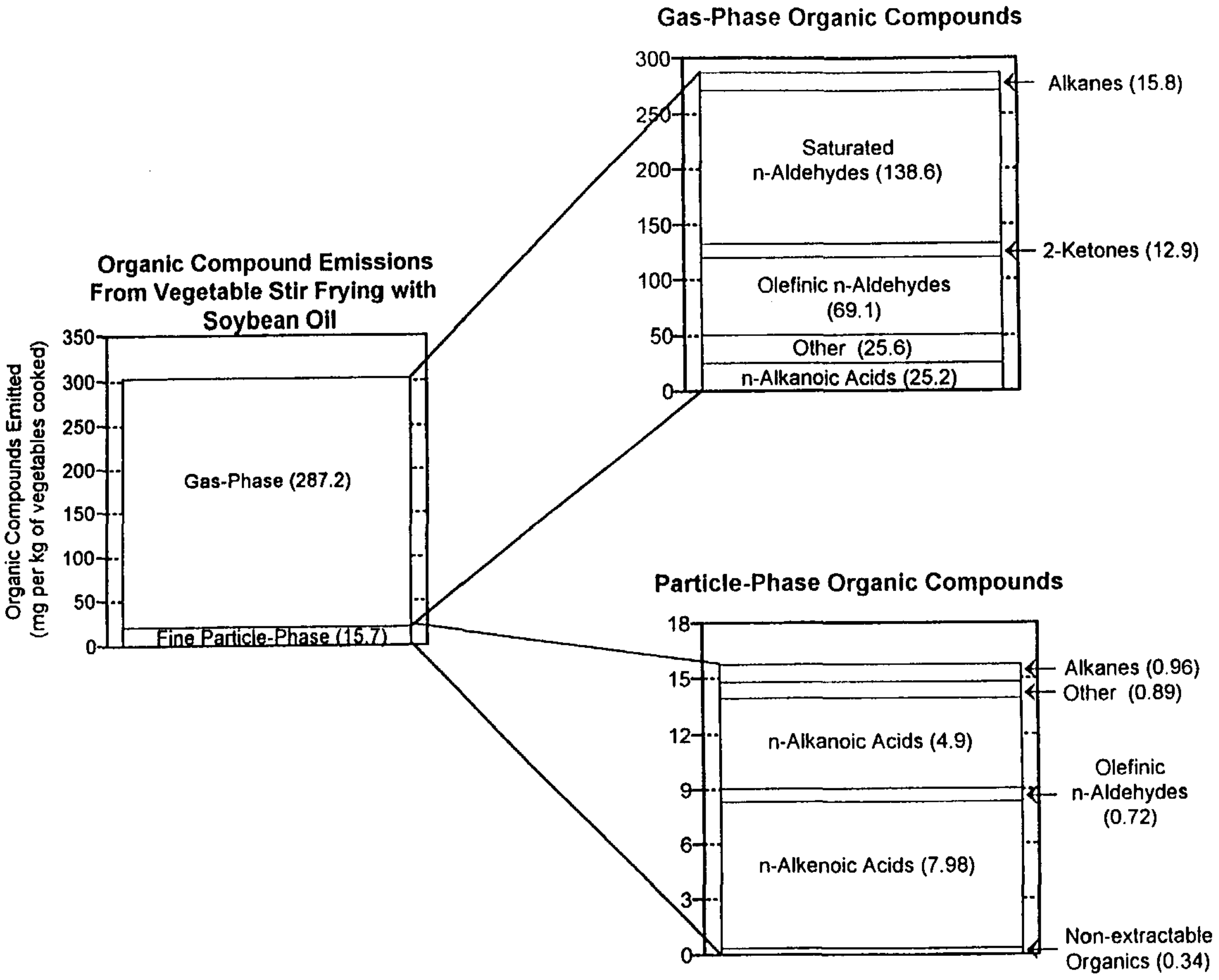


Figure 3.1. Material balance on the gas-phase, semi-volatile, and particle phase organic compounds emitted from stir frying vegetables in soybean oil.

fine particulate matter emitted during the canola oil based stir fry and the deep fried potatoes source tests, and one finds that the free fatty acids also make up a major portion of the particle mass. The total fraction of the fine particle organic compound mass that can be identified on a single compound level for the canola oil based stir fry test and the deep frying of potatoes test are 83% and 73%, respectively.

The gas-phase organic compound emissions from stir frying vegetables in soybean oil are dominated by carbonyls, as shown in Figure 3.1. A total of 242 mg of carbonyls are emitted per kg of vegetables cooked, which accounts for 84 percent of the mass of quantified gas-phase organic compound emissions. Gas-phase n-alkanoic acids contribute the next largest fraction of the gas-phase emissions, accounting for 25.2 mg per kg of vegetables cooked. Although the C_7^+ gas-phase n-alkanoic acids measured make up only 9.5% of the gas phase organic compound emissions, these gas-phase n-alkanoic acids emissions are more than 5 times greater than the emissions of higher molecular weight fine particulate n-alkanoic acids.

Gas-phase carbonyl emissions were measured at 252 and 108 mg per kg of vegetables cooked for stir frying in canola oil and deep frying in hydrogenated soybean oil, respectively. The total mass of C_7^+ gas-phase emissions of n-alkanoic acids is known based on analysis of the denuder samples, and is found to account for 18.8 and 5.5 mg per kg of vegetables cooked for stir frying in canola oil and deep frying potatoes in hydrogenated soybean oil, respectively. Since gas-phase hydrocarbon emissions were found to be small during the soybean oil frying experiment, the hydrocarbons were not measured during the canola oil based stir frying and the potatoes frying experiments.

3.3.1 Fine Particle Mass and Chemical Composition

Fine particulate matter was collected for mass emissions rate determination and inorganic chemical analysis by directly drawing the diluted cooled cooking exhaust through a Teflon membrane filter. Fine particle mass emissions rates were measured to be 21.5 ± 1.2 and 29.5 ± 1.3 mg per kilogram of vegetables cooked for the soybean oil and canola oil stir fry tests, respectively. The average fine particle emission rate for these two tests on a seed oil use basis is 190 mg of fine particle mass per liter of seed oil used in stir frying. The composition the fine particulate matter generated from the soybean oil stir fry test is shown in Table 3.1. As expected the aerosol is predominately organic matter consisting of 69.6 ± 5.5 percent organic carbon. Several ionic species also were measured in the fine particle emissions at lower but noticeable percentages. Nitrate ion was found to contribute 2.2% of the fine particle mass. Sodium, ammonium, and sulfate each made up about 1.0% of the fine particle mass. Potassium and chloride both contributed approximately 0.27% to the fine particle mass. These ionic species are believed to be derived from the vegetables and the stir fry sauce. The fine particle mass emitted during

Table 3.1. Average Fine Particle Mass Emission Rate and Fine Particle Chemical Composition Emitted From Cooking Vegetables in Seed Oils

	Vegetables Stir Fried in Soybean Oil	Vegetables Stir Fried in Canola Oil	Deep Frying of Potatoes
Mass Emission Rate (mg kg^{-1} of vegetables cooked)	21.5 ± 1.2	29.5 ± 1.3	13.1 ± 1.2
Particle Composition:			
Organic Carbon (wt %)[b]	69.6 ± 5.50	58.3 ± 4.7	62.7 ± 5.1
Elemental Carbon (wt %)	< 4.0	< 3.4	< 4.0
Na^+ (wt % by IC)	1.0 ± 0.1	a	a
NH_4^+ (wt % by IC)	0.94 ± 0.06	a	a
Cl^- (wt % by IC)	0.27 ± 0.06	a	a
NO_3^- (wt % by IC)	2.2 ± 0.06	a	a
$SO_4^=$ (wt % by IC)	1.08 ± 0.08	a	a
Potassium (wt% by XRF)	0.27 ± 0.10	a	a
Sulfur (wt% by XRF)	0.28 ± 0.06	a	a

Notes: (a) not measured

(b) measured downstream of the organics denuder the canola oil stir frying experiment was measured to be 58.3 ± 4.7 percent organic carbon.

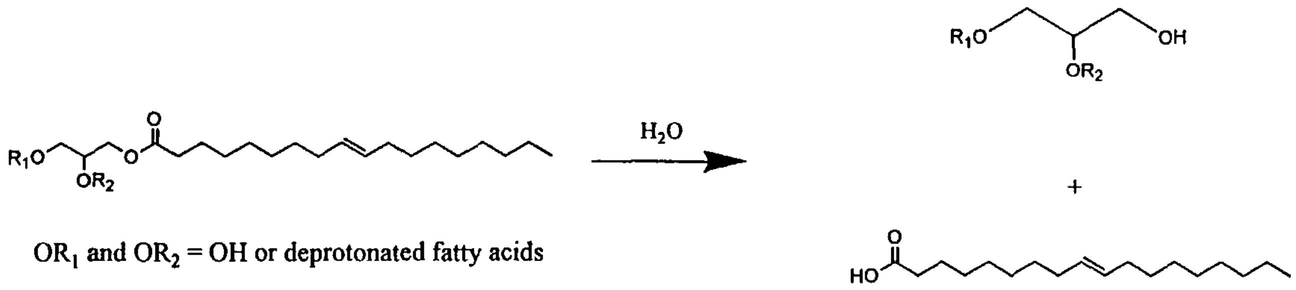
The emission rate of fine particle mass was measured to be 13.1 ± 1.2 mg per kg of potatoes cooked from the potatoes deep frying process. If these deep fryers were operated for 8 hours per day then the emission rate of fine particle mass would be 5.7 grams per day for both fryers while processing a total of 435 kg of fried potatoes. The fine particle mass was determined to be comprised of 62.7 ± 5.1 percent organic carbon.

Total organic carbon mass was also measured for each of the seed oil cooking tests on the quartz fiber filters located downstream of the organics denuder and on undenuded quartz fiber filters. Previous work has shown that certain gas-phase semi-volatile organic compounds can sorb to undenuded quartz fiber filters or to the particulate matter collected on the filters causing the addition of a positive artifact to the organic compound mass and the total mass collected on the filter. The emission rate of fine particle organic carbon measured downstream of the denuder averaged over all three tests was 80.6 ± 3.5% of the fine particle organic carbon measured from the undenuded samples collected on quartz fiber filters. This result is consistent with the strong sorption artifact for gas-phase fatty acids when passed through a quartz fiber filter as observed in Chapter 2 when sampling meat smoke.

3.3.2 Organic Compound Emissions

Refined seed oils used for cooking are largely comprised of fatty acid esters of glycerol (1,2,3-propanetriol) (5) with typically less than a few percent of hydrocarbons and other organic compounds (9). Samples of the seed oils used in the current experiments were derivatized with diazomethane to convert any free fatty acids to their methyl ester analogs. Analysis by GC/MS showed that virtually no free fatty acids were present in these refined seed oils. The n-alkanoic acids and the n-alkenoic acids present in the emissions from the seed oil cooking operations are likely due to the hydrolysis of glycerides present in the seed oils as shown in Figure 3.2.

As previously indicated the organic compound emissions from the seed oil cooking operations tested in this study are dominated by carbonyls and fatty acids. Table 3.2 lists the emission rate and gas/particle phase distribution of 99 organic compounds identified and quantified in the emissions from these seed oil cooking tests. Low molecular weight volatile hydrocarbons were only measured for the soybean oil stir fry test and were found to be very low except for methane and ethane, which are believed to be due to a small amount of unburned natural gas present in the atmosphere of the cooking facility. Methane and ethane are not expected to be emitted in any noticeable quantities from the seed oil cooking operation studied and since natural gas leakage from the cooking appliances is the likely source of the methane and ethane.



OR$_1$ and OR$_2$ = OH or deprotonated fatty acids

9-Octadecenoic acid

When OR$_1$ and OR$_2$ are both deprotonated fatty acids, then a triglyceride is converted to a diglyceride and a free fatty acid.

When OR$_1$ and OR$_2$ represent one OH and one deprotonated fatty acid, then a diglyderide is converted to a monoglyceride and a free fatty acid.

When OR$_1$ and OR$_2$ are both OH, then a monoglyderide is converted to glycerin and a free fatty acid.

Figure 3.2. Formation of free fatty acids from glycerol esters of fatty acids.

Table 3.2. Organic Compound Emission Rates from Frying Vegetables in Seed Oils

Compound	Stir Frying of Vegetables in Soybean Oil (μg kg^{-1} of Vegetables Cooked)		Stir Frying of Vegetables in Canola Oil (μg kg^{-1} of Vegetables Cooked)		Deep Frying of Potatoes in Hydrogenated Oil (μg kg^{-1} of Potatoes Cooked)		Notes
	Gas Phase	Particle Phase	Gas Phase	Particle Phase	Gas Phase	Particle Phase	
n-Alkanes							
Methane	168000$^{\Delta}$		*		*		a, e
Ethane	8690$^{\Delta}$		*		*		a, e
Propane	550		*		*		a, e
n-Butane	750		*		*		a, e
n-Pentane	800		*		*		a, e
n-Hexane	100		*		*		a, e
n-Heptane	110		*		*		a, e
n-Octane	110		*		*		a, e
n-Nonane	490		*		*		a, e
n-Decane	650		*		*		a, e
n-Tridecane	830		380		230		b, f
n-Tetradecane	930		530	25	340	5	a, f
n-Pentadecane	690		660	35	430	37	b, f
n-Hexadecane	720	150	450	33	230	18	a, f
n-Heptadecane	170	34	650	95	310	33	b, f
n-Octadecane	77	28	180	16	96	11	a, f
n-Nonadecane	82	14	97	22	49	9	b, f
n-Eicosane	38	26	100	14	37	6	a, f
n-Heneicosane	26	38	46	15	26	3	b, f
n-Docosane	19	10	36	10	20	1	b, f
n-Tricosane	25	18	36	5	19	1	b, f
n-Tetracosane	18	18	15	18	12		a, f
n-Pentacosane			7	13	9		b, f
n-Hexacosane		18		17			b, f
n-Heptacosane		340		470			a, f
Branched alkanes							
i-Butane	420		*		*		a, e
i-Pentane	280		*		*		a, e
n-Alkenes							
Ethene	760		*		*		a, e
Branched alkenes							
i-Butene	750		*		*		a, e
Alkynes							
Ethyne(Acetylene)	550		*		*		a, e
Aromatic hydrocarbons							
m-Xylene + p-Xylene	190		*		*		a, e
p-Ethyltoluene	150		*		*		a, e

Identification notes: (a) authentic quantitative standard. (b) authentic quantitative standard for similar compound in series. (c) secondary standard. (d) detected as a methyl ester.
Sample collection notes: (e) collected in SUMA canister (f) collected on denuder/filter/PUF sampling train. (g) collected on DNPH impregnated C$_{18}$ cartridges. * not measured. See text for details.
Additional Notes: †Compound is too volatile for complete collection by denuder at sampling conditions; mass of this compound reported in the gas-phase includes mass collected on PUF cartridge. $^{\Delta}$ Believed to be from natural gas and not from stir fry materials.

Table 3.2. (continued - page 2)

Compound	Stir Frying of Vegetables in Soybean Oil (µg kg^{-1} of Vegetables Cooked)		Stir Frying of Vegetables in Canola Oil (µg kg^{-1} of Vegetables Cooked)		Deep Frying of Potatoes in Hydrogenated Oil (µg kg^{-1} of Potatoes Cooked)		Notes
	Gas Phase	Particle Phase	Gas Phase	Particle Phase	Gas Phase	Particle Phase	
Aromatic hydrocarbons							
Naphthalene [†]	645		588		338		a, f
Acenaphthylene	38		37		19		a, f
Phenanthrene	138	7	120	8	83	2	a, f
Anthracene	11	1	8	2	6	2	a, f
Fluoranthene	40	7	24	5	19	1	a, f
Pyrene	28	4	15	5	19	1	a, f
Chrysene/Triphenylene	5	9		13	5	9	a, f
Aliphatic aldehydes							
Formaldehyde	20100		18600		12400		a, g
Acetaldehyde	50100		42200		20900		a, g
Propanal	12200		17000		7000		a, g
Butanal/Isobutanal	19700		17400		4500		a, g
Hexanal	4100		6400		6700		a, g
Heptanal	4300		8000		5200		a, g
Octanal	7900		9700		5700		a, g
Nonanal	12400		14800		13500		a, g
Decanal	5200		1090		2900		a, g
Undecanal	3000		200		1200		a, g
Dodecenal	1260		920				a, f
Tridecenal	550		180				a, f
Tetradecenal	410						a, f
Pentadecenal	440		411				a, f
Dicarbonyls							
Glyoxal	9400		9600		6400		a, g
Methylglyoxal	7400		10000		5500		a, g
Biacetyl	4200		2800		1400		a, g
Ketones							
2-Nonanone	3300				78		c, f
2-Decanone	2670		3130		590		c, f
2-Undecanone	2310				145		c, f
2-Tridecanone					84		c, f
2-Tetradecanone					180		c, f
2-Pentadecanone	3900	170	8050	120	1100	30	c, f
2-Heptadecanone	720	60	860	75	300		c, f
Unsaturated carbonyls							
Crotonaldehyde	29100		24100		5200		a, g
Methacrolein	5500		1100		800		a, g

Identification notes: (a) authentic quantitative standard. (b) authentic quantitative standard for similar compound in series. (c) secondary standard. (d) detected as a methyl ester.
Sample collection notes: (e) collected in SUMA canister (f) collected on denuder/filter/PUF sampling train. (g) collected on DNPH impregnated C_{18} cartridges. * not measured. See text for details.
Additional Notes: [†] Compound is too volatile for complete collection by denuder at sampling conditions; mass of this compound reported in the gas-phase includes mass collected on PUF cartridge. [Δ] Believed to be from natural gas and not from stir fry materials.

Table 3.2. (continued - page 3)

Compound	Stir Frying of Vegetables in Soybean Oil (μg kg^{-1} of Vegetables Cooked)		Stir Frying of Vegetables in Canola Oil (μg kg^{-1} of Vegetables Cooked)		Deep Frying of Potatoes in Hydrogenated Oil (μg kg^{-1} of Potatoes Cooked)		Notes
	Gas Phase	Particle Phase	Gas Phase	Particle Phase	Gas Phase	Particle Phase	
Unsaturated carbonyls							
2-Decenal	16100	400	26400	650	2630		a, f
2-Undecenal	18400	420	29400	550	2880		a, f
n-Alkanoic acids							
Heptanoic acid	5940		530	162	370	2	a, d, f
Octanoic acid	5930	160	4330	170	640	27	a, d, f
Nonanoic acid	11890	180	12200	180	3270	51	a, d, f
Decanoic acid	780	28	700		190	9	a, d, f
Dodecanoic acid	320	59	210	20	100	4	a, d, f
Tetradecanoic acid	130	93	87	42	60	52	a, d, f
Pentadecanoic acid		58		59		12	a, d, f
Hexadecanoic acid (palmitic)	238	2980	690	2280	800	1760	a, d, f
Heptadecanoic acid				50		23	a, d, f
Octadecanoic acid (stearic)	15	1250	65	1040	37	848	a, d, f
Nonadecanoic acid				7			a, d, f
Eicosanoic acid		38		65		48	a, d, f
Docosanoic acid		29		35		7	a, d, f
n-Alkenoic acids							
9-Hexadecenoic acid		174		36		18	b, d, f
9-Octadecenoic acid (oleic)		3250		6310		1940	a, d, f
9,12-Octadecadienoic acid (linoleic)		4190		3030		1750	a, d, f
9,12,15-Octadecatrienoic acid (linolenic)		310		270		77	a, d, f
Alkadioic acids							
Hexanedioic acid				33			a, d, f
Octanedioic acid		58		165		3	a, d, f
Furanones (γ-Lactones)							
5-Ethyldihydro-2(3H)-furanone †	470		370		41		a, f
5-Propyldihydro-2(3H)-furanone †	170		170		11		b, f
5-Butyldihydro-2(3H)-furanone	430	17	670	30	240	10	a, f
5-Pentyldihydro-2(3H)-furanone	280	30	470	38	75	7	b, f
5-Hexyldihydro-2(3H)-furanone	74	45	130	40	49	9	a, f
5-Heptyldihydro-2(3H)-furanone	33	5		5		3	b, f
5-Octyldihydro-2(3H)-furanone		43		53		1	b, f
5-Nonyldihydro-2(3H)-furanone		29		33		2	b, f
5-Decyldihydro-2(3H)-furanone		3		4		1	b, f
5-Undecyldihydro-2(3H)-furanone		41		30		2	b, f
5-Dodecyldihydro-2(3H)-furanone		12		10		1	b, f
Other Compounds							
Chlorpyrifos		54		76	23	33	a, f

Identification notes: (a) authentic quantitative standard. (b) authentic quantitative standard for similar compound in series. (c) secondary standard. (d) detected as a methyl ester.
Sample collection notes: (e) collected in SUMA canister (f) collected on denuder/filter/PUF sampling train. (g) collected on DNPH impregnated C_{18} cartridges. * not measured. See text for details.
Additional Notes: † Compound is too volatile for complete collection by denuder at sampling conditions; mass of this compound reported in the gas-phase includes mass collected on PUF cartridge. Δ Believed to be from natural gas and not from stir fry materials.

The emission rates and phase distributions of the fatty acids for all three seed oil cooking tests are shown in Figure 3.3. The distributions of C_{18} fatty acids (octadecanoic acid, 9-octadecenoic acid, 9,12-octadecadienoic acid, and 9,12,15-octadecatrienoic acid) in the emissions are consistent with the compositions of the seed oils used for cooking. Refined soybean oil contains the highest relative content of octadecadienoic esters compared to the other seed oils used (10). Since octadecadienoic acid contains two double bonds, it is expected to break down more readily during the cooking process than the other more saturated fatty acids. For this reason we do not expect that the ratio of this fatty acid to other n-alkanoic acids will be the same within the emissions as the ratio of the parent esters in the original seed oils used. Nevertheless, the octadecadienoic acid emissions from cooking with soybean oil are the highest among the three oils used in the tests. In canola oil, oleic acid (9-octadecenoic acid) makes up a higher fraction of the acids present as esters than in any other commercial edible seed oil (10). As can be seen in Figure 3.3, the largest monounsaturated C_{18} acid (9-octadecenoic acid) emissions are observed when using canola oil. Hydrogenated soybean oil has been processed to remove the tri-olefinic C_{18} acid (linolenic acid) present as esters and to convert some of the linoleic acid (9,12-octadecadienoic acid) esters to the monounsaturated (9-octadecenoic acid) and the saturated fatty acid (stearic acid) esters (5). Consistent with this operation, the smallest linolenic acid emissions are seen when deep frying with hydrogenated soybean oil. In addition, stearic acid

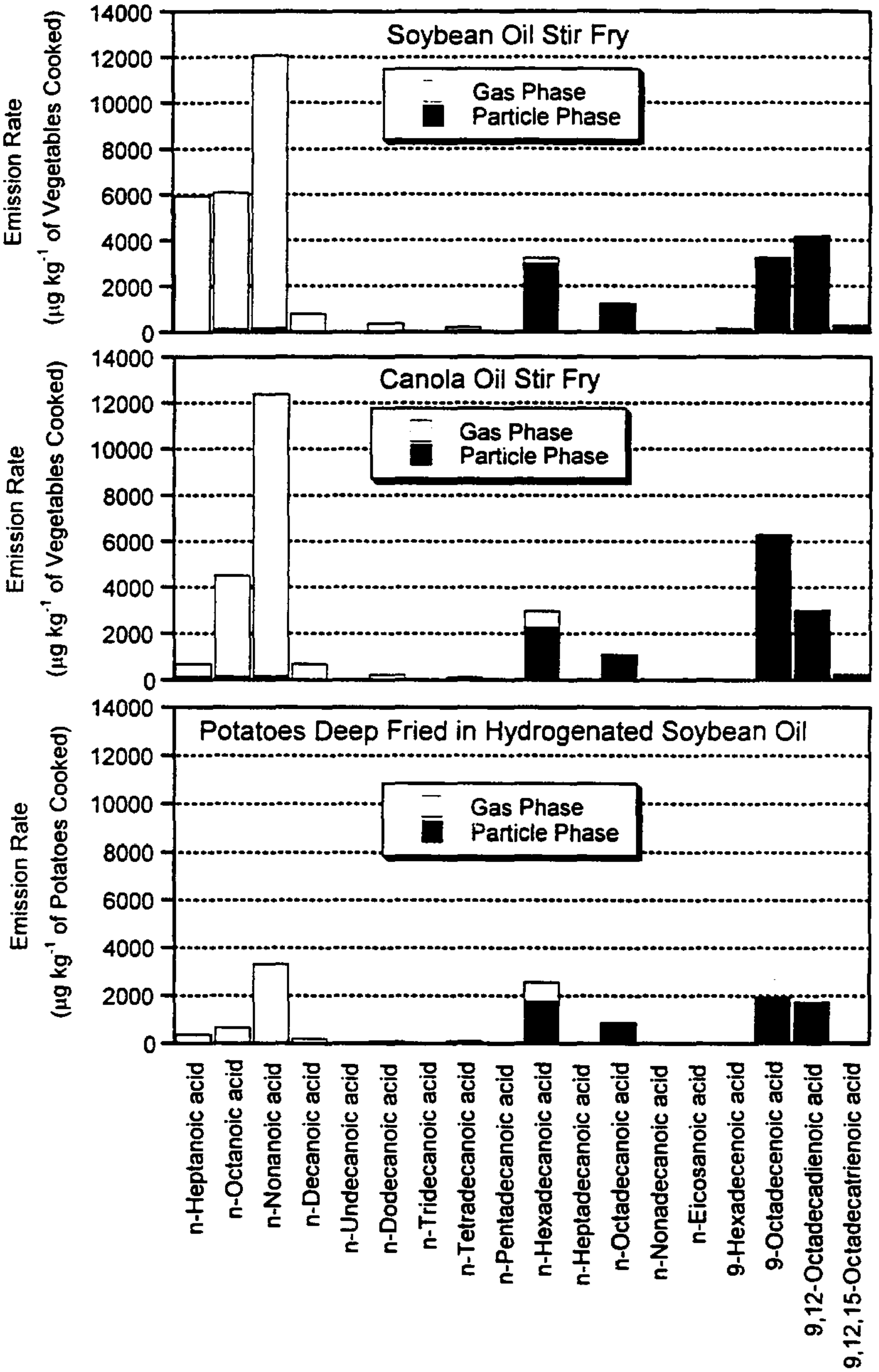


Figure 3.3. Emission rates and phase distributions of n-alkanoic acids emitted from cooking vegetables in seed oil.

makes up a higher percentage of the C_{18} fatty acids in the exhaust from deep frying than from either of the seed oils used for stir frying.

Nonanoic acid is emitted at the highest rate of all the C_7 and greater n-alkanoic acids from all of the food cooking operations tested. Nonanoic acid is expected to be formed from the breakdown of oleic acid present in the seed oils. The distributions of the C_{14}, C_{16}, and C_{18} saturated fatty acids are consistent with the compositions of the seed oils (5, 10), indicating that these acids are likely formed directly from the hydrolysis of their glycerol ester precursor analogs.

Acetaldehyde is emitted at the highest rate of any of the carbonyls for all three cooking operations. Figure 3.4 shows the emission rates of the paraffinic aldehydes, the olefinic aldehydes, and glyoxals for all three of the seed oil cooking tests. Significant quantities of crotonaldehyde, 2-decenal, and 2-undecenal were emitted from the stir fry cooking with soybean oil and canola oil. 2-decenal and 2-undecenal have been previously identified in the exhaust of heated seed oil (6). It should also be noted that the relative abundance of the C_5 through C_{10} aldehydes peaks at nonanal, which is consistent with the relative distribution of the alkanoic acid emissions which peak at nonanoic acid. Again, nonanal formation from the decomposition of the unsaturated fatty acid, 9-octadecenoic acid (oleic acid), is a likely cause of the elevated emissions observed.

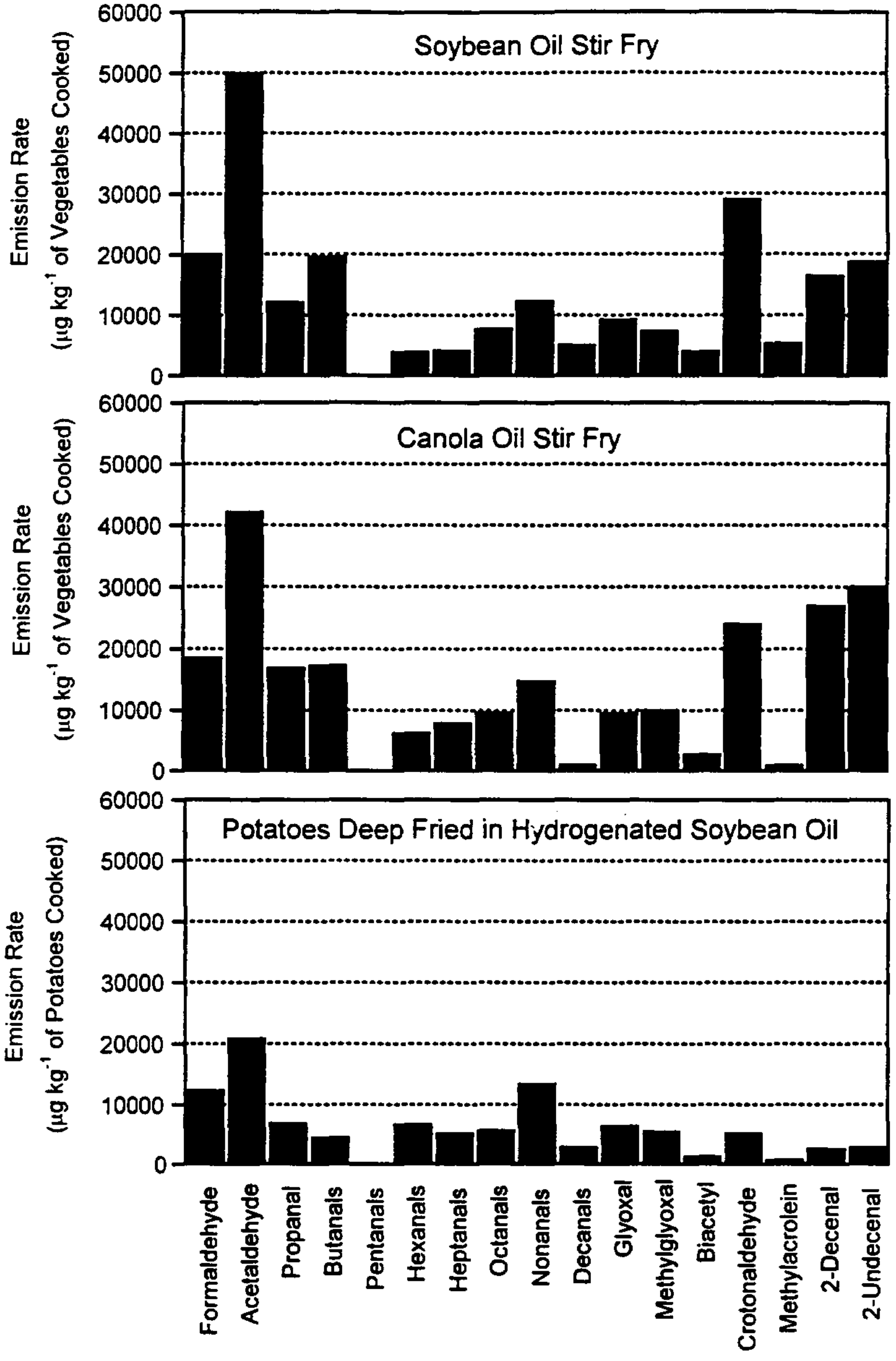


Figure 3.4. Emission rates of selected aldehydes emitted from cooking vegetables in seed oil.

In addition to the aldehyde emissions, noticeable amounts of 2-ketones also are emitted from the seed oil cooking operations. 2-Pentadecanone is emitted in the highest amount from all three cooking processes at much greater levels than pentadecanal. 2-Nonanone, 2-decanone and 2-undecanone are all emitted in relatively large quantities from the soybean oil-based stir frying experiment.

γ-Lactones spanning the range from gas-phase 5-ethyldihydro-2(3H)-furanone to particle-phase 5-dodecyldihydro-2(3H)-furanone are quantified in the emissions from the seed oil cooking operations. These compounds are not emitted in great quantities but may serve as tracers for food cooking exhaust in some cases. These compounds are also emitted from meat charbroiling operations.

A chlorinated insecticide, chlorpyrifos, was found in the exhaust of all three seed oil cooking processes. An analysis of the seed oils used for the cooking tests indicated that this compound was not present in the oils. It is unclear if the chlorpyrifos found in the cooking exhaust originated from the vegetables that were stir fried or if it was present in the cleaning materials used in the kitchen. In addition relatively small emissions of polycyclic aromatic hydrocarbons (PAH) and alkanes were quantified. Significantly more n-heptacosane is emitted than the other high molecular weight n-alkanes from vegetable stir frying; however, the emission rate of this compound is very minor compared to other urban sources of this compound (2).

3.3.3 Gas/Particle Partitioning: Experiment Versus Theory

According to gas/particle partitioning theory (11, 12), the phase distribution of a semi-volatile organic compound is determined by its absorption into the particle phase matrix. This phase distribution can be described by a partitioning coefficient, $K_{p,opm}$, defined as:

$$K_{p,opm} = \frac{F/OPM}{A} \qquad (1)$$

where $K_{p,opm}$ is the gas/particle partitioning coefficient based on organic particulate matter as the receiving particle phase substrate in units of $m^3\ \mu g^{-1}$. OPM is the total organic particulate matter concentration into which the compound can partition ($\mu g\ m^{-3}$). A is the gas-phase mass concentration of the compound of interest ($\mu g\ m^{-3}$), F is the particle-associated mass concentration of the semi-volatile organic compound of interest ($\mu g\ m^{-3}$). It is expected that the gas/particle partitioning coefficient, $K_{p,opm}$, will depend on the vapor pressure of the various organic compounds (12):

$$Log(K_{p,opm}) = m_{r,opm} Log(p_L^0) + b_{r,opm} \qquad (2)$$

where p_L^0 is the vapor pressure over a liquid pool of the semi-volatile organic compound of interest in torr, and $m_{r,opm}$ and $b_{r,opm}$ are coefficients that can be estimated by regressing a series of experimentally measured values of $K_{p,opm}$ on the corresponding liquid vapor pressure values, p_L^0, for the members of a given organic compound class. The coefficient $-m_{r,opm}$ should be close to unity if the compounds have similar activity coefficients when present in the particulate organic matrix and the partitioning process has reached equilibrium. The coefficient $b_{r,opm}$ is a constant characteristic of the partitioning for that class of compounds with the specific particle matrix.

Figure 3.5 shows a partitioning plot for n-alkanoic acids emitted during the seed oil cooking experiments based on the relationship proposed by Pankow (12) as measured during the present experiments using the denuder/filter/PUF sampling train. Good agreement with the model is observed. All three data sets have R^2 values of greater than 0.96, and have slopes of -0.97 ± 0.10, -1.01 ± 0.12, and -1.13 ± 0.13 for the deep frying of potatoes, the canola oil vegetable stir fry and the the soybean oil vegetable stir fry, respectively. Partitioning coefficients, $b_{r,opm}$, for the n-alkanoic acids in the exhaust from the deep frying of potatoes, stir frying vegetables in canola oil, and stir frying vegetables in soybean oil are 6.5 ± 0.3, 6.7 ± 0.5, and 7.1 ± 0.5, respectively. This result is very different than the phase distribution of these same compounds observed in meat smoke exhaust (Chapter 2), where the alkanoic acids did not

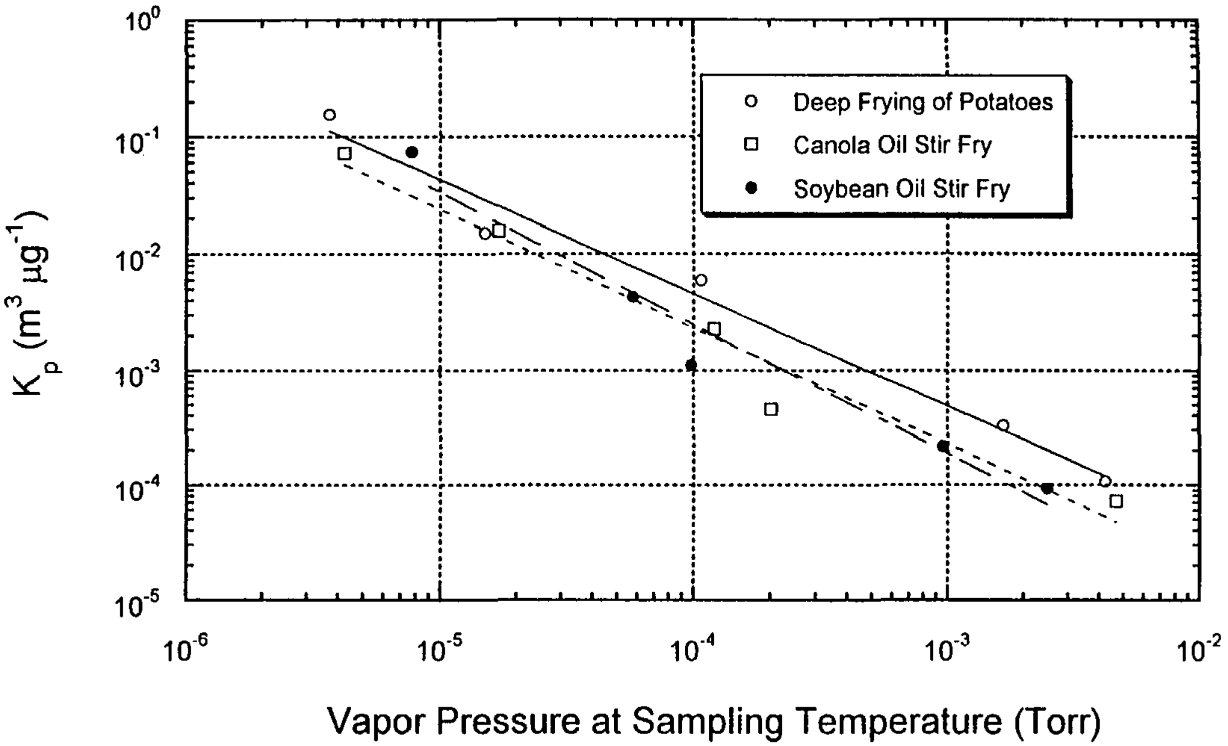


Figure 3.5. Partitioning of n-alkanoic acids in the diluted exhaust from cooking in seed oil as a function of the vapor pressure of the pure compound as measured by a denuder/filter/PUF sampling train.

follow the above partitioning theory, most likely because they were to some degree trapped within solidified meat fat particles.

3.3.4 Contribution to Concentrations of Alkanoic Acids in the Los Angeles Atmosphere

An analysis of the source contributions to atmospheric fine particle mass concentrations and fine organic aerosol concentrations in Southern California has been presented by Schauer et al. (2) using particulate organic tracers for the sources studied. In that study, nine sources of organic compounds accounted for most of the ambient fine aerosol concentrations in the Los Angeles Basin during the year 1982. It was found that the sources studied could not completely account for the n-alkanoic acids concentrations measured in the fine particles, and it was suggested that emissions from cooking with seed oils might constitute a missing primary source of n-alkanoic acids. Based on the results of the present source testing program, the seed oil cooking contribution to the n-alkanoic acids in the atmospheric fine particles during the 1982 time period studied by Schauer et al. (2) can be estimated.

The California Air Resources Board estimates that one commercial deep fryer is operated seven days per week for each 252 people living in an urban area (13). If the deep fryers tested in this study are considered to be typical of commercial deep fryers and if we assume that a typical commercial deep fryer is operated an average of 8 hours per day, then the emission rate of hexadecanoic acid and octadecanoic acid for the study 1982 period from deep fryers would be 11.1 and 5.3 kg per day, respectively, for the South Coast Air Basin that surrounds Los Angeles.

The emissions from stir frying and grill frying with seed oils can be estimated from the consumption of the oils used for these cooking operations. The United States Census Bureau reported that the consumption of salad and cooking oils in the U. S., which does not include baking and frying fats, was 3.0 million kilograms in 1994. Additionally, 0.91 million kilograms of margarine were consumed (14). The estimated consumption of these edible oils can be back-calculated to 1982 using an annual growth factor which is extrapolated from the seed oil consumption increase of 32% in the United States that occurred from 1981 to 1992 (10). If we assume that 75% of the salad and cooking oils were consumed for frying, and 25% of the margarine was consumed for frying and that the per capita consumption of cooking oils is similar for the entire United States and Southern California, then the emissions from stir frying and grill frying with seed oils can be estimated in the South Coast Air Basin to be 11.2 and 4.2 kg per day of n-hexadecanoic acid and n-octadecanoic acid emitted by commercial establishments. These combined emissions from both types of seed oil cooking account for approximately a 9% increase in these alkanoic acids emissions when compared to the primary sources previously assessed (2).

As mentioned previously, nananoic acid is emitted in relatively large quantities from cooking with seed oils. The nonanoic acid emission rate is only 28% of the hexadecanoic acid emission rate in meat smoke, but the ratio for the same compounds in the emissions when cooking with seed oils is approximately 400%. Therefore, if seed oil cooking accounts for 9% of the C_{16} and C_{18} alkanoic acid emissions and meat cooking accounts for approximately 45% of the C_{16} and C_{18} alkanoic acid emissions in this study area, then seed oil cooking emissions of nonanoic acid from cooking with seed oils should dominate over the emissions of nonanoic acid from meat charbroiling operations. It is uncertain whether there are other major primary sources of nonanoic acid emissions to the atmosphere, but clearly an investigation of these lighter organic acids is warranted. If cooking with seed oils is shown to dominate the primary emissions of nonanoic acid to the atmosphere, then the differences in the relative distribution of organic acids in source emissions and in the atmosphere discussed above may help to distinguish the effluent of seed oil use from the effluent from meat cooking operations when measured in the atmosphere.

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Chapter 4

Organic Compounds from Medium Duty Diesel Trucks

4.1 Introduction

Since diesel fuel consists largely of aliphatic hydrocarbons containing 10 to 25 carbon atoms, it is expected that these components and their thermally-altered breakdown products also will be present in diesel exhaust. The inorganic and organic composition of fine particulate matter emitted in the exhaust from diesel-powered motor vehicles has been characterized in the past (1, 2) at a level sufficient to determine the contribution of primary emissions from diesel engines to atmospheric fine particle mass concentrations via transport modeling and organic chemical tracer techniques (3, 4). Specific volatile and semi-volatile gas-phase polycyclic aromatic hydrocarbons (PAH) emitted from diesel-powered motor vehicles also have been examined (5-7). However, a detailed analysis of the remaining semi-volatile gas-phase emissions from contemporary diesel trucks has not been reported. These semi-volatile organic compounds (SVOC) can play a role in photochemical smog formation and are likely candidates to become the precursors of secondary organic aerosol (SOA) that is produced from the low vapor pressure products of atmospheric chemical reactions. The lack of emissions data for these compounds from diesel engines, however, has prevented current air quality models from assessing their importance in urban air pollution. In the present work, new measurements of diesel engine exhaust emissions have been undertaken with an emphasis on defining the mixture of semi-volatile organic compounds emitted and their distribution between the gas and particle phases.

The ratio of methyl-substituted PAH to unsubstituted PAH has been used previously to help determine the origin of hydrocarbon contamination in aquatic environments (8) and in the atmosphere (9). Crude oils and many refined petroleum products have a higher ratio of methyl-substituted PAH to unsubstituted PAH than is found in engine exhaust emissions due to thermal dealkylation within the engine (10). In the present study, the composition of the commercial diesel fuel burned in the diesel trucks tested is compared to the composition of the organic compounds emitted from the diesel trucks during the source tests. The change in the degree of methyl-substitution of the PAH in the exhaust emissions when compared to the fuel as well as other selective changes in the relative distribution of organic compounds is assessed, with an emphasis on quantifying those features that show potential for distinguishing diesel fuel vapors in the atmosphere from the organic compounds emitted from diesel truck exhaust as well as distinguishing diesel truck exhaust from gasoline-powered motor vehicle exhaust.

4.2 Experimental Methods

4.2.1 Comprehensive Source Sampling

A two-stage dilution sampler is used in the present study. It consists of two sections, a pre-dilution tunnel followed by the primary sampling system. The pre-dilution tunnel is connected directly to the tailpipe of the diesel truck being tested on the dynamometer via a stainless steel hose. At the entrance of the pre-dilution tunnel, HEPA-filtered and activated carbon-filtered dilution air is turbulently mixed with the vehicle exhaust. The pre-dilution tunnel is operated at a fixed combined flowrate of 9910 lpm, such that the exhaust concentration in this tunnel is always proportional to the total emission rate from the tailpipe. At the downstream end of the pre-dilution tunnel, a small portion of the total flow is drawn through a cyclone separator which removes particles larger than a nominal 10 μm in aerodynamic diameter. The gas-phase and particulate species that exit the cyclone pass through a venturi meter into the primary sampling system where they are diluted a second time. Stages 1 plus 2 of this system dilute the vehicle exhaust by a total average dilution factor of approximately 140 fold.

The primary sampling system is a modified version of the portable dilution sampler originally developed by Hildemann et al. (11). The modified sampling system has been previously described in Chapter 2, but briefly consists of a dilution tunnel, which in the current study provides the second stage of dilution, followed by a residence time chamber that retains the diluted source sample while further condensation of organic gases onto the particles takes place. A diagram of the original dilution sampler as used in a motor vehicle test configuration is shown in Figure 1b of Hildemann et al. (1) and the added details of the particulate and gas-phase measurement systems now placed at the downstream end of the source sampler are shown in Figure 2.1 in Chapter 2. At the downstream end of the dilution sampler, instruments for measuring fine particulate and gas-phase species concentrations and chemical composition are attached to the residence time chamber from which samples are withdrawn for chemical analysis. Samples are drawn through AIHL-design cyclone separators (12) which are operated at flowrates such that fine particles with aerodynamic diameters smaller than 1.8 μm pass through the cyclone separator along with gas-phase species. Gas-phase, semi-volatile and fine particle-phase organic compounds are collected downstream of the cyclones using three types of sampling trains that are operated simultaneously in parallel at this location. Semi-volatile and particulate organic compounds are collected by both a denuder/filter/PUF sampling train and filter/PUF sampling trains. A description of these sampling units is included in Chapter 2. Fine particle emission rates and chemical composition, as well as the emissions rates of carbonyls, organic acids, and gas-phase hydrocarbons are collected with the third type of cyclone based sampling train discussed in Chapter 2.

The internally exposed area of the entire two-stage dilution sampler is constructed only of aluminum, Teflon, and stainless steel. The entire sampler is assembled with Teflon o-rings and is completely free of grease coatings and rubber gaskets.

Electronic particle sizing instruments and a pair of MOUDI impactors are also connected to the residence time chamber during the diesel vehicle source tests to obtain particle size distributions and particle chemical composition as a function of particle size. The size distributions and the results obtained from the MOUDI impactors will be reported elsewhere.

4.2.2 Source Testing Procedure

The two medium duty diesel trucks tested in the present study were both sampled during 1996 from the current in-use vehicle fleet in southern California and were fueled with commercially-obtained California reformulated diesel fuel. The first vehicle tested was a 1995 model year Isuzu intercooled turbo diesel truck with a 3.8 liter, 4 cylinder engine. The second vehicle was a GMC Vandura 3500 full-sized commercial van with a 6.5 liter, 8 cylinder diesel engine. The Isuzu truck and the GMC van had accumulated 39,993 miles and 30,560 miles of driving, respectively, prior to being tested.

Due to vehicle testing facility operating procedures, the diesel trucks could not be moved onto the dynamometer directly from cold storage. The truck has to be driven onto the dynamometer, which entails first starting the engine, so the diesel trucks had to be tested with a hot start FTP cycle. Prior to the start of each source test, the truck tested was warmed up on the dynamometer for approximately ten minutes. The engine was then shut off and the truck tailpipe was connected to the source sampler. The flows through the source samplers were established and the truck was started and driven over the dynamometer cycle shown in Figure 4.1. For both vehicle tests the two roller hydraulic dynamometers were operated at a load of 7500 pounds and an actual horsepower (AHP) of 17.5. The second diesel truck was tested directly after the first truck was finished. The filters used for fine particle mass and bulk chemical composition determination and the denuder were changed between tests, and all other samples destined for detailed analysis of individual organic compounds were collected as a composite sample of the exhaust from the two trucks.

4.2.3 Organic Chemical Analysis

The sample extraction and GC/MS techniques used to quantify the emissions of semi-volatile and particle-phase organic compounds from diesel trucks are the same as was used for the meat charbroiling source tests and are described in Chapter 2.

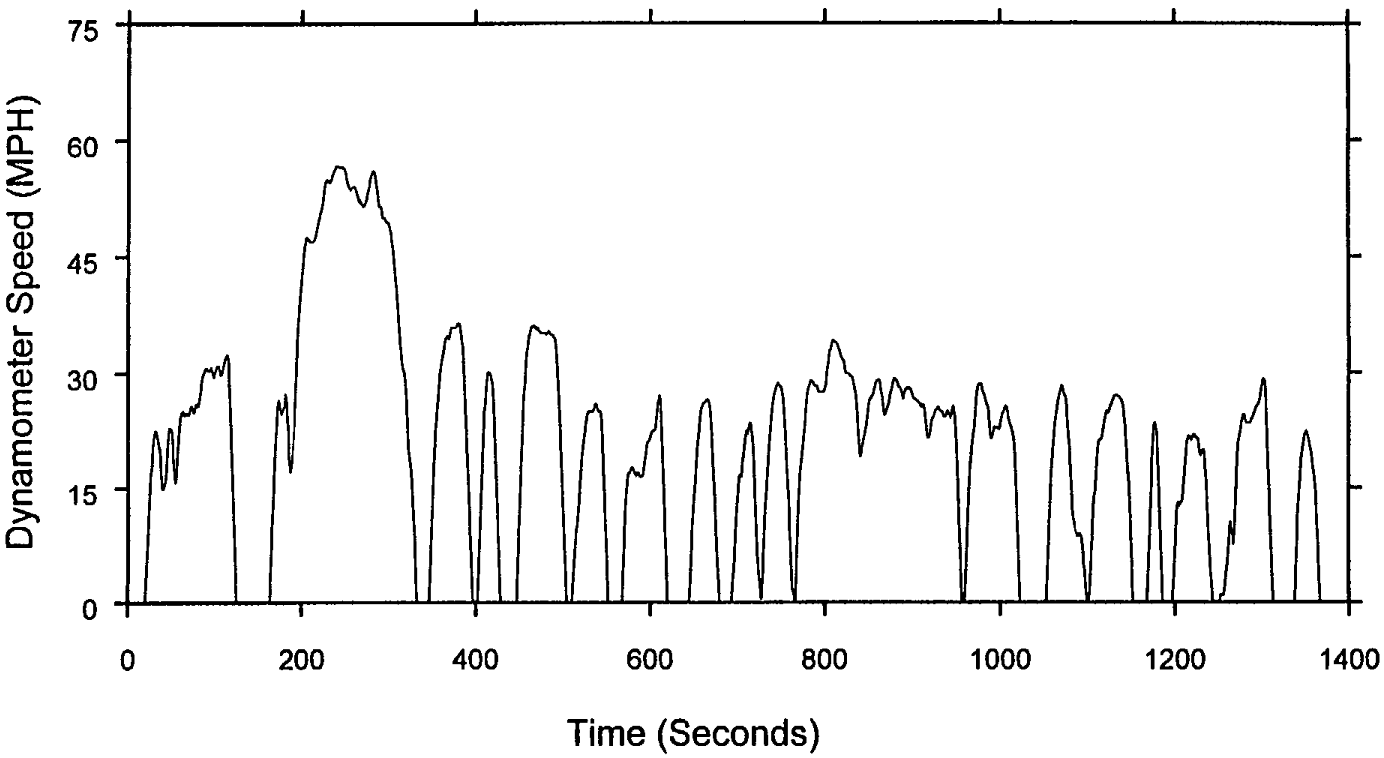


Figure 4.1. Dynamometer cycle used for medium duty diesel truck emissions testing.

Filter, PUF, and denuder field blanks were analyzed in conjunction with the diesel truck source test. The field blanks were prepared, stored and handled by exactly the same procedures as used for the source samples.

Hundreds of authentic standards have been prepared for the positive identification and quantification of the organic compounds found in the current source test program. When quantitative standards could not be obtained for a given compound or compound class, significant effort was made to obtain a non-quantitative secondary standard that could be used for unique identification of the organic compounds. An example of such a secondary standard is the use of motor oil as a source of hopanes and steranes that was used to help identify these compounds in the fine particle diesel exhaust. Quantification of compounds identified using secondary standards has been estimated from the response factors for compounds having similar retention times and chemical structure. In the case of the hopanes and steranes an authentic standard of cholestane was used to estimate the response factors of the remaining hopanes and steranes that were quantified.

Total non-methane organic gases (NMOG, EPA method TO12) and individual organic vapor-phase hydrocarbons ranging from C_1 to C_{10} were analyzed from the SUMA canisters by gas chromatography/flame ionization detection (GC/FID). Carbonyls collected using the DNPH-impregnated C_{18} cartridges were analyzed by liquid chromatography/UV detection.

4.3 Results and Discussion

4.3.1 Fine Particle Mass and Chemical Composition

Fine particle mass and chemical composition measurements made by directly filtering a known volume of the diluted cooled vehicle exhaust without the use of the semi-volatile organic vapor denuder system are shown in Table 4.1. Chemical species for which the emissions rates are significantly greater than zero are shown in bold-face type. Fine particle mass emission rates for the medium-duty diesel trucks tested averaged 185 ± 22 mg per kilometer driven on the FTP urban driving cycle (195.6 ± 3.1 mg per kilometer for the Isuzu truck and 173.7 ± 16.1 mg per kilometer for the GMC van). The fine particle mass collected in this fashion consisted of 30.4 percent organic carbon and 30.8 percent elemental carbon. Sulfate and ammonium ion were found to compose 1.0 percent and 0.73 percent of the mass, respectively, accompanied by detectable amounts of silicon, iron, and zinc.

Organic and elemental carbon also were measured on the quartz fiber filters located downstream of the XAD-coated denuders. The emission rate of fine particle elemental carbon as measured on the filter downstream of the denuder showed good agreement with the undenuded filter sample at 56 mg of elemental carbon per kilometer driven. Significantly less organic carbon was collected on filters located downstream of the denuders than was the case for

Table 4.1. Average Fine Particle Emission Rate and Fine Particle Chemical Composition for Medium-Duty Diesel Truck Exhaust. (Values shown in boldface are greater than zero by at least two standard errors.)

Fine Particle Mass Emissions Rate (AVG ± STD)		**185 ± 22 mg km^{-1}**	
Elemental and Organic Carbon (Wt % of Fine Particle Mass)			
Organic Carbon[a]	**19.7 ± 1.6**	Elemental Carbon	**30.8 ± 2.6**
Ionic Species (Wt % of Fine Particle Mass)			
Chloride	0.00 ± 0.18	Sulfate	**1.00 ± 0.25**
Nitrite	0.01 ± 0.01	Ammonium	**0.73 ± 0.11**
Nitrate	0.23 ± 0.38		
X-ray Fluorescence (Wt % of Fine Particle Mass)			
Aluminum	0.08 ± 0.14	Selenium	0.00 ± 0.01
Silicon	**0.63 ± 0.04**	Bromine	0.00 ± 0.01
Phosphorus	0.01 ± 0.06	Rubidium	0.00 ± 0.01
Sulfur	**0.22 ± 0.02**	Strontium	0.00 ± 0.01
Chlorine	0.00 ± 0.06	Yttrium	0.00 ± 0.02
Potassium	0.00 ± 0.09	Zirconium	0.00 ± 0.02
Calcium	0.03 ± 0.08	Molybdenum	0.00 ± 0.04
Titanium	0.00 ± 0.29	Palladium	0.01 ± 0.10
Vanadium	0.00 ± 0.12	Silver	0.01 ± 0.11
Chromium	0.01 ± 0.03	Cadmium	0.06 ± 0.12
Manganese	0.01 ± 0.02	Indium	0.06 ± 0.14
Cobalt	0.01 ± 0.01	Tin	0.00 ± 0.18
Iron	**0.05 ± 0.01**	Antimony	0.00 ± 0.21
Nickel	0.00 ± 0.01	Barium	0.00 ± 0.79
Copper	0.01 ± 0.01	Lanthanum	0.00 ± 1.04
Zinc	**0.07 ± 0.01**	Mercury	0.00 ± 0.03
Gallium	0.01 ± 0.02	Lead	0.01 ± 0.04
Arsenic	0.00 ± 0.03		

Notes: (a) measured by downstream of the organics denuder. Organic carbon measured on undenued filter is 30.4 percent of fine particle mass.

the undenuded filter sample taken in parallel. Figure 4.2 shows the emission rates of organic and elemental carbon measured by the two sampling techniques. A detailed analysis of the organic carbon distribution between the collection substrates of the denuder/filter/PUF sampling system indicated that there was very little organics mass on the two PUF plugs located downstream of the XAD-coated denuder/filter combination as compared to the difference between the undenuded filter and the denuded filter measurement of the fine particle organic carbon concentration. This indicates that the lower particulate organic carbon mass on the filter in the denuder/filter/PUF system could not be due to organic carbon volatilizing off that filter as the volatilization of organic aerosol would have resulted in higher concentrations measured on the PUF located downstream. These facts indicate that the larger quantity of organic carbon collected on the undenuded filter was due mainly to sorption of semi-volatile gas-phase organic compounds to the undenuded filter and not due to vaporization of particulate matter from the filter located downstream of the denuder.

4.3.2 Distribution of Organic Compounds

The quantities of individual gas-phase plus particle-phase organic compounds and elemental carbon emitted from the medium-duty diesel trucks are shown in Table 4.2 and are summarized in Figure 4.3. The composition of diesel fuel also is given in Table 4.2, as measured by diluting diesel fuel with

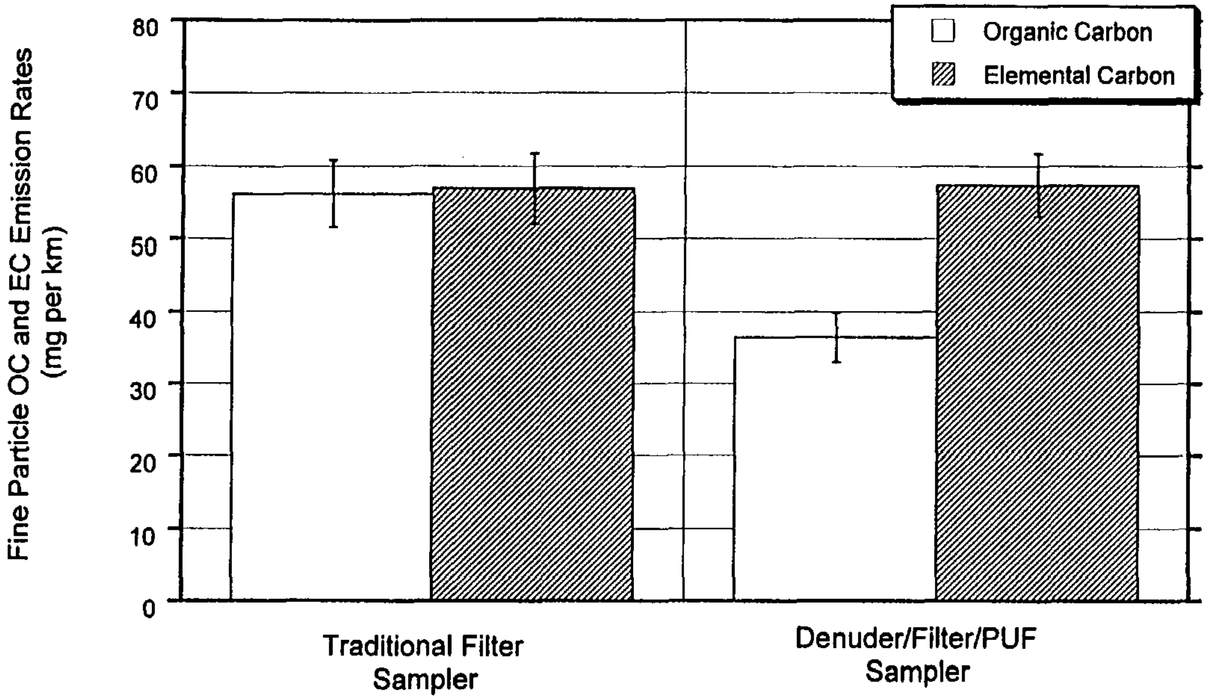


Figure 4.2. Comparison of fine particle organic and elemental carbon emitted from the diesel trucks tested as measured by a traditional filter sampler and a denuder/filter/PUF sampler.

Table 4.2. Organic Compounds Present in Diesel Fuel and in Medium Duty Diesel Truck Exhaust

Compound	Diesel Powered Medium Duty Truck Emissions ($\mu g\ km^{-1}$)		Diesel Fuel Composition ($\mu g\ gram^{-1}$)	Notes
	Gas Phase	Particle Phase		
n-Alkanes				
n-Butane	3830		*	a, e
n-Pentane	1860		*	a, e
n-Heptane	470		*	a, e
n-Octane	260		*	a, e
n-Nonane	160		*	a, e
n-Undecane	*		*	
n-Dodecane†	503		15500	a, f
n-Tridecane	477		15700	b, f
n-Tetradecane	629		13500	a, f
n-Pentadecane	398	2.12	10500	b, f
n-Hexadecane	711	8.62	10100	a, f
n-Heptadecane	614	5.92	5700	b, f
n-Octadecane	601	2.84	9212	a, f
n-Nonadecane	411	3.82	7020	b, f
n-Eicosane	206	95.7	6530	a, f
n-Heneicosane	65.8	40.5	5220	b, f
n-Docosane		52.0	4340	b, f
n-Tricosane		45.5	2670	b, f
n-Tetracosane		40.7	1680	a, f
n-Pentacosane		26.1	730	b, f
n-Hexacosane		34.9	290	b, f
n-Heptacosane		25.7	180	b, f
n-Octacosane		19.7	36	a, f
n-Nonacosane		6.1		b, f
Branched alkanes				
i-Pentane	2740		*	a, e
2,2-Dimethylbutane	310		*	a, e
2,3-Dimethylbutane	570		*	a, e
2-Methylpentane	930		*	a, e
3-Methylpentane	670		*	a, e
2,4-Dimethylpentane	410		*	a, e
2-Methylhexane	570		*	a, e
2,3-Dimethylpentane	720		*	a, e
3-Methylhexane	310		*	a, e
2,2,4-Trimethylpentane	1240		*	a, e
2,5-Dimethylhexane	50		*	a, e
2,4-Dimethylhexane	50		*	a, e
2,3,4-Trimethylpentane	310		*	a, e

Identification notes: (a) authentic quantitative standard. (b) authentic quantitative standard for similar compound in series. (c) secondary standard. (d) detected as a methyl ester.
Exhaust sample collection notes: (e) collected in SUMA canister. (f) collected on denuder/filter/PUF sampling train. (g) collected on DNPH impregnated C_{18} cartridges. (*) not measured. See text for details. Additional Notes: † Compound is too volatile for complete collection by denuder at sampling conditions; mass of this compound reported in the gas-phase includes mass collected on PUF cartridge.

Table 4.2. (continued - page 2)

Compound	Diesel Powered Medium Duty Truck Emissions (μg km^{-1})		Diesel Fuel Composition (μg gram^{-1})	Notes
	Gas Phase	Particle Phase		
Branched alkanes				
2,3-Dimethylhexane	160		*	a, e
2-Methylheptane	100		*	a, e
3-Ethylhexane	210		*	a, e
Norfarnesane[†]	360		16300	b, f
Farnesane[†]	434	4.1	9220	b, f
2,6,10-Trimethyltridecane	367	1.2	8830	b, f
Norpristane	566	4.9	8670	b, f
Pristane	443		5840	a, f
Phytane	439		5770	b, f
n-Alkenes				
Ethene	8560		*	a, e
Propene	780		*	a, e
trans-2-Butene	520		*	a, e
cis-2-Butene	260		*	a, e
trans-2-Pentene	50		*	a, e
trans-2-Hexene	160		*	a, e
cis-2-Hexene	100		*	a, e
Branched alkenes				
Isobutene	1140		*	a, e
3-Methyl-1-butene	160		*	a, e
2-Methyl-1-butene	260		*	a, e
2-Methyl-2-pentene	210		*	a, e
Diolefins				
1,3-Butadiene	310		*	a, e
Alkynes				
Ethyne	4600		*	a, e
Saturated cycloalkanes				
Cyclopentane	410		*	a, e
Methylcyclopentane	620		*	a, e
Cyclohexane	210		*	a, e
Methylcyclohexane	520		*	a, e
Pentylcyclohexane	83.9			b, f
Hexylcyclohexane	14.9		830	b, f
Heptylcyclohexane	20.0		730	b, f
Octylcyclohexane	26.2		500	b, f
Nonylcyclohexane	24.7		490	b, f
Decylcyclohexane	38.2		420	b, f
Undecylcyclohexane	23.9		430	b, f

Identification notes: (a) authentic quantitative standard. (b) authentic quantitative standard for similar compound in series. (c) secondary standard. (d) detected as a methyl ester.
Exhaust sample collection notes: (e) collected in SUMA canister. (f) collected on denuder/filter/PUF sampling train. (g) collected on DNPH impregnated C_{18} cartridges. (*) not measured. See text for details. Additional Notes: [†] Compound is too volatile for complete collection by denuder at sampling conditions; mass of this compound reported in the gas-phase includes mass collected on PUF cartridge.

Table 4.2. (continued - page 3)

Compound	Diesel Powered Medium Duty Truck Emissions (μg km^{-1})		Diesel Fuel Composition (μg gram^{-1})	Notes
	Gas Phase	Particle Phase		
Saturated cycloalkanes				
Dodecylcyclohexane	16.8		200	b, f
Tridecylcyclohexane	16.5	4.34	170	b, f
Tetradecylcyclohexane	15.9	3.96	160	b, f
Pentadecylcyclohexane	12.8	9.88	150	a, f
Hexadecylcyclohexane		12.9		b, f
Heptadecylcyclohexane		16.7		a, f
Octadecylcyclohexane		11.5		b, f
Nonadecylcyclohexane		9.0		b, f
Unsaturated cycloalkenes				
Cyclopentene	210		*	a, e
Aromatic hydrocarbons				
Benzene	2740		*	a, e
Toluene	3980		*	a, e
Ethylbenzene	470		*	a, e
m & p-Xylene	2330		*	a, e
o-Xylene	830		*	a, e
n-Propylbenzene	100		*	a, e
p-Ethyltoluene	520		*	a, e
m-Ethyltoluene	210		*	a, e
1,3,5-Trimethylbenzene	260		*	a, e
1,2,4-Trimethylbenzene	880		*	a, e
Naphthalene†	617		600	a, f
2-Methylnaphthalene†	611		980	a, f
1-Methylnaphthalene †	378		580	a, f
C_2-Naphthalenes	542		2050	a, f
C_3-Naphthalenes	240	130	1360	b, f
C_4-Naphthalenes	97.3	98.6	760	b, f
Acenaphthylene	70.1			a, f
Acenaphthene	19.3			a, f
Fluorene	34.6	9.5	52	a, f
C_1-Fluorene	65.2	83.0	190	b, f
Phenanthrene	93.1	47.0	57	a, f
Anthracene	12.5	10.9	5	a, f
3-Methylphenanthrene	30.3	29.4	51	b, f
2-Methylphenathrene	42.0	35.6	45	b, f
2-Methylanthracene	10.4	10.4	6	a, f
9-Methylphenanthrene	22.9	22.0	35	b, f
1-Methylphenanthrene	17.0	17.8	28	a, f

Identification notes: (a) authentic quantitative standard. (b) authentic quantitative standard for similar compound in series. (c) secondary standard. (d) detected as a methyl ester.
Exhaust sample collection notes: (e) collected in SUMA canister . (f) collected on denuder/filter/PUF sampling train. (g) collected on DNPH impregnated C_{18} cartridges. (*) not measured. See text for details. Additional Notes: † Compound is too volatile for complete collection by denuder at sampling conditions; mass of this compound reported in the gas-phase includes mass collected on PUF cartridge.

Table 4.2. (continued - page 4)

Compound	Diesel Powered Medium Duty Truck Emissions (μg km^{-1})		Diesel Fuel Composition (μg gram^{-1})	Notes
	Gas Phase	Particle Phase		
Aromatic hydrocarbons				
C_2-MW 178 PAH	196	57.2	2080	a, f
C_3-MW 178 PAH	97.4	97.5	120	b, f
Fluoranthene	53.0	56.6		a, f
Acephenanthrylene	12.0	16.2		b, f
Pyrene	71.9	88.5	64	a, f
C_1-MW 202 PAH	39.0	81.0	290	b, f
Benzo[ghi]fluoranthene	5.82	19.8		b, f
Cyclopenta[cd]pyrene	2.06	3.50		a, f
Benz[a]anthracene	2.98	7.76		a, f
Chrysene & Triphenylene	3.35	15.6		a, f
C1-MW 228 PAH		6.54		b, f
Tricyclic terpanes				
8β,13α-Dimethyl-14β-n-butylpodocarpane	44.0	10.6	2.1	c, f
8β,13α-Dimethyl-14β-[3'-methylbutyl]podocarpane	13.8	4.50	0.6	c, f
Diasteranes				
20S-13β(H),17α(H)-Diacholestane		1.37		c, f
Hopanes				
18α(H)-22,29,30-Trisnorneohopane		2.74		c, f
17α(H)-22,29,30-Trisnorhopane		0.99		c, f
17α(H),21β(H)-29-Norhopane		11.3		c, f
17α(H),21β(H)-Hopane		11.4		c, f
Steranes				
20R,5α(H),14β(H),17β(H)-Cholestane		0.78		c, f
20R,5α(H),14α(H),17α(H)-Cholestane		1.19		c, f
20R&S,5α(H),14β(H),17β(H)-Ergostane		3.15		c, f
20R&S,5α(H),14β(H),17β(H)-Sitostane		2.61		c, f
Aliphatic aldehydes				
Formaldehyde	22300		*	a, g
Acetaldehyde	41800		*	a, g
Propanal	14000		*	a, g
Butanal	1300		*	a, g
Hexanal	2200		*	a, g
Heptanal	3200		*	a, g
Octanal	3100		*	a, g
Nonanal	4400		*	a, g

Identification notes: (a) authentic quantitative standard. (b) authentic quantitative standard for similar compound in series. (c) secondary standard. (d) detected as a methyl ester.

Exhaust sample collection notes: (e) collected in SUMA canister. (f) collected on denuder/filter/PUF sampling train. (g) collected on DNPH impregnated C_{18} cartridges. (*) not measured. See text for details. Additional Notes: † Compound is too volatile for complete collection by denuder at sampling conditions; mass of this compound reported in the gas-phase includes mass collected on PUF cartridge.

Table 4.2. (continued - page 5)

Compound	Diesel Powered Medium Duty Truck Emissions ($\mu g\ km^{-1}$)		Diesel Fuel Composition ($\mu g\ gram^{-1}$)	Notes
	Gas Phase	Particle Phase		
Aliphatic aldehydes				
Decanal	2800		*	a, g
Undecanal	2600		*	a, g
Dodecanal	1200		*	a, g
Tridecanal	2000		*	a, g
Olefinic aldehydes				
Crotonaldehyde	13400		*	a, g
Acrolein	3400		*	a, g
Methacrolein	4000		*	a, g
Aliphatic ketones				
Acetone	22000		*	a, g
Butanone / Methylacrolein	7500		*	a, g
Aromatic aldehydes				
Benzaldehyde	3800		*	a, g
Acetophenone	5100		*	a, g
2,5-Dimethylbenzaldehyde	4100		*	a, g
Aromatic ketones				
Indanone†	69.5			a, f
Fluorenone	34.6	9.84		a, f
Xanthone	12.4			a, f
Dicarbonyls				
Glyoxal	2100		*	a, g
Methylglyoxal	1700		*	a, g
Biacetyl	900		*	a, g
n-Alkanoic acids				
Octanoic acid	125		*	a, f, d
Nonanoic acid	240		*	b, f, d
Decanoic acid	72.9		*	a, f, d
Undecanoic acid	206		*	b, f, d
Dodecanoic acid	58.5		*	a, f, d
Tridecanoic acid	13.1		*	b, f, d
Tetradecanoic acid	5.3		*	a, f, d
Heptadecanoic acid		22.3	*	b, f, d
Octadecanoic acid		362	*	a, f, d
Nonadecanoic acid		5.7	*	b, f, d
Eicosanoic acid		14.2	*	a, f, d

Identification notes: (a) authentic quantitative standard. (b) authentic quantitative standard for similar compound in series. (c) secondary standard. (d) detected as a methyl ester.
Exhaust sample collection notes: (e) collected in SUMA canister. (f) collected on denuder/filter/PUF sampling train. (g) collected on DNPH impregnated C_{18} cartridges. (*) not measured. See text for details. Additional Notes: † Compound is too volatile for complete collection by denuder at sampling conditions; mass of this compound reported in the gas-phase includes mass collected on PUF cartridge.

Table 4.2. (continued - page 6)

Compound	Diesel Powered Medium Duty Truck Emissions (µg km^{-1})		Diesel Fuel Composition (µg gram^{-1})	Notes
	Gas Phase	Particle Phase		
Alkanedioic acids				
Octadecanedioic acid		138	*	a, f, d
Nonadecanedioic acid		176	*	a, f, d
Aromatic acids				
Benzoic acid	1260		*	b, f, d
Methylbenzoic acids	772	26.7	*	a, f, d
Other compounds				
Benzofuran	53.2			a, f
Dibenzofuran	28.7	6.0	29	a, f
Dibenzothiophene	1.98			a, f
Dibenzothiazole	251			a, f
Unresolved Complex Mixture	53800	41400	*	b, f

Identification notes: (a) authentic quantitative standard. (b) authentic quantitative standard for similar compound in series. (c) secondary standard. (d) detected as a methyl ester.
Exhaust sample collection notes: (e) collected in SUMA canister. (f) collected on denuder/filter/PUF sampling train. (g) collected on DNPH impregnated C_{18} cartridges. (*) not measured. See text for details. Additional Notes: † Compound is too volatile for complete collection by denuder at sampling conditions; mass of this compound reported in the gas-phase includes mass collected on PUF cartridge.

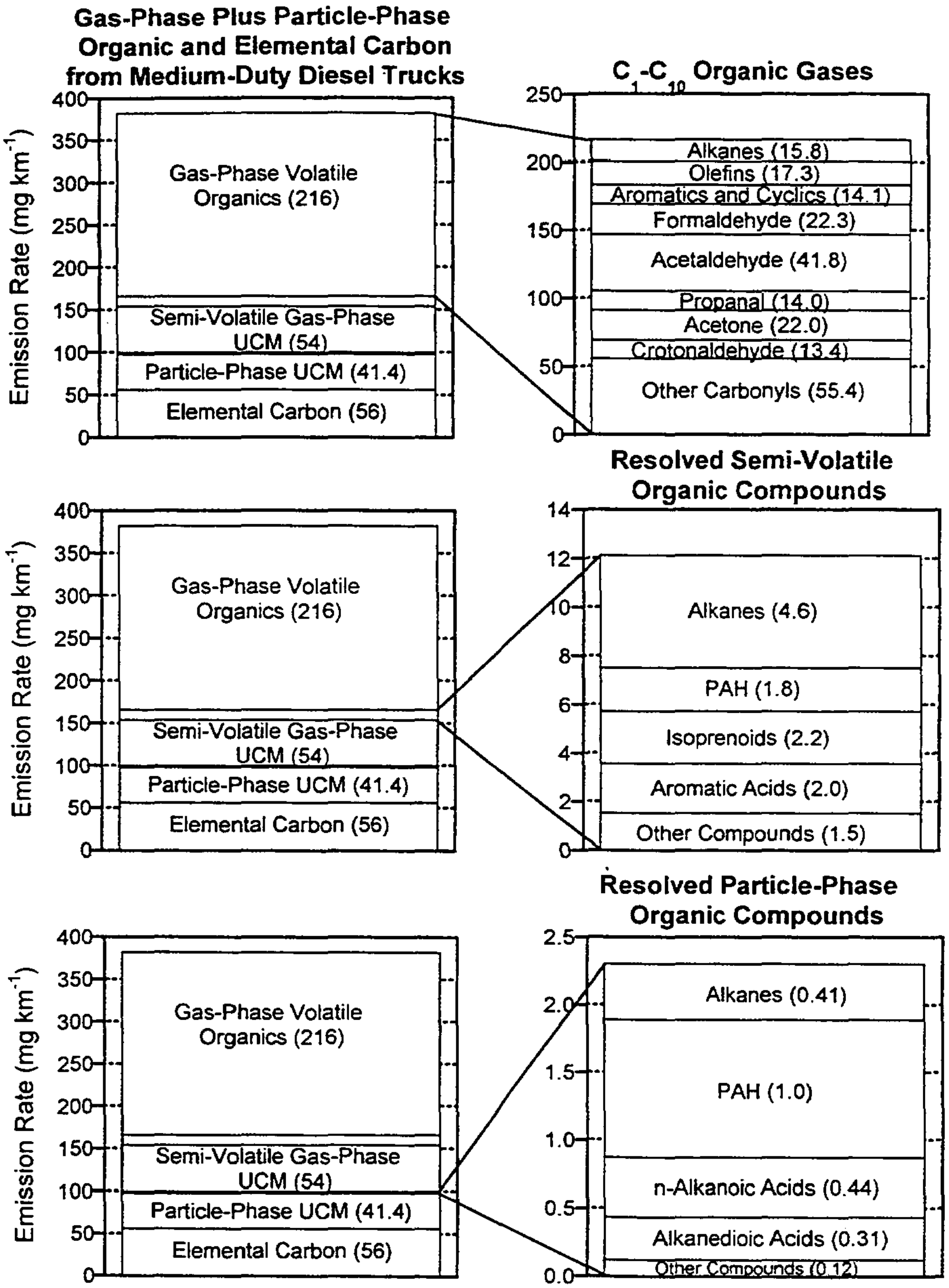


Figure 4.3. Material balance on the gas-phase, semi-volatile, and particle-phase organic compounds emitted from medium duty diesel trucks driven over the hot start Federal Test Procedure urban driving cycle on a chassis dynamometer.

extraction-grade solvents and then analyzing the diluted fuel by the same GC/MS techniques as are used for the exhaust samples in this study. Light gas-phase carbonyls make up the largest fraction of the gas-phase exhaust emissions; they are emitted at a rate of 126 mg per kilometer driven. Over half of the carbonyl emissions consist of formaldehyde plus acetaldehyde, accompanied by significant quantities of propanal, acetone, butanone, and crotonaldehyde. It is known from previous work (13, 14) that the carbonyl emissions from diesel trucks are substantial. The present study is unique because the emissions of high molecular weight carbonyls up to tridecanal are also quantified. Gas-phase alkanes are emitted at a rate of 11.2 mg per kilometer driven, accompanied by smaller quantities of aromatics, PAH, olefins and other vapor-phase organic compounds. A noticeable quantity of the gas-phase alkane mass emitted is in the carbon number range from C_{12} through C_{20}, which is consistent with the composition of diesel fuel.

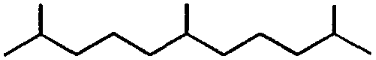
A major part of the remaining gas-phase and particle-phase organic compound emissions is made up of an unresolved complex mixture (UCM) comprised of aliphatic branched and cyclic hydrocarbons that are not separable as individual GC peaks. The gas-phase portion of the UCM consists of high molecular weight semi-volatile organics that are in the aggregate emitted at a rate of 54 mg km^{-1}, slightly less than half that of the total carbonyl mass emission rate, while the particle-phase UCM contributed an additional 41.4 mg km^{-1}.

The composition of the UCM found in the particle phase was very similar to motor oil when analyzed by GC/MS. The distribution of hopanes and steranes in the fine particle exhaust emissions and in motor oil was found to be very similar as well. For these reasons, the UCM contained in the fine particulate matter emitted was quantified according to a GC/MS response factor obtained by using motor oil as a standard. Quantifying the UCM by this method closely closed a mass balance on the organic carbon collected on the quartz fiber filters as analyzed by thermal evolution and combustion analysis and by GC/MS analysis. The vapor phase semi-volatile UCM collected on the denuders and the PUF cartridge was quantified by the same procedure, because the GC/MS response factor for motor oil was close to that of n-alkanes in the carbon number range from C_{14} to C_{24} on a total ion current (TIC) basis.

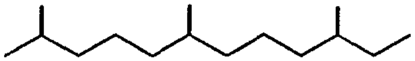
The remaining high molecular weight carbonaceous species emitted in the diesel exhaust include resolved vapor-phase semi-volatile and particle-phase organic compounds plus elemental carbon, as summarized in Figure 4.3. Elemental carbon contributes 56 mg km^{-1}, while an additional 14.4 mg km^{-1} can be accounted for in terms of the individual organic compounds shown in Table 4.2. Included in the resolved organic compounds are n-alkanes, PAH, isoprenoids, saturated cycloalkanes, organic acids, hopanes and steranes.

The n-alkane emission rates are greatest in the carbon number range from C_{12} through C_{20}, averaging over 400 μg km^{-1} for most individual n-alkanes in this range. n-Butane and n-pentane also are emitted at high rates at 3830 and 1860 μg per kilometer, respectively. As the concentration of the C_4 and C_5 alkanes was not analyzed in the diesel fuel, it is unclear whether these compounds are formed in the diesel engine combustion process or if they were originally present in solution in the diesel fuel. Likewise, iso-pentane and other low molecular weight branched alkanes shown in Table 4.2 are emitted at relatively high rates.

Individual organic compounds in the class of branched C_{14} through C_{20} alkanes known as the isoprenoids are emitted at rates in the range of 360 to 570 μg per vehicle kilometer traveled. The structures of selected isoprenoid hydrocarbons are shown in Figure 4.4. These compounds are naturally present in crude oil (15) and therefore would be expected to be found in lightly processed or straight run diesel fuel cuts in the petroleum refining process. The isoprenoids, in conjunction with certain PAH, hopanes, steranes and elemental carbon as will be described shortly, have the potential to be used as tracers for diesel engine exhaust. Figure 4.5 shows the distribution of the n-alkanes and isoprenoids in the commercial California diesel fuel used in the current source tests compared to the emission rate and phase distribution of these compounds in the diesel truck exhaust. As can be seen in Figure 4.5, the tailpipe emissions are depleted in the lowest molecular weight homologues in each series of these branched and straight chain alkanes when compared to the parent fuel. It

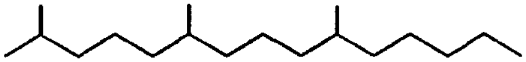


Norfarnesane
2,6,10-Trimethylundecane



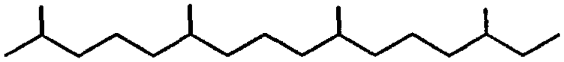
Farnesane
2,6,10-Trimethyldodecane

2,6,10-Trimethyltridecane

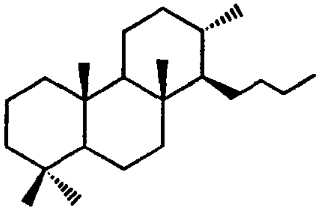


Norpristane
2,6,10-Trimethylpentadecane

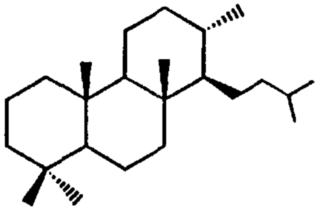
Pristane
2,6,10,14-Tetramethylpentadecane



Phytane
2,6,10,14-Tetramethylhexadecane



8β,13α-Dimethyl-14β-n-butylpodocarpane



8β,13α-Dimethyl-14β-[3'methylbutyl]podocarpane

Figure 4.4. Chemical structures of isoprenoids and tricyclic terpanes present in diesel fuel and emitted from diesel trucks.

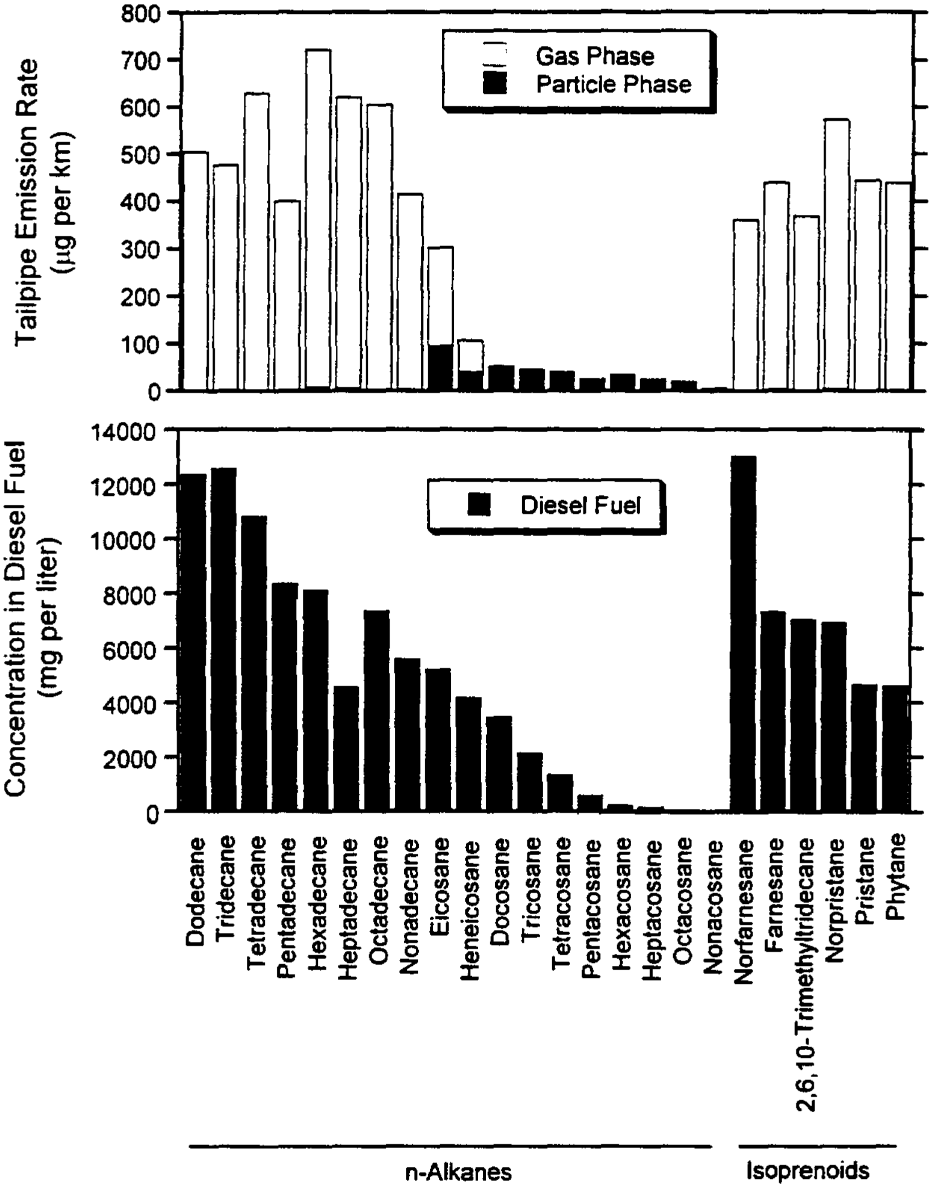


Figure 4.5. Comparison of the distribution n-alkanes and isoprenoids in medium-duty diesel truck exhaust and present in the diesel fuel supplied to those trucks.

should be noted that the overall distribution of the organic compounds between the gas and particle phases summed over the entire FTP driving cycle may not behave according to gas/particle partitioning theory (16) applied to the bulk compound emission rate data averaged over the whole test. At any given point during the FTP cycle, the organic compounds in the diluted exhaust should partition as expected by theory; however, the primary emission rates and organic compound compositions are changing continuously throughout the cycle such that the linear sum of these instantaneous equilibrated phase distributions may not add to produce gas/particle concentration ratios for the test as a whole that correspond to the equilibrium distribution at the average conditions during the test.

A similar comparison between the PAH present in the fuel and in the diesel truck emissions is shown in Figure 4.6. Significant differences can be seen in the ratio of methyl-substituted PAH to unsubstituted PAH between the fuel and the tailpipe emissions. The dimethyl phenanthrenes and anthracenes (C_2-MW 178 PAH in Table 4.2) contribute the overwhelming majority of the PAH with three or more ring structures in the diesel fuel. The ratio of these compounds to phenanthrene plus anthracene decreases from 33.5 in the diesel fuel to 1.55 in the tailpipe emissions. An analogous but less extreme difference is observed for the methyl fluoranthenes, acephenanthrylenes, and pyrenes

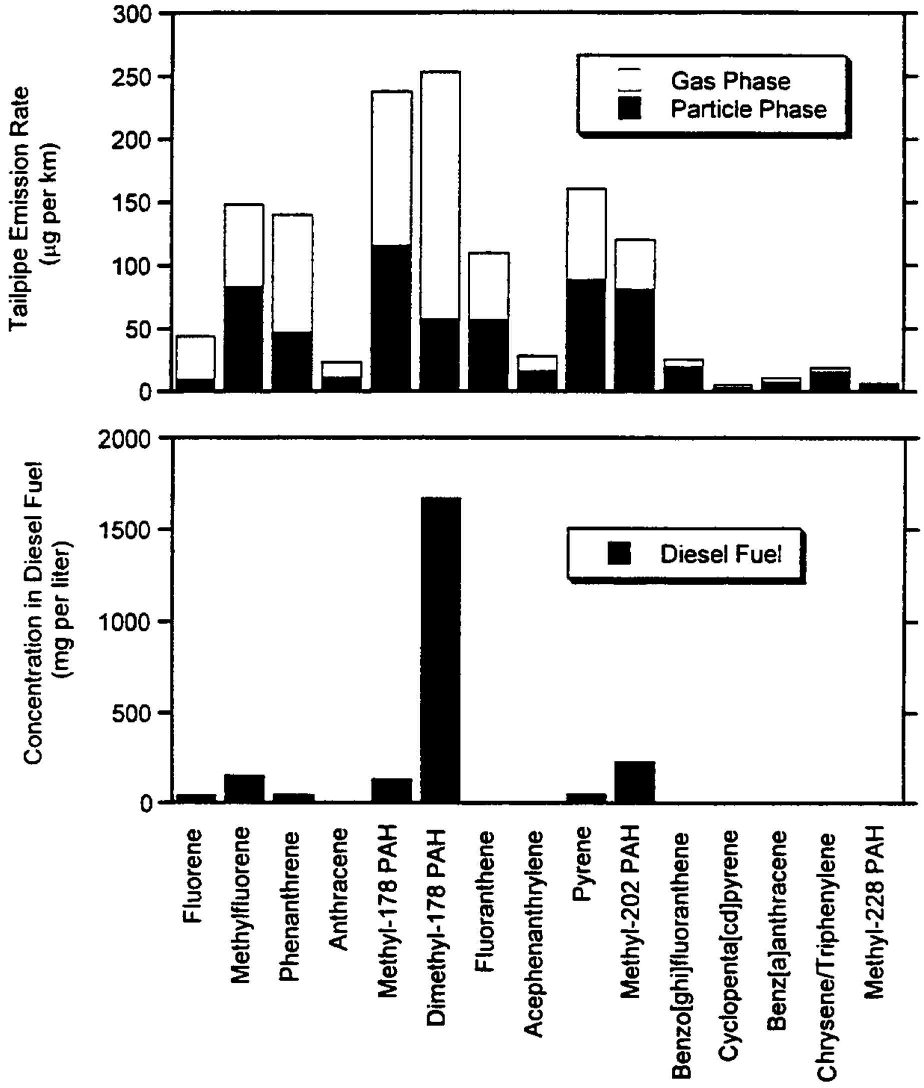


Figure 4.6. Polycyclic aromatic hydrocarbons (PAH) emitted from medium-duty diesel trucks and present in diesel fuel.

(C_1-MW 202 PAH in Table 4.2) when compared to the unsubstituted PAH with molecular weights of 202.

The particle-phase hopanes and steranes present in vehicle exhaust have been used in the past as tracers for motor vehicle exhaust contributions to atmospheric fine particle samples (3, 4). To this set of particle-phase exhaust molecular tracers we can now add two semi-volatile tricyclic terpanes, 8β,13α-dimethyl-14β-n-butylpodocarpane and 8β,13α-dimethyl-14β-[3'-methylbutyl]podocarpane, which are quantified in the diesel truck exhaust and have been previously quantified in the atmosphere of Los Angeles (17). The structures of these compounds are shown in Figure 4.4. These compounds are also present in the diesel fuel used in these experiments at 2.1 and 0.6 $\mu g\ g^{-1}$, respectively, as shown in Table 4.2.

The question posed at the outset of the study is now revisited, "How can diesel fuel vapors in the atmosphere be distinguished from diesel truck exhaust and how can diesel truck exhaust be distinguished from gasoline-powered motor vehicle exhaust?" Since diesel exhaust contains unburned diesel fuel, whole fuel vapors share many features in common with the tailpipe exhaust, as we have just seen. However, the diesel truck exhaust is clearly distinguished from unburned fuel by its high black elemental carbon content, by its hopanes and sterane content, by its higher ratio of unsubstituted PAH to methyl-PAH, and by its high aldehyde content (although the aldehydes are too reactive to be considered as tracer species for diesel exhaust). The hopanes and steranes are not present in large amounts in the fuel (e.g., see Table 4.2) but are present in motor oil (see discussion of standards in text) and thus must be contributed largely by the lubricant oil used by the engines. Diesel exhaust is readily distinguished from gasoline-powered auto exhaust by its higher elemental carbon content and by the relatively high quantity of pristane and phytane in diesel exhaust. Auto exhaust in turn can be distinguished from non-tailpipe derived gasoline vapors because there is a limit placed on the atmospheric concentration of the sum of the gasoline plus diesel engine tailpipe emissions by the total quantity of hopanes and steranes in the atmosphere (3).

Ambient concentrations of semi-volatile n-alkanes, isoprenoids, and tricyclic terpanes were measured by Fraser et al. (17) in Southern California during the summer of 1993. Shown in Figure 4.7 is the 2-day average ambient concentration of n-octadecane, n-nonadecane, n-eicosane, pristane, phytane, and the tricyclic terpanes as measured by Fraser et al. (17) at Azusa, California, along with the diesel engine emission rates of these compounds from the present study. The data from Fraser et al. (17) are scaled upward across all compounds by a factor of 1.7 to correct an error in the reported air volumes sampled. Good agreement is observed between the relative distribution of these compounds measured in the atmosphere and the emission rates of these compounds from the diesel trucks tested in the present study, which further

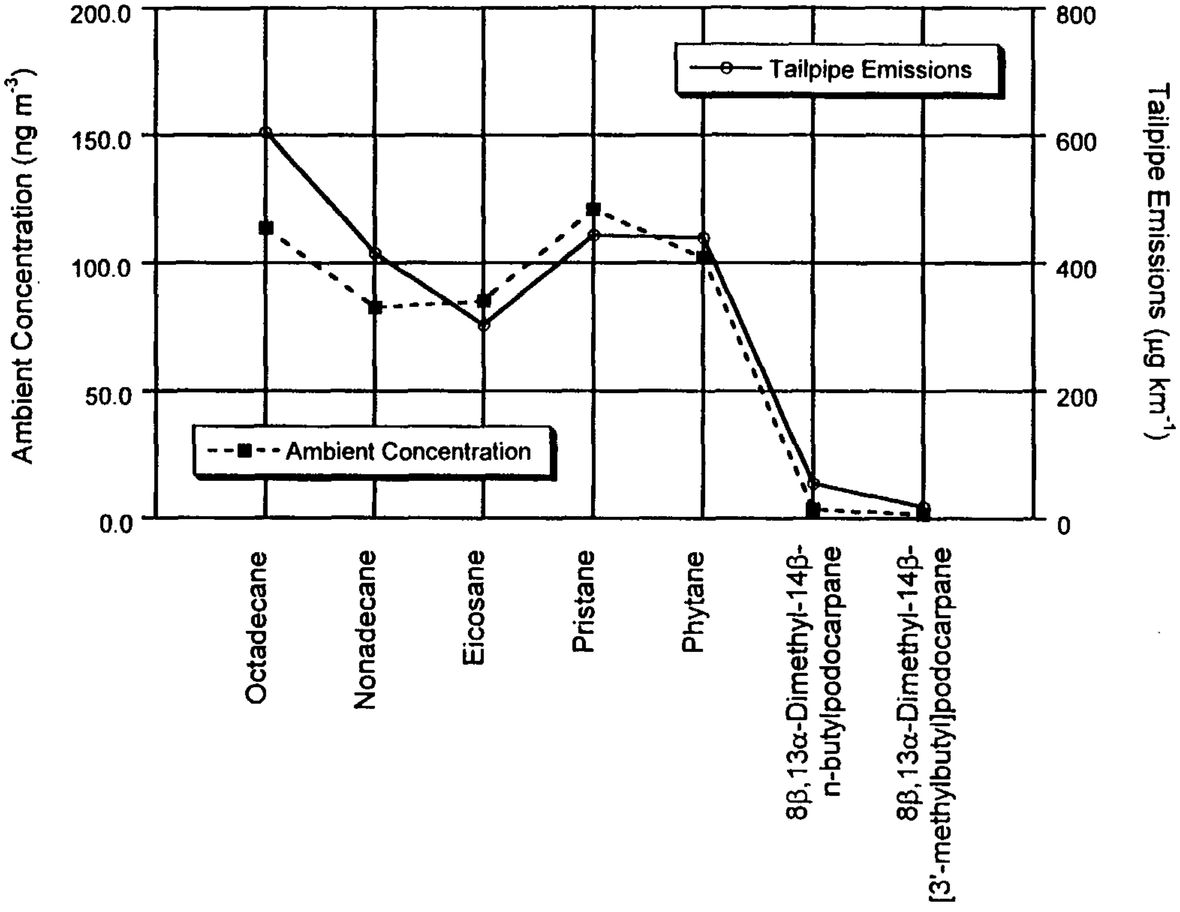


Figure 4.7. Semi-volatile n-alkane, isoprenoid, and tricyclic terpane ambient concentrations measured in Azusa, California, in the summer of 1993 compared to the tailpipe emission rates of these compounds from medium-duty diesel trucks on the FTP hot start driving cycle.

indicates that these compounds will likely be useful as part of the group of tracers for motor vehicle exhaust.

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