Evaluating the Contribution of PM2.5 Precursor Gases and Re-entrained Road Emissions to Mobile Source PM2.5 Particulate Matter Emissions

Prepared by MACTEC Under Contract to the Federal Highway Administration
Authors: William M. Hodan and William R. Barnard
MACTEC Federal Programs
5001 South Miami Boulevard, Ste. 300
Research Triangle Park, NC 27703
Tel. 919-941-0333
Fax. 919-941-0234
E-mail: wmhodan@mactec.com
wrbarnard@mactec.com

A number of literature sources have attributed varying contributions from mobile sources to the current PM2.5 ambient concentration levels. PM2.5 emissions from mobile sources are generated from three general processes: 1) it is directly emitted from the tailpipes of cars, trucks and other on-road vehicles, 2) it is re-entrained from materials found on the roadway (typically known as fugitive dust), and 3) it is created by secondary formation from precursor emissions such as sulfur dioxide (SO2), nitrogen oxides (NOx), volatile organic compounds (VOCs) and ammonia (NH3). Items 1 and 2 are generally known as primary emissions of PM2.5. Secondary formation occurs due to chemical reaction in the atmosphere generally downwind some distance from the original emission source. Efforts to determine the contribution of each of these PM2.5 emission mechanisms has shown a great deal of variability, as seen from an examination of current literature. A thorough review of current literature pertaining to PM2.5 emissions from mobile and other sources provides a foundation for comparison and contrast of the chemical and physical mechanisms involved in emission and formation of PM2.5. The effects of various precursor compounds emitted from mobile sources will be reviewed as well as the contribution of re-entrained dust from tire wear, brake wear, and road dust. The contributions of gasoline and diesel vehicles will be discussed individually, and the affects of atmospheric conditions on secondary PM2.5 formation in different areas of the United States will be addressed. This understanding of the contribution of all aspects of mobile source contribution to PM2.5 problems will be necessary to develop accurate inventories of PM2.5 and implement effective control strategies.

TABLE OF CONTENTS

GLOSSARY

Agglomerate:	*Particles formed by nucleation and/or coagulation.*
Ammonia:	*Ammonia is the chemical NH3.*
Ammonium Nitrates:	*Compound formed from chemical reaction of ammonia and nitrate (typically from NOx).*
Ammonium Sulfates:	*Compound formed from chemical reaction of ammonia and sulfate (typically from SO2).*
Carbonaceous Material:	*Material containing carbon. Essentially the sum of all materials or particles containing organic carbon (OC) and/or elemental carbon (EC).*
Carbonaceous Aerosol:	*Aerosol material containing carbon. The same as carbonaceous material, except that it refers to the aerosol form.*
Coagulation:	*The cooling of exhaust gases resulting in transformation of some exhaust vapors into particles.*
DEOG:	*Diesel Emitted Organic Gases. DEOG generally refers to precursor compounds that have not yet formed particulate matter.*
DPM:	*Diesel Particulate Matter. 90% of the total number of particles in diesel exhaust are in a median size range of about 0.02µm. Most of the mass in diesel exhaust is represented by a median particle size of about 0.25µm. This mass is known as DPA, and is primary particulate matter.*
EC:	*Elemental Carbon. Elemental carbon is pure carbon or soot that is usually formed by incomplete combustion of organic fuels such as gasoline or diesel fuel.*
MSAT:	*Mobile Source Air Toxic (see Table 1-1 of this report for a list).*
NAAQS:	*National Ambient Air Quality Standard.*
NFRAQS:	*Northern Front Range Air Quality Study.*

NOx:	*Nitrogen oxides. These chemicals are responsible for the formation of nitrate ($NO3^{-}$) chemicals in the atmosphere. NOx is one of the specific groups responsible for secondary PM2.5 formation.*
Nitrates:	*Nitrates are chemicals containing the $NO3^{-}$ group, or can refer to the $NO3^{-}$ ion.*
Nitric Acid:	$HNO3$
Nucleation:	*Occurs when inorganic or organic vapors begin to form particles by collecting around an existing solid particle or nucleus.*
OC:	*Organic Carbon. Organic carbon refers to a molecule containing carbon-hydrogen bonds. OC is a term that is mainly used to discuss or quantify the carbon portion of a molecule while differentiating this carbon from elemental carbon (EC). All volatile organic compounds (VOC) contain OC.*
PAH:	*Polyaromatic Hydrocarbon. This is a subset of POM (Polycyclic Organic Matter), and VOC (Volatile Organic Compounds).*
PM2.5:	*Particulate matter that is less than or equal to 2.5 micrometers in diameter.*
PM2.5 Precursor:	*Any chemical that contributes to the formation of PM2.5 particles, but is not emitted directly from a source as PM2.5. PM2.5 precursors react in the atmosphere to form PM2.5.*
POM:	*Polycyclic Organic Matter. POM is a subset of VOC (Volatile Organic Compounds). POM includes organic compounds with more than one benzene ring, and which have a boiling point greater than or equal to 100 degrees centigrade.*
Primary PM2.5:	*PM2.5 that is formed directly from a combustion source, or is otherwise emitted as PM2.5 without having to react with other chemicals, and is not formed from the cooling of hot gases.*
Re-entrained dust:	*Dust kicked up from a roadway surface – considered one of the sources of particulate matter and PM2.5.*

SOA:	*Secondary Organic Aerosol. SOA is formed by the gas-phase photooxidation of hydrocarbons that condense into the aerosol phase – also referred to as "Organic Aerosol".*
Secondary PM2.5:	*PM2.5 that is formed in the atmosphere through reaction, coagulation, or nucleation of chemicals some time after emission from a source.*
SO2:	*Sulfur dioxide.*
SOx:	*Sulfur oxides. These chemicals are responsible for the formation of sulfate (SO4) chemicals in the atmosphere. SO4 is one of the specie groups responsible for secondary PM2.5 formation.*
Sulfates:	*Sulfates are chemicals containing the* $SO4^{2-}$ *group, or can refer to the* $SO4^{2-}$ *ion.*
VOC:	*Volatile Organic Compounds. VOCs are defined as any compound containing carbon that participates in photochemical reactions and is not specifically excluded because it has been shown that the chemical does not contribute to the formation of ozone/smog. POM and PAH are subsets of VOC.*

Evaluating the Contribution of PM2.5 Precursor Gases and Re-entrained Road Emissions to Mobile Source PM2.5 Particulate Matter Emissions

EXECUTIVE SUMMARY

The purpose of this report has been to identify, review, and discuss current scientific literature to provide a consensus on the contribution of PM2.5 precursor compounds from on-road mobile sources. Additionally, we researched the contribution of the re-entrained dust component of on-road emissions to PM2.5 concentrations. The first section of the report consists of an introduction to PM2.5 from on-road sources. In the second section we define the relative magnitudes of PM2.5 formation from primary and secondary PM2.5 from the emissions of on-road vehicles. The third section of the report presents an analysis of the contribution of re-entrained road dust to PM2.5 ambient concentrations.

Five specific questions were addressed in the statement of work for this project effort. The questions and summary answers to these questions are provided here. Detailed information describing the answers to these questions in depth is provided within the body of this report.

Questions:

1. What does the research and data reviewed for this project indicate the percentage and variability (simple differences are acceptable) are for PM2.5 particles in the atmosphere as measured on the PM2.5 monitors? What percentages were formed from PM2.5 precursor NOx and VOC compounds versus those directly emitted?

Answer: The percentage and variability of PM2.5 in the atmosphere vary significantly by location or region within the United States. This is shown in Figure 1-2 of this report, where the PM2.5 concentration and composition of the PM2.5 are shown to be widely different. The highest PM2.5 concentrations were measured in the western United States. The PM2.5 concentration measurements in the continental United States vary between $3.0\mu g/m^3$ and $39.2\mu g/m^3$. (Higher measurements were observed in Mexico).

Based on an analysis of the composition of the PM2.5 measured in the United States, the percentages of the PM2.5 formed by precursor NOx and VOC compounds is quite variable. The portion of PM2.5 comprised of all secondary components (sulfates, nitrates, ammonium, organic carbon) varies anywhere from 30% to 90% of all PM2.5 (see Table 1-2). The percentage of PM2.5 formed from VOC precursors varies from approximately 11% to 41%, and the percentage of PM2.5 formed from NOx precursors varies from approximately 4% to 37%. NOx precursors become particulate nitrates, and VOC precursors become particulate organic carbon. According to these calculations, directly emitted PM2.5 accounts for approximately 10% to 70% of all PM2.5 in the United States.

2. What does the research and data indicate is the percentage and variability of precursor NOx and VOC gases forming PM2.5 particles that are generated by on-road mobile sources?

Answer: The formation of PM2.5 from NOx and VOC gases from on-road mobile sources is not a constant value or conversion factor. Many environmental factors are responsible for the conditions that make it favorable or unfavorable for formation of PM2.5 from these compounds. Studies suggest that on-road emission sources contribute between 26% and 45% of all NOx, and between 16% and 33% of all VOC from sources in the United States. Although based on emission estimates, these values provide an idea of the contribution of on-road mobile sources. Applying this to the ambient measurements in Table 1-2 for NOx gives us a range of approximately 1% to 2% on the low end, and 10% to 18% on the upper end from mobile sources. Of the amounts of NOx and VOC from on-road sources, the formation of PM2.5 from these chemicals varies greatly, and was not able to be conclusively determined from the literature. In general, all mobile sources (including on- and off-road) are thought to contribute approximately 20% of total PM2.5 annual emissions in the United States.

3. What does the research and data indicate is the percentage and variability of re-entrained road dust emissions as a contributor to PM2.5?

Answer: Depending on the method used to estimate the emissions of road dust from on-road vehicle travel, the contribution varies greatly. Emission inventories often use estimated emission rates and vehicle miles traveled to calculate re-entrained road dust emissions. Typically, the emissions calculated using this method are much higher than the emissions calculated using receptor models. From the inventories, it is estimated that re-entrained road dust from paved roads contributes between 3% and 16% of total directly emitted PM2.5, and unpaved roads contribute between 9% and 22% of total directly emitted PM2.5. Estimates from other sources discussed in this report indicate that the total contribution from re-entrained road dust emissions is more likely just a few percent of all PM2.5. On a per-vehicle basis unpaved roads are higher emitters than paved roads, but the traffic volume on paved roads offsets the emission rate difference.

4. What factors, such as geographic region of the country, does the research indicate is associated in the variability of these percentages and what is the level of certainty that the researchers can ascribe to these variabilities?

Answer: Geographic region of the country and seasonal factors play a huge role in the variability of the estimates used to determine the formation of PM2.5 from precursor components. This is due to the significant differences in climate that play a major role in the chemistry involved in PM2.5 formation from precursors. The complex nature of atmospheric chemistry with respect to PM2.5 formation also plays a large role in the uncertainty of PM2.5 formation from precursors. These two factors are tied together since regional differences change the atmospheric chemistry scenario. Note that nitrates are more important in the western United States and sulfates are more important in the east, but sulfates are driven by combustion for power generation rather than transportation.

The variability of the percentages of PM2.5 formed from re-entrained road dust are mostly due to the very different values calculated from emission inventories versus the results from receptor model calculations. Geographic differences are also responsible for the variabilities in PM2.5 from on-road vehicles.

5. Is there general consensus on these questions or is there significant uncertainty among the various research reports?

Answer: There is a general consensus that the formation of PM2.5 from precursor compounds is highly uncertain and varies regionally and seasonally due to weather conditions and other related variables that affect atmospheric chemistry. Contributions from mobile sources are ascertained primarily from evaluating emissions rather than direct attribution at receptors, although receptor models have also been used to infer mobile source contributions to ambient concentrations. However, in most receptor model studies the difference between on-road and non-road contributions is not delineated.

There is not a general consensus on the differences in PM2.5 emission estimates from re-entrained dust. Although, several factors such as PM2.5 transport and deposition rates are in question, emission inventories are still calculated using estimation techniques that lead to much higher values than those derived from receptor models. Recent studies have indicated that current emission rates for fugitive dust sources do not match well with ambient measurements. Studies to look at transport and removal mechanisms for these types of emissions indicate that removal may play a large role in the apparent discrepancy.

Evaluating the Contribution of PM2.5 Precursor Gases and Re-entrained Road Emissions to Mobile Source PM2.5 Particulate Matter Emissions

1. INTRODUCTION

In response to the implementation of the PM2.5 National Ambient Air Quality Standard (NAAQS), States will begin developing State Implementation Plans (SIPs) for those areas designated to be in non-attainment of the standard.

A number of sources have attributed varying contributions from mobile sources to the current PM2.5 ambient concentration levels. PM2.5 emissions from mobile sources are generated from three general processes: 1) it is directly emitted from the tailpipes of cars, trucks and other on-road vehicles, 2) it is re-entrained from materials found on the roadway (typically known as fugitive dust), and 3) it is created by secondary formation from precursor emissions such as sulfur dioxide (SO2), nitrogen oxides (NOx), volatile organic compounds (VOCs) and ammonia (NH3). Items 1 and 2 are generally known as primary emissions of PM2.5. Secondary formation occurs due to chemical reaction in the atmosphere generally downwind some distance from the original emission source. Primary emissions can be solid, liquid or gaseous. Solid or liquid particles that are directly emitted are considered primary as are particles that are formed solely due to cooling after release into the atmosphere (these types of particles are also known as condensibles). Secondary particles are formed exclusively from gases that react in the atmosphere.

Concerning the tailpipe emissions from diesel and gasoline engines, tests have shown that almost all primary particles emitted from these engines are less than 2.0µm in diameter. This means that they are less than 2.5µm, and in the size range of concern regarding PM2.5 NAAQS. In fact, concerning diesel exhaust from mobile sources, 90% of the total number of particles are in a median size range of about 0.02µm. Most of the mass in diesel exhaust is represented by a median particle size of about 0.25µm. These statistics concerning diesel engine emissions refer to diesel particulate matter (DPM), which is generally considered to be primary particulate. Diesel emitted organic gases (DEOG) generally refers to precursor compounds that have not yet formed particulate matter. DEOG components can condense after cooling, and form particulate matter – likely in the size range of <0.1µm. (Baldauf, et. al.)

The terms DPM and DEOG are not well defined, often causing confusion about their intended meanings. We attempted to locate a firm definition of DPM and DEOG, so that these terms would not add confusion to the already fine line that differentiates particulate matter from some gases. Unfortunately, even after researching these definitions it has become clear that the rules associated with use of these terms are ambiguous and inconsistent between agencies and authors. In fact, DPM is generally defined as a complex aggregate of solid and liquid material. Its origin is carbonaceous particles generated in the engine cylinder during combustion. These carbon particles form larger agglomerates (particles formed by nucleation and/or coagulation) and combine with several other, both organic and inorganic, components of diesel exhaust. DPM is divided into three basic fractions: 1. solids (soot); 2. heavy hydrocarbons adsorbed to the carbon; and 3. hydrated sulfuric acid. The composition of DPM depends on the particular engine and its load and speed conditions as well as fuel sulfur content. (Gertler, 2003), (Nett Technologies) No definition of DEOG was located in the literature.

The EPA's list of mobile source air toxics (MSATs) includes DPM and DEOG as constituents. Table 1-1 includes the list of compounds included in the EPA's list of MSATs.

Table 1-1. List of Mobile Source Air Toxics (MSATs)
(EPA; December 2000)

Acetaldehyde	Ethylbenzene	Nickel Compounds
Acrolein	Formaldehyde	POM
Arsenic Compounds	n-Hexane	Styrene
Benzene	Lead Compounds	Toluene
1,3-Butadiene	Manganese Compounds	Xylene
Chromium Compounds	Mercury Compounds	
Dioxins/Furans	MTBE	
DPM & DEOG	Naphthalene	

In order to control those sources contributing to PM2.5 concentrations, emission inventories will need to be developed and associated control programs implemented. The emission inventories (and control strategies) will need to consider how, and to what degree precursor compounds contribute to PM2.5 concentrations.

Figure 1-1. Schematic showing pathways and reactions leading to atmospheric particulate loadings (from figure 3.1 of the Particulate Matter Science for Policy Makers - A NARSTO Assessment February 2003 Part 2 report)

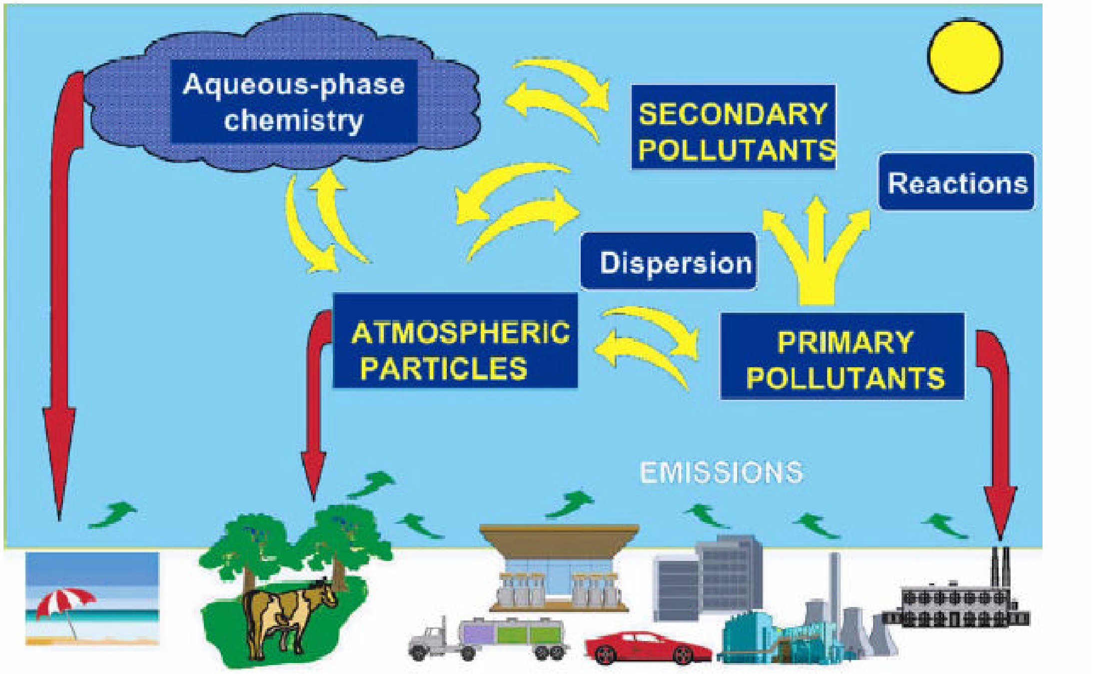
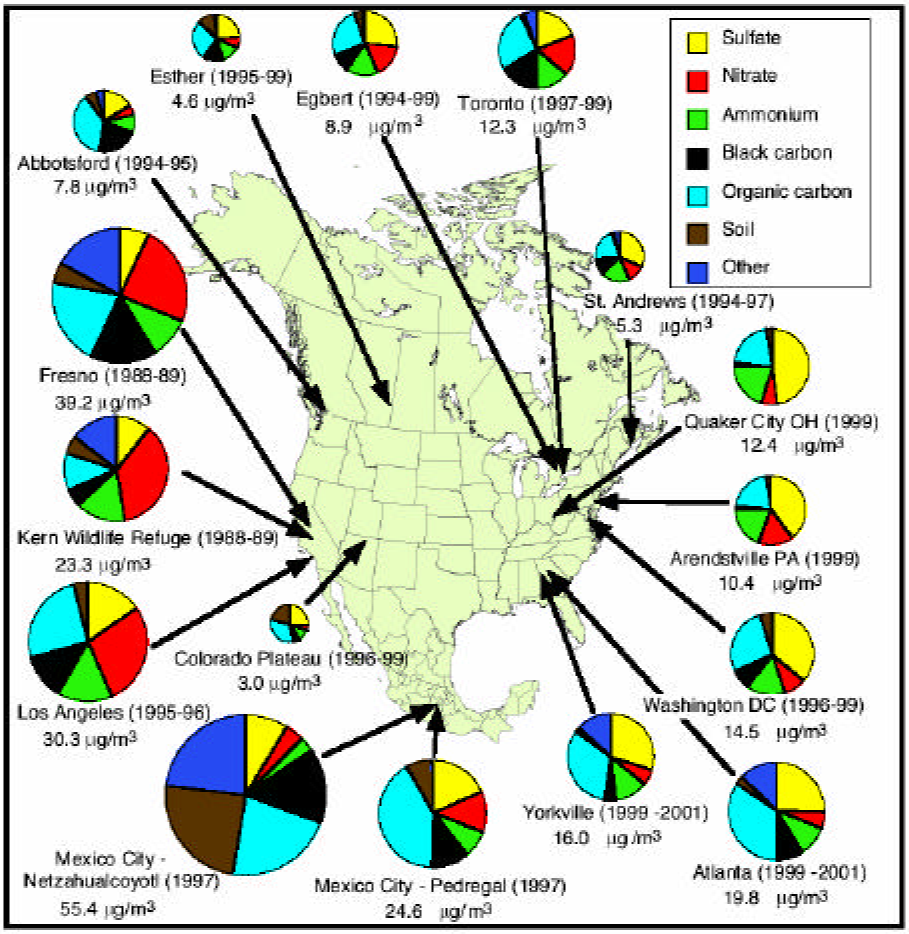


Figure 1-1 shows a schematic representation of the emissions of particulates and precursor emissions and the pathways into the atmosphere and for formation of particles.

However, it is unclear what the contribution of the precursor gases are to PM2.5 nonattainment, and more specifically what the contribution of the on-road mobile sources are to these precursors and to the primary PM2.5 emissions.

The variability in the contribution of both precursor and the various components of primary PM2.5 emissions from all emission sources throughout the U.S. (and parts of Canada and Mexico) is shown in Figure 1-2. This figure clearly indicates that secondary particulates dominate most ambient monitoring stations with ammonium, sulfate and nitrate contributions (resulting from ammonia, SOx, and NOx emissions respectively), at ambient monitors in the U.S. contributing approximately 30-75% of total filter mass, with significantly smaller fractions from directly emitted particles (as represented by the soil, black carbon and other fractions). The secondary component increases further if organic carbon is added to the other secondarily formed components and increases the percentage from 30-75% to approximately 50-90%. This is due to the increase in overall mass resulting from the incorporation of the organic carbon to the secondarily formed components.

Figure 1-2. Composition of PM2.5 at representative urban and rural locations, based on annual averages except Mexico City. (From Figure 6.12 of the Particulate Matter Science for Policy Makers - A NARSTO Assessment Feb. 2003 Part 2 report)



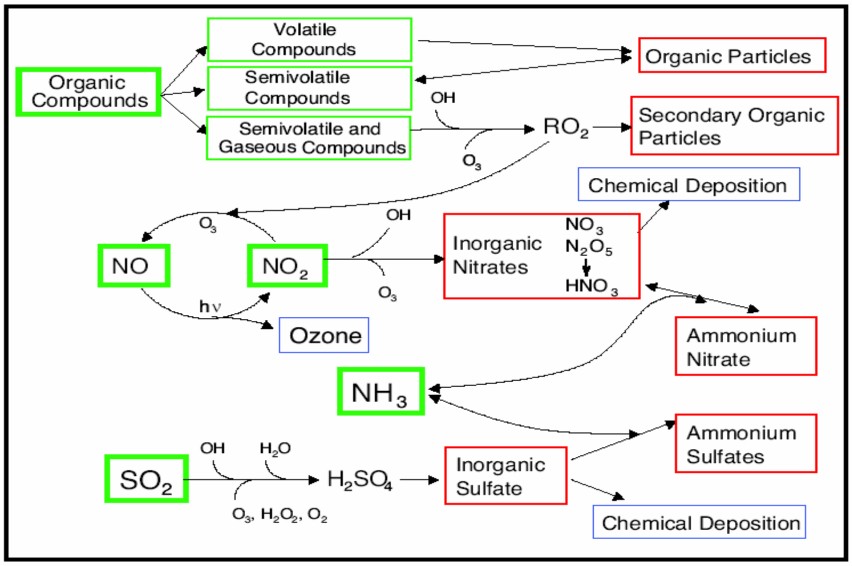
Minimum, maximum and average values for each of the seven species shown in the pie charts in Figure 1-2 are provided in Table 1-2. These concentration values represent ambient concentration values from monitors located in the areas shown on the map. Note that the maximum values represent the maximum value found for each individual species without regard to the other species. Thus the total of the values in the maximum column sums to more than 100 percent.

Table 1-2. Minimum, maximum and average contributions of major species to ambient PM2.5 concentration levels.

PM2.5 Component	Min.	Max.	Avg.
Sulfate (secondary)	7%	47%	24%
Nitrates (secondary)	4%	37%	13%
Ammonium (secondary)	3%	20%	13%
Black Carbon (primary)	2%	22%	10%
Organic Carbon (secondary)	11%	41%	27%
Soil (primary)	2%	25%	7%
Other (primary/secondary)	0%	23%	6%

The PM2.5 components listed in Table 1-2 represent the major components of PM2.5, and thus the precursors that form secondary PM2.5 through the reactive process. Black carbon, which is essentially soot, and soil are the main sources of primary PM2.5. The other components that are listed as secondary components of PM2.5 are not emitted from mobile sources as primary PM2.5, but contribute to PM2.5 through chemical reaction, coagulation and other mechanisms discussed in this report. As indicated previously, secondarily formed PM2.5 particles typically are derived from the formation of either ammonium sulfate or ammonium nitrate, through the chemical reaction of ammonia and SO2 (in the presence of water) or ammonia and NOx (again in the presence of water). In addition, secondary particles are developed via the chemical reaction of ozone and organic gases (organic carbon) in the atmosphere. Figure 1-3 shows the primary formation mechanisms for secondary particle formation in the atmosphere. Ammonium nitrate and ammonium sulfate formation are shown in the lower right of the figure while secondary particle formation from organic compounds is shown at the top. Other ancillary chemical reactions associated with ozone and PM are shown in the middle of the diagram.

Figure 1-3. Chemical links between the ozone and PM formation processes. The major precursors are shown in green squares. The organic compounds can be gaseous (always in the gas phase), non-volatile (always in the condensed phase), and semivolatile (partitioned between the gas and condensed phases). (From Figure 3.16 of the Particulate Matter Science for Policy Makers - A NARSTO Assessment February 2003 Part 2 report)



Attribution Methods

Given the variability in the contributions to ambient concentrations of PM2.5 from all sources, how are on-road mobile source contributions attributed? Attribution to specific sources is usually accomplished in one of three ways.

Source-specific Methods

Direct emission contributions can be developed using a differential method where the concentrations are measured both upwind and downwind of the source and the difference in concentrations is then attributed to the source (typically using a dispersion model). The main drawback to this approach is that 1) it typically only captures and identifies direct particle emissions (rather than secondary particle emissions) since the source normally has to be close to the monitor in order to eliminate other potentially interfering sources and thus, time for reactions is insufficient, and 2) it can’t typically be used to perform source attribution for regional sources again due to the requirement that the source be close to the monitor.

Receptor Based Models

The second method used to attribute sources to monitored ambient concentrations is receptor modeling. Typically the models used are either mass balance models or regression type models. The most popular model used for this type of attribution is the Chemical Mass Balance (CMB) model. The CMB model uses known information about the chemistry of the source to solve a system of equations that attributes measured species concentrations on the ambient filters to the various sources. The resiliency of the CMB model depends primarily on finding chemical source signatures that provide "marker" elements (or compounds) that help specifically identify source types. Regression type models use similar methods but typically use emission inventories (or other measures of emission source strengths) to allocate the measured concentrations to the sources.

One of the biggest drawbacks to the CMB model is that it can suffer from "co-linearity" issues. When several sources have very similar chemical signatures, it is frequently impossible to completely allocate the source contributions to the individual components with similar chemical speciation information. For example, many geologic sources (including some of interest in this review – paved and unpaved roads) are extremely difficult to separate chemically from other geologic materials such as a soil signature profile. Thus frequently a soil or geologic signature is input into the model but it truly represents all geologic sources including soil, paved and unpaved, cattle feedlot, and other agricultural emissions. Similarly, since they burn the same or similar fuels and since the combustion processes are similar, attribution using CMB for directly emitted tailpipe emissions from on-road mobile sources is complicated because of non-road sources.

Inventory Attribution

The third method of allocation (and an integral component of most regression type model attributions) is to use emission inventories. For this type of attribution, the concentrations of interest are measured by the ambient monitors and then the sources that contribute to these components are allocated out to the sources based on the fraction of the total emissions of each component attributed to each source. The major drawback to using emissions based attribution is that there is frequently a large uncertainty in the methods used to estimate emissions. In addition, the uncertainty in the methods used to estimate emissions from various sources varies from source type to source type. For example, emission estimates from utility sources that originate from continuous emissions monitoring (CEM) are highly certain, while estimates from sources like unpaved roads or wildfires are highly uncertain.

Inventory and receptor models are frequently used together generally to try and improve the emission inventory. Measured concentrations are attributed using a receptor model (like CMB) to ascertain the contributions from various sources. These attributions are then compared to determine whether they are similar in value to attributions made using the emission inventory. If they are then the inventory is regarded as being generally reflective of the emission sources. If it isn't then methods used for estimating a particular sector or source type are evaluated for improvements. This type of comparison is one of the reasons that the transport fraction (discussed later in this document) was developed for fugitive dust sources. Inventories were showing that fugitive dust sources were contributing 70 percent or more to primary particulate emissions but receptor models applied to ambient monitoring values were showing a considerably smaller contribution (see Figure 1-2 for example), clearly indicating that there was a disconnect between the inventory and the measured concentrations found in atmosphere.

Table 1-3 provides some examples of the different types of models/techniques that are used to generate estimates of the contributions of mobile (or other) sources.

Table 1-3. Methods/techniques used to estimate the contributions of various sources to the atmosphere.

Model/Technique	Application	Information Developed by Method	Model of Type	Comments
Source Model	Used to estimate directly emitted material from the source	Typically emission factors or emission rates	Upwind/downwind; exposure profiling	This type of method can only typically be used close to the source and thus is hard to use to estimate regional emission rates
Receptor Model	Used to estimate the contribution of various sources to measured ambient concentrations.	Percentage contribution to measured concentration	CMB, Principal Component Analysis (PCA), Positive Matrix Factorization (PMF)	Frequently need to have knowledge of the source composition. May not cover all sources due to similarities between sources (similar sources not resolved). Can be used over wide regions to determine source contributions.
Emission Inventories	Used to estimate the quantity of pollutants emitted into the atmosphere	Total emissions for some time period	Top down; bottom up	Inventories vary in their accuracy depending upon the source type.

Geographic Variability

In addition to the uncertainty associated with attributing sources to ambient concentrations, the contributions from different sources vary both geographically and temporally. The pie charts in Figure 1-2 show that the percentage of each component is highly variable geographically. One important aspect to notice in Figure 1-2 is that nitrate is significantly more important in the western U.S. than in the east while sulfate is higher in the eastern U.S. Both of these constituents are associated with ammonia as either ammonium nitrate or ammonium sulfate.

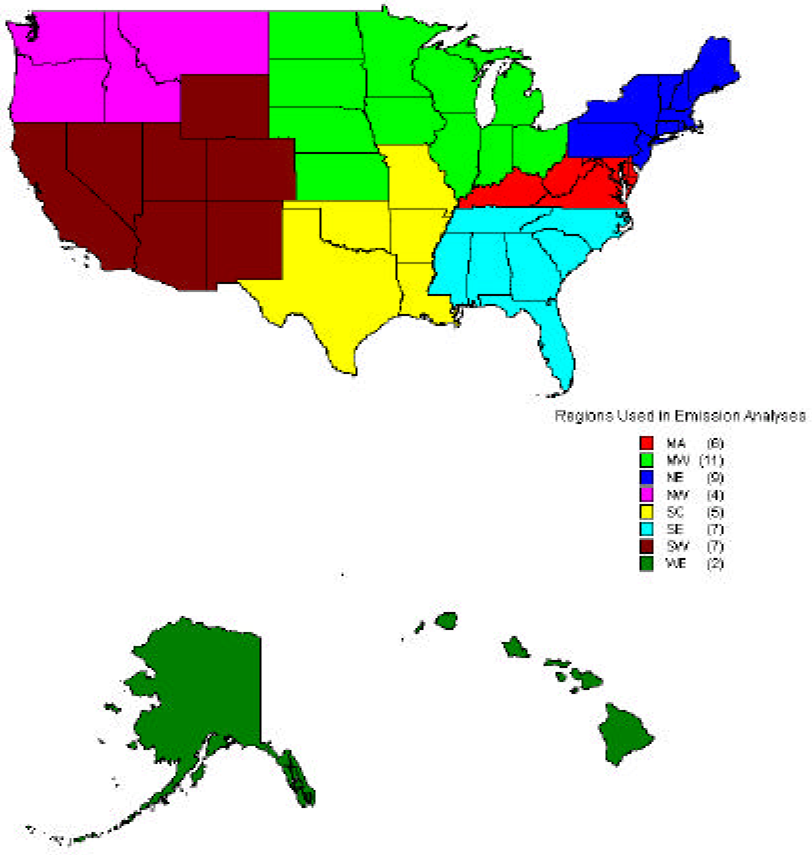
In performing the evaluations for this report concerning emissions of the various components that contribute to both primary and secondary PM2.5, we have determined emission contributions for a number of regions of the country. Figure 1-4 shows the region that each State was assigned to for this report. The regions are abbreviated as follows: mid-atlantic (MA); midwest (MW); northeast (NE); northwest (NW); south central (SC); southeast (SE); southwest (SW); west (WE).

Although not shown in this report, changes in these constituents also vary with time. For example, elemental carbon (EC) may comprise a large portion of ambient PM2.5 concentrations in areas where woodstoves are used frequently. Since this activity tends to be during the fall and winter, the elemental carbon component of PM2.5 would be significantly higher during those seasons.

Work on this project was comprised of two primary tasks which are covered in the next two sections of this report. Section 2 involves the investigation of studies that were undertaken to examine the influence of PM2.5 precursors in PM2.5 particle formation for on-road sources.

Section 3 presents an examination of reports concerning the re-entrained dust component of PM2.5 and the role that on-road mobile sources play in that component.

Figure 1-4. Regional Map of the United States



2. THE INFLUENCE OF PRECURSOR COMPOUNDS IN PM2.5 PARTICLE FORMATION

PM2.5 emissions resulting from the exhaust of on-road mobile sources come from two mechanisms. First, there are emissions of PM2.5 particles directly from the tailpipe of on-road mobile sources. These emissions can be visible as white or black smoke if they are in large enough quantities, although all on-road combustion engines emit a certain amount of PM2.5. Diesel vehicles are known for emitting black smoke, especially under a significant load, and gasoline vehicles that are out of repair can emit visible quantities of white smoke. Secondly, and more difficult to quantify, are the emissions from on-road vehicles that can be considered PM2.5 precursors. These precursors are the chemicals that react to form particles after exiting through the exhaust stream of on-road mobile sources in a gas-to-particle conversion process. (Dominguez et. al., 2001). Precursor compounds can be generally characterized by one of several groups of chemicals such as volatile organic compounds (VOC), nitrogen oxides (NOx), sulfur oxides (SOx), or ammonia (NH3). One reason that it is difficult to quantify contributors to PM2.5 is due to the fact that many of the products formed can fluctuate between the particulate and vapor states depending on conditions. The degree to which these precursors react to form PM2.5 depends on environmental conditions and various drivers for complex chemical reactions which will be discussed in this report.

In order to obtain an idea of the significance of the various PM2.5 precursors, a broad literature search was conducted to locate information from recent studies of PM2.5 formation. The studies discussed in this section of the report represent available literature on PM2.5 formation from emissions of precursor compounds from on-road emission sources. This section covers the species involved, reaction rates of the various species, and regional differences in the formation of PM2.5 from these precursors.

The time required for the PM2.5 precursors to react and form PM2.5 is highly variable, and depends on the specific precursor chemical, temperature, and humidity. Reaction times for sulfate precursors show that oxidation of sulfate occurs at an average rate of 0.1 to 1 percent of sulfate per hour. Nitrates continuously change between the gas and condensed phases in the atmosphere, so a reaction time is nearly impossible to quantify. The equilibrium of the reactions shifts depending on temperature, humidity, and other compounds present in the atmosphere. The formation of PM2.5 from organic compounds depends on four factors: its atmospheric abundance, its chemical activity, the availability of oxidants, and the volatility of the products. All these factors contribute to reaction times, but volatility plays a predominant role, since highly volatile chemicals such as alkanes and alkenes with less than six carbon atoms are unlikely to form PM2.5. Larger alkenes and alkanes are able to react to form PM2.5, or condense on existing particles.

A review of recent technical papers included in environmental journals, EPA publications, information published on the internet, and pre-print versions of some literature articles are condensed in this report in an effort to evaluate the degree to which the direct and precursor PM2.5 emissions contribute to the on-road PM2.5 emissions. Our review of the technical literature suggests that there are regional differences in the source of PM2.5 depending on the number of on-road mobile and other sources, as well as the atmospheric conditions present in different parts of the country. Assessments of mobile source contribution to the PM2.5 problem is also highly variable depending on the methods used to calculate the contributions. The formation of PM2.5 from precursors is heavily dependent on the availability of a variety of chemical components in the atmosphere. Different parts of the United States are known for contributing different chemical components toward the formation of PM2.5 from precursors. Mobile and industry sources are largely responsible for precursor emissions of carbon, NOx, SOx, and VOC from fuel combustion, while rural areas contribute NH3 from agricultural sources. The conditions that influence the formation of PM2.5 from organic aerosol are also seasonal, with significant differences in the formation mechanisms of PM2.5 in the winter vs. summer.

Particles in the atmosphere originate either by direct emission of the particle from a source, or formation by nucleation from the gas phase. Nucleation occurs when inorganic or organic vapors begin to form particles by collecting around an existing solid particle or nucleus. The particles that are formed secondarily by nucleation can originate in different levels of the atmosphere, and be created by a variety of chemical and physical mechanisms. The life cycle of particles in the atmosphere begins with emission from a source, or formation by nucleation; the particles are changed further by processes such as dilution, dispersion, coagulation, and chemical reaction. The term "coagulation" is used to describe the cooling of exhaust gases resulting in transformation of some exhaust vapors into particles. Some coagulation usually occurs very quickly near the source of the emission due to the rapid cooling of combustion exhaust. The process of coagulation slows rapidly as the particles move away from the source of the emission. Coagulation can result in the settling of some particulate matter, thereby removing those particles from the atmosphere. Particles that are not removed by coagulation eventually interact with other chemical vapors in the atmosphere such as sulfuric acid (H2SO4), organics, nitric acid (HNO3), and ammonia (NH3). Continued reactions cause the particles to grow in size. Atmospheric conditions such as relative humidity can also have a bearing on particle size and reactions that occur. If a large portion of a particle consists of water, the dissolution of SO2 can occur forming SO4, which then joins to the particle (typically as ammonium sulfate). Eventually, coagulation results in the formation of a particle that is too large to remain airborne, and resettles to earth. This is one of the deposition mechanisms that acts to regulate the concentration of PM in the atmosphere. The results of the recent literature search used to assemble this section of the report focuses on estimating the contribution of precursor gases, particularly from mobile sources toward PM2.5 non-attainment. (NARSTO report, 2003)

Formation of PM2.5 from VOC Precursors

The volatile organic gases in secondary organic aerosol (SOA) are oxidized by species such as the hydroxyl radical (OH), ozone (O3), and nitrate (NO3). After oxidation of the VOC, some of the oxidation products have low volatilities and condense on available particles becoming part of the PM. SOA formation demands that the oxidation products must have vapor pressures low enough for them to be able to partition into the vapor phase. (Odum et. al., 1997) Several factors determine whether the oxidized VOC will result in production of SOA: atmospheric abundance, chemical reactivity, oxidant availability, and product volatility. Most smaller VOCs (e.g. VOCs with six or less carbons), do not form aerosols due to the high vapor pressure of their products. Diesel engines are relatively low VOC emitters, but do emit polyaromatic hydrocarbons (PAH), and other straight chain hydrocarbons containing more than 10 carbon atoms. PAHs are considered to be a subset of the category of chemicals defined as VOCs, as well as a subset of the broad term polycyclic organic matter, (POM). POM includes organic compounds with more than one benzene ring, and which have a boiling point greater than or equal to 100 degrees centigrade. VOCs from the aromatic group are the most significant contributor to SOA from anthropogenic sources. In a 1999 report on SOA resulting from traffic emissions in Athens, Greece, it was determined that m-xylene and toluene were responsible for producing approximately 50% of the organic aerosol. The main aerosol product resulting from reaction of these components was expected to be nitrophenols. The NARSTO report (2003) suggests that toluene, xylenes, and trimethylbenzenes emitted by mobile and industrial sources are responsible for 50-70% of SOA. The same report goes on to explain that the contribution of SOA to the organic particulate matter varied from 20-80% during the same day. (Grosjean, et. al. 1989), (NARSTO report, 2003), (Kourtidis et. al., 1999)

A study completed in the Baltimore, MD area used the UNMIX receptor model to apportion ambient samples of VOC collected via a PAMS network site over a period of three summers. The results of that study showed that on-road vehicle exhaust contributed approximately 29% of the VOC in the area, although there were other factors to be considered. For instance, it was discovered that during high ozone days, the contribution of VOC from biogenic sources doubled, whereas the contribution from anthropogenic sources was not significantly different. This difference was attributed to the generally higher temperatures on high ozone days, causing the release of additional VOC compounds from biogenic sources (Choi, et. al., 2003). Although the focus of that study was aimed at analyzing sources of VOC to guide ozone reduction strategies, the VOC measurements can be considered valid in evaluating the contribution of mobile sources to SOA and PM2.5.

Formation of PM2.5 from NOx and SOx Precursors

The results from the Northern Front Range Air Quality Study, (NFRAQS) in Colorado (1998) showed that the majority of particulate ammonium nitrate (NH4NO3) results from NOx emissions from mobile sources. The percentage of PM2.5 made up of NH4NO3 was much less in the summer than in the winter, because the NH4NO3 evaporates at warmer temperatures. Additionally, it was pointed out that a reduction in NOx emissions would have only a small effect on the production of NH4NO3 due to the chemical mechanism equilibriums that result in formation (NFRAQS, 1998).

NOx emissions from combustion sources are comprised mostly of nitric oxide (NO), and must be oxidized before becoming particulate nitrate. SOx emissions are mostly gas-phase sulfur dioxide (SO2), and also must be oxidized to become particulate sulfate. The amount and chemical mechanism used in formation of PM2.5 by the NOx and SOx emissions depends largely on atmospheric conditions. Formation of PM2.5 from NOx and SOx in the winter time is limited by the presence of atmospheric oxidants and water vapor. NOx must be converted to nitric acid prior to reaction with other chemicals to form PM2.5, and the atmosphere is not favorable for formation of nitric acid in the winter months in most areas of the United States. NH3, on the other hand, can participate directly to form PM2.5 as ammonium nitrate (NH4NO3) in the winter months, while this reaction is reversed by higher temperatures in the summer months. NH3 can also react to produce ammonium sulfate $[(NH4)_2SO4]$ in the winter months. (NFRAQS, 1998). This would suggest that mobile sources of NOx emissions (whether on-road or off-road), would contribute more heavily towards PM2.5 formation during the summer and in warmer winter climates such as those found in the southern United States. Conversely, emissions of NH3 from agricultural and other sources would contribute to PM2.5 formation during the winter months when mobile source emissions are not as active in PM2.5 formation.

The most significant PM2.5 precursors that are reported by the EPA through the National Emissions Inventory (NEI) are VOC, NOx, SO2, and NH3. Although VOC actually refers to any organic compound not specifically exempted due to extremely low atmospheric reactivity, the subset of VOCs that are aromatic organics and organic compounds with more than six carbons are mostly responsible for formation of SOA. Since this subset of VOC is not tracked by the EPA, it is difficult to determine exactly how much of the VOC from various sources results in the formation of SOA. Exhaust emission profiles from gasoline and diesel engines offer some clues toward making this estimation. NOx emissions from vehicles are a significant PM2.5 precursor component of on-road vehicle exhaust. SO2 and NH3 precursor compounds play a significant role in PM2.5 formation, but on-road mobile sources are only responsible for a small fraction of emissions of these compounds. Table 2-1 shows reported estimates of precursor emissions from eleven categories of emission sources from the NEI. The relative PM2.5 precursor contributions from these source categories can easily be compared in the table and charts that follow.

Table 2-1. Tons of Primary PM2.5 and PM2.5 Precursors Emitted in the US in 1999
Source: EPA 1999 NEI version 2

Emission Source	VOC (*tons*)	NOx (*tons*)	SO2 (*tons*)	NH3 (*tons*)	PM25-PRIMARY (*tons*)
Stationary Source Fuel Combustion	1,447,093	9,586,125	15,513,970	74,088	1,040,590
Industrial	1,266,570	781,227	1,313,789	155,106	447,356
Solv/Store/Waste/Misc.	8,235,940	541,635	51,730	98,831	515,180
Non-road Mobile	2,829,261	4,417,707	444,302	35,825	318,398
On-road Mobile	5,612,344	8,347,746	300,093	263,776	184,390
Ag. Crops	0	0	0	723,990	871,027
Agriculture Livestock	0	0	0	3,585,403	86,163
Fires	0	0	0	0	1,196,301
Paved	0	0	0	0	628,863
Unpaved	0	0	0	0	1,097,294
Other Fugitive	0	0	0	0	525,466
TOTAL	**19,391,208**	**23,674,440**	**17,623,884**	**627,626**	**2,505,914**

As shown in the table above, the emissions from paved and unpaved roads make up the largest source of *primary* PM2.5 emissions in the United States. However, on-road mobile sources contribute significant amounts of PM2.5 precursor VOC and NOx emissions as well, making up approximately 30 and 35% of the totals respectively. On-road mobile sources contribute to SO2 emissions, but on a much smaller scale compared to stationary source fuel combustion categories. Likewise, on-road mobile sources contribute to NH3 emissions, but on a much smaller scale compared to agricultural sources of NH3. Although there is some regional variation concerning the contribution of these sources to the total emissions of PM2.5 precursors, the variation is relatively small. Regionally, within the United States, on-road mobile source contributions of VOC are between 16% in the west, and 33% in the southwest, and contributions of NOx are between 26% in the west and 45% in the northeast. Table 2-2 shows the regional contributions of VOC and NOx emissions in 1999.

Table 2-2. Regional Percentage Contributions of VOC and NOx From All Sources
Source: EPA 1999 NEI version 2

Emission Source	MA		MW		NE		NW		SC		SE		SW		WE	
	VOC (%)	NOx (%)	VOC (%)	NOx (%)	VOC (%)	NOx (%)	VOC (%)	NOx (%)	VOC (%)	NOx (%)	VOC (%)	NOx (%)	VOC (%)	NOx (%)	VOC (%)	NOx (%)
Stationary Source Fuel Combustion	14	52	7	45	10	34	4	19	8	44	6	41	5	32	4	26
Industrial	7	3	5	3	4	3	4	2	14	4	8	3	4	3	0	3
Solv/Store/ Waste/Misc.	37	1	47	2	40	2	62	14	35	1	43	2	37	2	67	18
Non-road Mobile	12	13	15	19	16	16	11	25	12	20	13	16	20	25	13	27
On-road Mobile	30	31	26	32	30	45	19	41	31	31	30	38	33	37	16	26
TOTAL	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**

In a Journal of Air and Waste Management Association report it is estimated that a range of 10 to 65 percent of all PM2.5 in the United States consists of carbonaceous material directly emitted as primary PM2.5, or formed in the atmosphere from precursor components. Carbonaceous aerosol is composed of elemental carbon (EC) and organic carbon (OC) chemical compounds, of which the EC is essentially graphite material emitted as primary PM, and the OC is one of a large group of compounds (VOC), that can be primary PM, or form PM through reaction in the atmosphere. In a study of the "carbon" emission inventory for Pittsburgh, PA in 1995, it was calculated that on-road mobile sources contributed approximately 13% of the total *primary* OC and 32% of the total *primary* EC. The contribution of mobile sources toward the production of PM2.5 from *secondary* mechanisms of PM2.5 was not quantified for the Pittsburgh area in that paper, but overall it was calculated that secondary organic aerosol (SOA) contributed between 10% and 35% to the total mass of PM2.5 for the area. Additionally, the SOA contribution to PM2.5 is also quite seasonal, with the SOA reacting to form PM2.5 at a rate of 50% during the summer and close to 0% during the winter. This difference is due to the same conditions that influence the formation of tropospheric ozone in the summer. In central and southern California, studies have shown that SOA is an important contributor to the organic PM2.5 concentration, with SOA contributing between 15% and 40% of the total annual OC. The seasonal distribution of SOA in this area shows that the contributions are about 60% in the summer and 20% in the winter. (Cabada et. al., 2002).

NFRAQS (1998) estimated that the most important sources or contributors to PM2.5 in the study area (Colorado) were gasoline vehicle and engine exhaust and diesel vehicle and engine exhaust at 28% and 10% of the total respectively. The NFRAQS study did not differentiate between on-road and non-road mobile source emissions, so the estimates from that report refer to the emissions from both types of mobile sources. Table 2-1 of this report shows that VOC and NOx emissions from on-road mobile sources are approximately twice the amount from non-road sources on a national basis. It can therefore be estimated that the percentage contribution from on-road mobile sources makes up about two thirds of the above NFRAQS estimates. Of the PM from these mobile sources, it was estimated that 75% of the *primary* PM was produced by gasoline-powered vehicles, with the remaining 25% coming from diesel vehicles. This would seem to indicate that gasoline powered vehicles emit more primary PM. In reality, however, diesel vehicles were only responsible for five percent of the local VMT, so the emissions per vehicle were much higher than the gasoline vehicles. Additionally, high-emitting and smoking gasoline vehicles which comprise a very small fraction of all gasoline vehicles were responsible for about half of the PM2.5 emissions from gasoline vehicles.

The EPA's National Emission Inventory (NEI) shows that on a national basis, total mobile source PM2.5 emissions account for about 20% of total PM2.5 from anthropogenic sources. (Baldauf, et. al.) The individual contributions of gasoline vs. diesel vehicles to PM2.5 is highly variable depending on region and further complicated by the uncertainty of the calculations used to apportion emissions to various sources. Table 2-3 demonstrates the variability of the results from 17 source apportionment studies conducted in different locations in the U.S. The percent contributions of gasoline and diesel mobile sources (on- and non-road), together with other significant contributors to PM2.5 are included in the table. Several of the studies note a particular season of analysis. It is apparent from Table 2-3 that mobile sources are responsible for the largest percent contribution towards PM2.5 concentration. Another interesting point from Table 2-3 is that the relative contributions of diesel and gasoline mobile sources are not consistent. Six of the studies show that diesel engines contribute significantly more towards PM2.5, but four of the studies show that gasoline engines contribute more. The other seven studies did not differentiate between diesel and gasoline engine emissions. The PM2.5 concentration is located in the rightmost column of Table 2-3, and shows a large degree of variability as well. The standard for PM2.5 is less than 65µg/m^3 in a 24-hour period and less than 15µg/m^3 annual average concentration.

Table 2-3. Source Apportionment Studies Investigating Mobile Source Contributions to PM2.5 Emissions
Source: Baldauf et. al.

Sampling Location	Time Period	Percent Contribution								PM2.5 Concentration *($\mu g/m^3$)*
		Diesel	**Gasoline**	**Total Mobile Sources**	**Road Dust/Soil**	**Biomass Burning**	**Secondary Sulfate**	**Secondary Nitrate**	**Misc. Sources**	
Pasadena, CA (Schauer, 1996)	1982	18.8	5.7	24.5	12.4	9.6	20.9	7.4	24.1	28.2
Downtown, LA (Schauer, 1996)	1982	35.7	6.5	42.2	11.1	5.8	20.3	9.2	18.9	32.5
West LA (Schauer, 1996)	1982	18.0	5.7	23.7	12.2	11.0	24.1	7.8	23.3	24.5
Rubidoux, CA (Schauer, 1996)	1982	12.8	0.7	13.5	13.1	1.2	13.8	24.7	21.6	42.1
Bakersfield, CA (Schauer, 2000)	1995	9.5	3.5	13.0	1.5	16.9	5.0	29.2	25.8	53.8
Fresno, CA (Schauer, 2000)	1995	9.7	2.5	12.2	1.8	49.5	3.5	25.7	19.3	65.9
Sacramento, CA (Motallebi, 1999)	Winter, 1991-96	---	---	24.5	1.2	18.1	4.5	36.6	---	39.5
Bakersfield, CA (Magliano, 1998)	Winter, 1996	---	---	16	<3	20	7	34	---	52
Fresno, CA (Magliano, 1998)	Winter, 1996	---	---	13	<3	19	5	32	---	63
Philadelphia, PA (Dzubay, 1988)	Summer, 1982	---	---	8.5	4.4	---	81.9	---	4.5	27.0
Camden, NJ (Dzubay, 1988)	Summer, 1982	---	---	9.2	3.2	---	81.3	0.4	5.7	28.3
Clarksboro, NJ (Dzubay, 1988)	Summer, 1982	---	---	5.8	2.7	---	84.6	---	2.7	26.0
Welby, CO (Lawson, 1998)	Winter, 1997	10	28	38	16	5	10	24	6	No data
Brighton, CO (Lawson, 1998)	Winter, 1997	10	26	36	11	2	15	32	4	No data
Reno, NV (Gillies, 2000)	Summer, 1998	---	---	68	14.5	4	11	2	0.6	7.8
Phoenix, AZ (Ramadan, 2000)	Summer, 1995-98	10.9	36.2	47.1	1.8	15.0	---	---	36.0	8.3
Phoenix, AZ (Ramadan, 2000	Winter, 1995-98	14.5	38.9	53.4	1.1	8.9	---	---	36.8	13.8

In another study using the UNMIX receptor model, PM2.5 aerosol was apportioned to determine the largest sources of PM2.5 in the Phoenix, AZ area. Ambient data from a three year period beginning in 1995 was used in the analysis. The results from that study showed that gasoline engines were responsible for 33% of the PM2.5 emissions on an annual basis. This value reflects the gasoline engine emissions which make up 42% of the total PM2.5 emissions during the winter, and 20% of the total PM2.5 emissions during the summer. During the summer, PM2.5 emissions in Phoenix are only approximately 62% of the winter values. It was also determined that diesel engines contributed approximately 16% to the overall PM2.5 emissions, with only a slight seasonal variation. (Lewis et. al., 2003)

Based on the research that was collected for this report, the contribution of PM2.5 precursors from on-road and off-road mobile sources is highly variable depending on several factors that have been discussed in this chapter. Regional climate and other atmospheric influences have a significant bearing on the formation of PM2.5 from precursor chemicals. Additionally, due to the difficulty in separating primary PM2.5 from secondary PM2.5 using sampling techniques, the contribution of precursors toward PM2.5 concentrations remains somewhat inconclusive. A review of the studies covered in this chapter of the report shows that on-road mobile sources contribute significant amounts of VOC and NOx precursors to the atmosphere, and that these precursor compounds result in the formation of PM2.5 under the right conditions. The VOC emitted from on-road mobile sources is approximately 30% of the national total, and the NOx emissions from on-road mobile sources are approximately 35% of the national total. The conditions that give way to the formation of PM2.5 from precursor components tend to be warm temperatures close to metropolitan areas where NOx and VOC are both plentiful in the atmosphere. Although other chemicals contribute to PM2.5 formation these two components are the main precursor emissions from on-road mobile sources.

3. RE-ENTRAINED DUST COMPONENT OF PM2.5

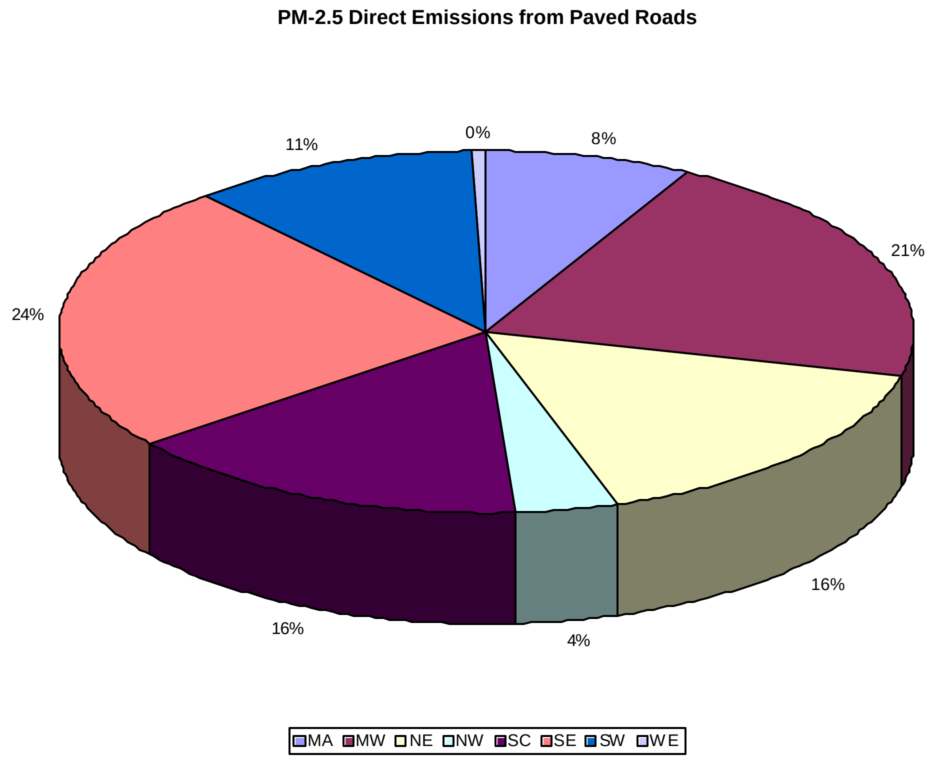
For our evaluation of paved and unpaved road emissions we looked at both national emission levels as well as the geographic variability in emissions from the different regions of the country (see Figure 1-4, Introduction for State-by-State regional assignments). Table 3-1 shows 1999 emissions from major source categories for both PM precursors as well as primary PM10 and PM2.5 (fugitive and non-fugitive). In addition, the contribution from paved and unpaved road fugitive emissions is shown separately at the bottom of the table. Emissions directly associated with injection of surface materials from paved and unpaved roads only contribute to primary emissions of PM10 and PM2.5. The tailpipe, brake and tire wear emissions from vehicles using these roads are reflected in the highway vehicle entry in Table 3-1.

Table 3-1. 1999 National emissions of particulate precursors and primary particulates from various sources (All values in tons/year. Data Source 1999 NEI version 2)

SOURCE CATEGORY	VOC	NOx	SO2	NH3	PM10-PRIMARY	PM25-PRIMARY
Fuel Comb. Elec. Util.	55,435	5,664,757	12,531,092	16,272	265,300	169,734
Fuel Comb. Industrial	175,404	2,850,530	2,404,596	48,568	342,143	266,294
Fuel Comb. Other	1,216,254	1,070,838	578,282	9,248	625,222	604,561
Chem. & Allied Product Mfg.	292,343	112,280	312,824	94,873	51,455	43,866
Metals Processing	65,821	86,961	327,083	2,129	157,605	130,776
Petroleum & Related Inds.	413,585	124,666	302,549	10,218	37,882	25,751
Other Industrial Processes	494,820	457,319	371,332	47,886	371,627	246,963
Solvent Utilization	4,996,335	3,532	777	321	4,429	111
Storage & Transport	1,216,822	9,751	5,440	4,596	81,165	37,994
Waste Disposal & Recycling	525,456	161,043	33,229	84,911	475,214	448,660
Highway Vehicles	5,612,344	8,347,746	300,093	263,776	241,100	184,390
Off-Highway	2,829,261	4,417,707	444,302	35,825	347,712	318,398
Miscellaneous	1,497,327	367,309	12,284	4,315,189	8,908,924	2,688,554
Unpaved Roads	0	0	0	0	7,290,847	1,097,294
Paved Roads	0	0	0	0	2,511,293	628,863

Figure 3-1 shows the percentage of total national paved road PM2.5 fugitive emissions from each region in the county. This figure shows that almost a quarter of the national PM2.5 emissions for re-entrained fugitive dust from paved roads originate in the southeastern U.S. An additional 20 percent comes from the Midwest, with an additional 16 percent from both the northeast and south-central regions.

Figure 3-1. Regional contributions to national PM2.5 emissions from paved road re-entrainment.



For paved roads, the re-entrained dust is typically generated from pavement wear, tire fragments, or loose material that has either deposited on the road surface from windblown sources, was placed there during road sanding and salting operations for snow and ice removal, or was tracked onto the roadway from unpaved areas (e.g., construction sites). In general terms, re-entrained particulate emissions from paved roads originate from, and result in the depletion of, the loose material present on the surface (i.e., the surface loading). In turn, that surface loading is continuously replenished by other sources. In the absence of continuous addition of fresh material (through localized trackout or application of antiskid material), paved road surface loading should reach an equilibrium value in which the amount of material re-entrained matches the amount replenished. The equilibrium surface loading value depends upon numerous factors. It is believed that the most important factors are: mean speed of vehicles traveling the road; the average daily traffic volume (ADTV); the number of lanes and ADTV per lane; the fraction of heavy vehicles (buses and trucks); and the presence/absence of curbs, storm sewers and parking lanes.

While this section focuses on paved roads, we also present limited information on unpaved roads.

Assessment Methods

In order to assess the re-entrained dust component of on-road mobile sources to PM2.5 concentrations we examined information on three aspects of re-entrained (fugitive) on-road mobile source PM2.5. First, we looked at data from the U.S. Environmental Protection Agency (EPA)'s National Emission Inventory and other more local and regional inventory efforts. Second, we evaluated emission rates and alternative emission values from literature sources. Finally we looked at receptor modeling studies that have been performed and used to assess the contribution of paved and unpaved roads to ambient monitoring levels.

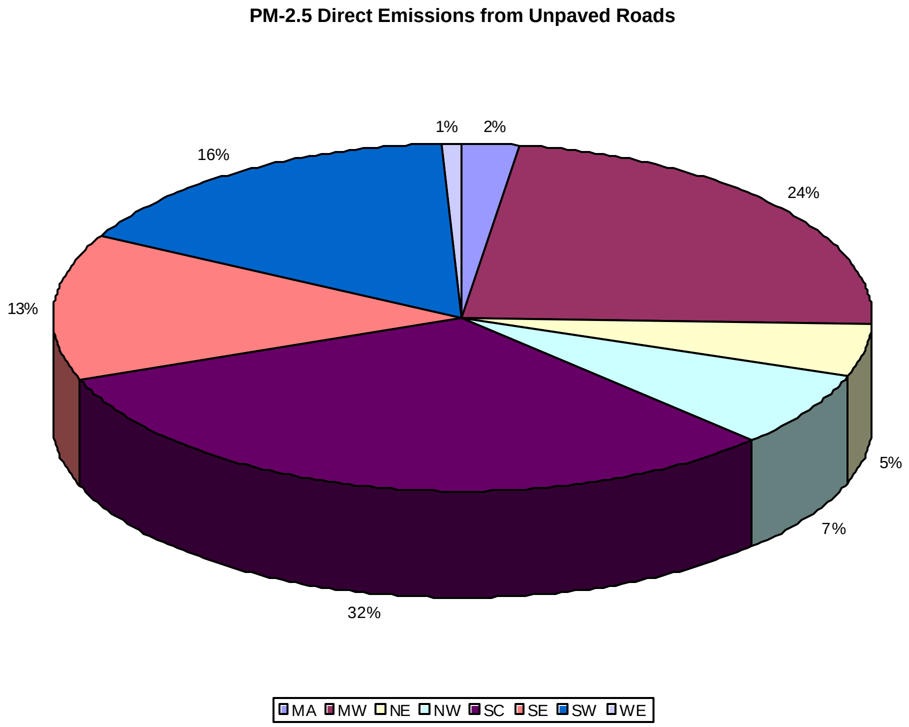
As indicated in the introduction, inventory and receptor models are frequently used together to try and improve our understanding of emissions (and to improve the inventory). Attributions determined by receptor models are compared to the inventory to determine whether they are similar in value. If they are then the inventory is regarded as being generally reflective of the emission sources. If it isn't then methods used for estimating a particular sector or source type are evaluated for improvements. One of the potential improvements would be to re-evaluate the emission rate (emission factor). In that case, source modeling would be performed to re-evaluate emission rates and to compare them to current values. Changes would then be reflected in new inventories which in turn would be re-evaluated with receptor models. This process is responsible for the recent introduction by U.S. EPA of the transport fraction (discussed later in this section) for fugitive dust sources. Inventories were showing that fugitive dust sources were contributing 70 percent or more to primary particulate emissions but receptor models were showing a considerably smaller contribution (see the soil component in Figure 1-2 for example), clearly indicating that there was a disconnect between the inventory and the measured concentrations found in atmosphere.

Emissions Assessment

For our evaluation of paved and unpaved road fugitive emissions we first looked at the geographic variability in emissions from the different regions of the country (see Figure 1-4, Introduction for State-by-State regional assignments). Figure 3-1 shows the percentage of total national paved road PM2.5 fugitive emissions from each region in the country. This figure shows that almost a quarter of the national PM2.5 emissions for re-entrained fugitive dust from paved roads originate in the southeastern U.S. An additional 20 percent comes from the Midwest, with an additional 16 percent from both the northeast and south-central regions.

For unpaved roads the regional emissions percentages are somewhat different. Figure 3-2 shows the breakout for unpaved roads. Figure 3-1 shows that 34 percent of the fugitive PM2.5 emissions from re-entrained dust from unpaved roads originate in the south-central U.S., while the Midwest contributes 24 percent followed by the southwest (16 percent) and the southeast (13 percent).

Figure 3-2. Regional contributions to national PM2.5 emissions from unpaved road re-entrainment.



These results may appear anomalous considering that for PM10 most nonattainment areas are driven by fugitive dust and are primarily located in the west while PM2.5 is generally regarded as being a combustion source yet fugitive emissions still dominate emissions especially in the Midwest and western regions of the country (MS, SW, SC, and NW regions discussed here). This result is largely an artifact of the emission inventory itself and the high levels of fugitive dust emissions found in the inventory. As has been noted earlier, the emission inventory does not match well with ambient measurements. U.S. EPA has developed a transport fraction (discussed below) which addresses this apparent dichotomy.

To provide an idea of the relative importance of both paved and unpaved road re-entrainment to direct on-road primary particulate emissions we prepared two figures, one without on-road fugitive dust sources and one with them included along with direct emissions of PM2.5 from tailpipe, tire and brake wear. Again the emissions are broken down by region for comparison purposes.

Figure 3-3 shows the tailpipe, tire and brake wear emissions from each region without including the re-entrained fugitive dust sources. You can see from this figure that tailpipe emissions dominate in every region and that emissions are highest in the Midwest and southeast with roughly equivalent emissions in the south-central, southwest and northeast.

Figure 3-4 shows the same graph as Figure 3-3 but with the directly emitted fugitive PM2.5 from paved and unpaved roads added in. This figure clearly shows that, for directly emitted PM2.5 according to the U.S. EPA 1999 National Emission Inventory (version 2), fugitive dust from unpaved and paved road re-entrainment dominates on-road emissions. Unpaved emissions are higher in every region than paved roads with the exception of the northeast and mid-atlantic and are roughly equivalent in the southeast.

In order to fully understand the relative significance of directly emitted fugitive PM2.5 from paved and unpaved roads however, the emissions need to be compared with total emissions from all sources since that (along with secondary particles) are typically what shows up on ambient filters.

Table 3-2 shows the relative contribution of paved and unpaved roads fugitive emissions to total directly emitted PM2.5 in each region of the country. For paved roads the percentage contribution range is between 3 and 16 percent. For unpaved roads, the range is from 9 to 22 percent.

Figure 3-3. Directly emitted PM2.5 emissions from tailpipe, tire and brake wear for each region of the U.S. without re-entrained dust from paved and unpaved roads.

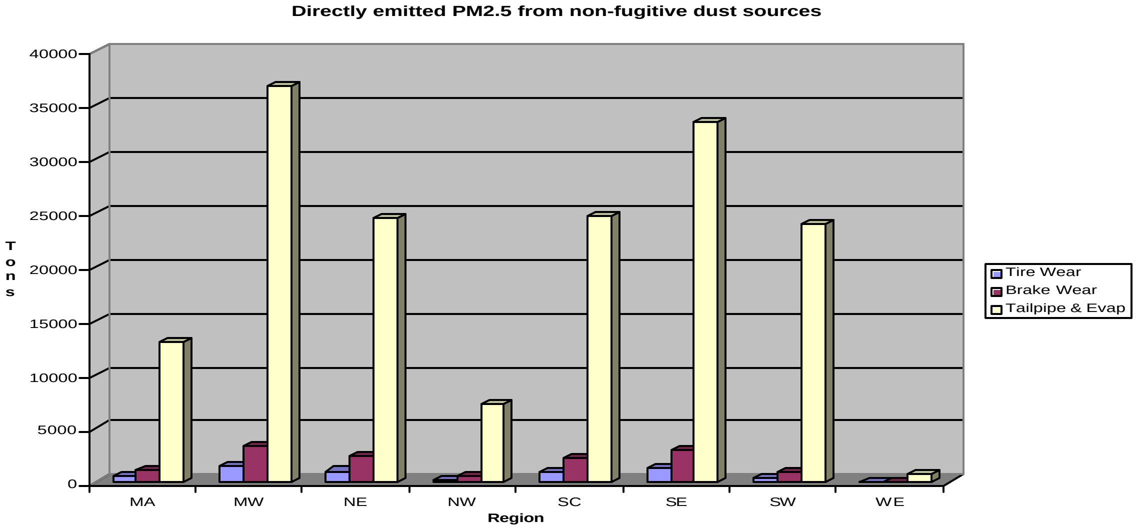


Figure 3-4. Directly emitted PM2.5 emissions from tailpipe, tire and brake wear for each region of the U.S. including re-entrained dust from paved and unpaved roads.

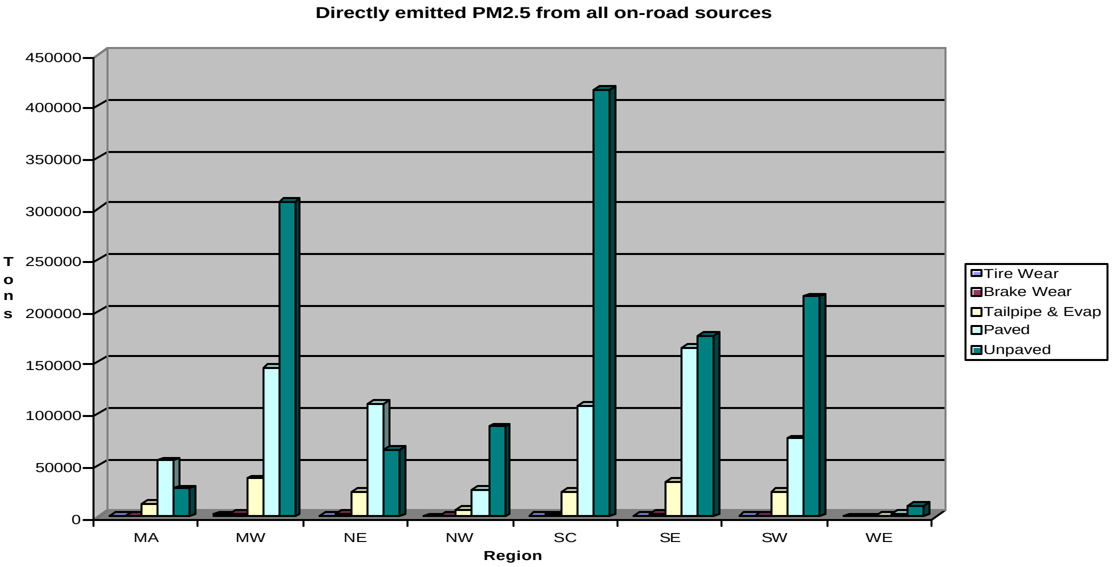
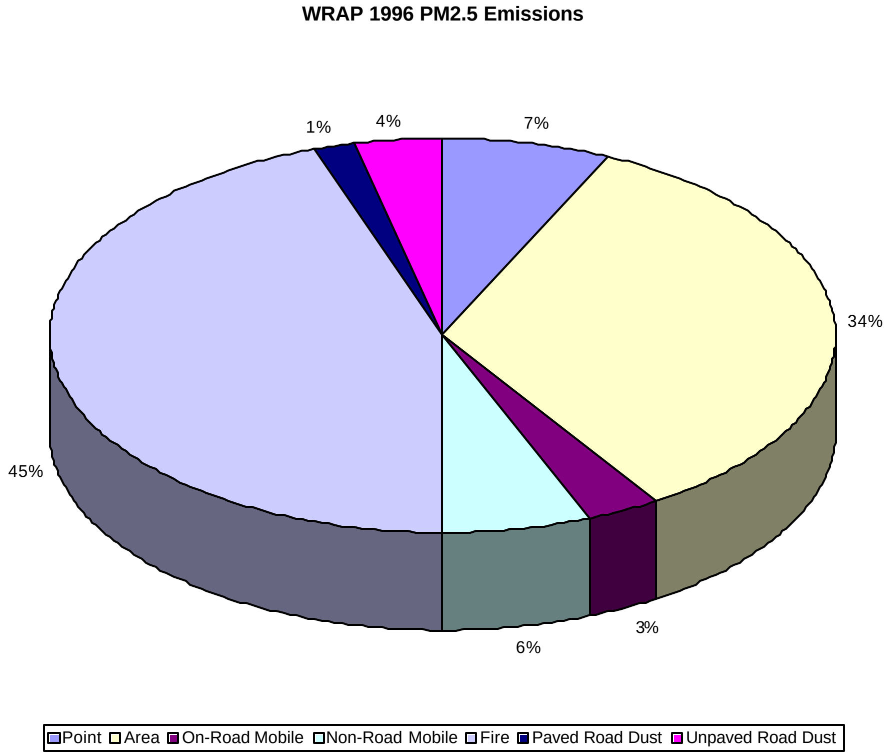


Table 3-2. Regional Percentage Contributions of Primary PM2.5 From All Sources
Source: EPA 1999 NEI version 2

Emission Source	MA (PM2.5 %)	MW (PM2.5 %)	NE (PM2.5 %)	NW (PM2.5 %)	SC (PM2.5 %)	SE (PM2.5 %)	SW (PM2.5 %)	WE (PM2.5 %)
Stationary Source Fuel Combustion	21	11	40	5	13	15	12	6
Industrial	8	6	7	4	6	8	9	1
Solv/Store/ Waste/Misc.	13	5	11	4	5	13	6	4
Non-road Mobile	5	5	5	2	5	4	5	2
On-road Mobile	4	2	4	1	3	3	2	1
Ag. Crops	5	28	3	8	17	6	4	0
Ag. Livestock	2	1	0	1	3	1	1	0
Fires	6	10	1	56	11	16	21	72
Paved	16	8	14	4	5	14	7	3
Unpaved	8	17	9	12	21	15	21	9
Other Fugitive	11	7	8	3	10	6	11	1
TOTAL	100	100	100	100	100	100	100	100

As a point of comparison to the regional contributions developed from the U.S. EPA NEI, we also looked at the emission inventory prepared for the Western Regional Air Partnership (WRAP) as part of their regional haze assessment for the western states (Alaska, Arizona, California, Colorado, Idaho, Montana, New Mexico, North Dakota, Oregon, South Dakota, Utah, Washington, and Wyoming - their states roughly correspond to our southwest, northwest and west regions). Data for this comparison was taken from http://www.wrapair.org/forums/ef/inventories/combined/2018-1996_Difference_Actual_to_Control_revised.xls. Their inventory is for 1996. Figure 3-5 shows that paved and unpaved roads fugitive emissions represent 1 and 4 percent of total directly emitted PM2.5 in the WRAP region. These values are significantly lower than those found in the 1999 NEI. It is not surprising that the comparison of the NEI versus the WRAP inventory shows significant differences due to the inherent uncertainty of these inventories (and in fact all emission inventories). Most of the data that is used in emission inventories are estimates of emissions. Different calculation methodologies yield a range of results that are interpreted and used to calculate the emission estimates used in emission inventories. It is important to recognize that the difference in these emission inventories is due to the uncertainty of estimates, and that comparison of inventories should not be considered in terms of absolute numerical comparison.

Figure 3-5. Percentage of primary PM2.5 emissions from all sources – WRAP 1996.



We also evaluated emission estimates at more localized levels. For example we evaluated emission estimates prepared for the San Joaquin Valley for 2000. Table 3-3 shows the emissions (in tons/day) of directly emitted PM2.5. This table shows that paved roads and unpaved road re-entrained fugitive dust accounts for 10 and 11 percent of the daily inventory, respectively, while mobile sources (which includes non-road engines) account for roughly 10 percent of the emissions. The values for San Joaquin Valley are roughly similar to values found for these sources in the NEI (Countess, 2003; Countess and Countess, 2003). Although the values in Table 3-3 do not reflect their application, Countess did find that applying a "transport fraction" to the emissions provided a better correspondence for source attribution to ambient measurements. Additional information on the transport fraction and its application to emissions is presented later in this chapter.

Table 3-3. San Joaquin Valley 2000 inventory (tons/day)

Source Category	Emissions	Percent of Total
Stationary Sources	32	20.6%
Agricultural Waste Burning	41	26.5%
Mobile Sources	15	9.7%
Paved Road Dust	16	10.3%
Unpaved Road Dust	17	11.0%
Construction & Demolition	4	2.6%
Farming Operations	22	14.2%
Windblown Dust	8	5.2%
Subtotal Fugitive Dust Sources	67	43.2%
Total All Sources	155	

Finally, we evaluated emission inventories prepared for the Pocatello, ID PM10 nonattainment area. An emission inventory was prepared for that area that included estimates of PM2.5. Two papers related to that inventory were presented at Air and Waste Management Association annual meetings (Schewe and Kellar, 2002; Schewe and Wagner, 2003) however those papers did not list the emissions from these (or other) categories. We contacted the authors and received data on the PM2.5 emissions for that area. Table 3-4 shows the emissions for the Pocatello area for PM2.5. It is interesting to note that paved road fugitive emissions are significantly higher than unpaved fugitive emissions in the area. Paved road fugitive emissions contribute approximately 6 percent to the overall inventory for the area. This is similar to the exhaust emission contributions (almost 5 percent). The largest source in the area is windblown fugitive dust from both agricultural and non-agricultural sources (contributing approximately 27 percent).

Table 3-4. PM2.5 Emissions for 2000 from the Pocatello, ID area (all values in tons/year).

Source	Emissions	Percentage contribution to inventory
Industrial Point Sources	153.45	22.66%
Fuel Comb. Comm/Inst.	6.67	0.98%
Fuel Comb. Res.	43.51	6.43%
Landfills	4.46	0.66%
Tilling	13.34	1.97%
Windblown Dust	194.21	28.68%
Fires	72.26	10.67%
Construction	78.13	11.54%
Storage Piles	0.05	0.01%
Nonroad exhaust	24.80	3.66%
Locomotives	13.16	1.94%
On-road exhaust	31.26	4.62%
Paved Roads	41.13	6.07%
Unpaved roads	0.73	0.11%
Total PM2.5 Emissions	**677.16**	

In evaluating the variability in emissions for this project, we found that substantially more research in the last few years has been focused on unpaved roads than on paved roads. In addition, the majority of research has been performed in the western U.S. with little carried out in the eastern part of the country. This dichotomy seems to be related to the fact that 1) western inventories seem to have a larger component of the inventory attributed to these source types, 2) fugitive dust is a more important component of the inventory in current PM10 nonattainment areas (PM2.5 areas have yet to be designated) and 3) eastern nonattainment areas are more likely to have components such as wood smoke and fires as the larger contributors to primary PM2.5.

Fugitive dust estimates are also poorly characterized because both the emission factors and the activity data are highly uncertain. Road dust emission factors depend on many variables including soil type, average driving speed, and average vehicle weight. Paved activity (vehicle miles traveled [VMT]) is relatively well characterized, but there is no reliable data on unpaved road activity. U.S. EPA has recently release a draft revision of the emission factor methodology for paved road dust that attempts to remove the tire wear, tailpipe, and brake wear components of emissions that were included in the initial formulation of the paved road emission factor.

This type of uncertainty is not typically mentioned in most of the research and published literature, even though a large part of the uncertainty and variability associated with emissions from these categories has to do with the parameters that are used in developing the emissions for different regions. For example, the current emission factor for paved and unpaved roads uses the silt loading (paved) or silt content (unpaved) as part of the emission factor equation. However, the supporting data for silt loading for EPA's AP-42 that EPA deems as values "that are most appropriate for typical road conditions" has a list of only 169 samples, from four states, three of which are western states (NV, OR, CA). The range of values is from 0.01 to 6.82 g/m2. A second table (designated as "paved road silt loading data base for areas with attainment problems related to road sanding and wind blown dust") contains 230 samples with a range from 0.014 to 103.7 g/m2. These data cover nine states, five from the west and four from the midwest. No samples in this data set are from the eastern U.S.

For unpaved roads, the silt database contains 368 samples, however 298 of these are from industrial roads that may not have characteristics similar to public unpaved roads. The silt content value for the public roads ranges from 0.1 to 68 percent. Unpublished data from over a hundred sites throughout the country collected by the Illinois State Water Survey as part of the 1985 NAPAP program on public unpaved roads found that the silt values were typically in the range from 1-15 percent.

Variability in the EPA emission factors is not limited to the silt content and loading but also to information related to vehicle weight, and moisture content (for unpaved roads only). It is also related to the activity data (which for both of these sources is vehicle miles traveled - VMT). Vehicle weight is typically "fleet average" vehicle weight. Thus the variability is related to the quality of the information concerning the typical fleet in the area where emissions are estimated. Moisture content is even more difficult to estimate since local soil moisture may not adequately reflect moisture conditions on an unpaved road that may 1) have a substantial drying effect associated with the traffic on the road and 2) may be surfaced with gravel or crushed stone that has different moisture retention properties than local soils. In addition, most soil moisture databases are measurements that were made at different points in the past and may not accurately reflect moisture contents conditions at the time estimates are made. EPA encourages emission estimators to use locally collected data whenever possible, however most of the large scale regional or national inventories are the result of national or regional databases of these information or are developed using default values.

Estimating VMT on unpaved roads is also highly uncertain. Few states collect data on unpaved road VMT. States do submit unpaved road mileage in average daily traffic volume classes to FHWA, however when those data are used to estimate VMT (by assuming a value for the ADT, multiplying by the number of miles of unpaved road and by 365 days to produce an annual number) the values obtained sometimes are larger than total VMT estimates produced by FHWA by functional class. Paved Road VMT estimates are generally regarded as better than unpaved road VMT estimates due to their inclusion in the FHWA HPMS statistics, however both VMT values are only estimates.

The WRAP has recently recognized the inherent variability in these factors in looking at unpaved road emissions in the western U.S. In a recent paper by Tran, Pollack, and Yu (2003), they evaluated and revised unpaved road emissions in the 13 WRAP states by updating and revising the silt content estimates, the ADT estimates and by applying a transport fraction to the estimates. Their revisions were triggered by unexpected inconsistencies that were observed in the Western states road dust emissions estimates developed using the standard AP-42 approach. They found that there were large variations in emission estimates from state to state, and in adjacent counties. In particular, there was unexpectedly large variation in the unpaved road dust emissions among the Colorado Plateau states. The underlying data used to estimate the road dust emissions were reviewed, and significant variation was found in both the emission factors (expressed in grams per mile) and the activity data (expressed as VMT), the product of which yields the emission estimates.

For this revision the authors obtained the raw silt content data from the Illinois State Water Survey (ISWS) and from these, it was determined that variability in the state-level emission factors was largely because of variability in the assumed state-level silt content values. They made two changes to the silt data. First, the Western states average of 3.2 percent was applied in states with inadequate data (less than three measurements), rather than the national average of 3.9 percent that EPA uses. Second, the largest value (17.99, an outlier) was deleted from the Montana average, which reduced the Montana average.

They also made changes regarding ADTV assumptions. As mentioned above, unpaved road VMT is commonly estimated as the product of the road mileage and the assumed ADTV (times the days per year for annual estimates). The 1996 FHWA Highway Statistics Report (FHWA, 1996) was the source for the mileage estimate used in the first WRAP inventory. The FHWA data were submitted by each state, with varying data collection methods across states and counties — some jurisdictions performed surveys; others relied on road owners/managers (usually Federal agencies). Data were reported separately for urban and rural roads. While the authors found that these factors question the consistency of the unpaved road length data, they were not revised since no alternative source was available to justify or facilitate their revision. However, the ADTV estimates were revised based on survey work done for the Clark County, NV June 2001 PM10 State Implementation Plan (SIP) and traffic volume estimates for National Forest Service unpaved roads (NFS is the largest manager of unpaved roads in the west).

The ADTV estimates for urban unpaved roads were based upon those in Clark County, NV June 2001 PM10 SIP (available at http://www.co.clark.nv.us/Comprehensive_planning/Environmental/AirQuality/PM10SIP.htm). VMT estimates on urban unpaved roads were estimated using the average ADTV value for Clark County (69.2), with adjustments for differences in population density. Urban unpaved road ADTV values for all counties were first estimated using the average Clark County ADTV and adjusting with the ratio of county population densities. Population densities were based upon 1990 U.S. Census Bureau population and land area data. The final ADTV for each state was obtained by computing the arithmetic average across all counties.

The results of these revisions were that fugitive dust PM10 (and PM2.5 as well since the PM2.5 emissions using AP-42 are a constant fraction of PM10) emissions were reduced by 15 percent due to revision of the silt loading values and revisions to the ADTV data resulted in a 68 percent reduction.

Estimates of Re-entrained dust contributions based on Emission Rates

Paved Roads

While emission rates themselves cannot provide a direct estimate of the contribution of mobile sources to re-entrained dust, they do provide a means for estimating the variability that can be expected in emissions estimates. In addition, since virtually all large scale regional or national emission inventories have been compiled using U.S. EPA's AP-42 emission factor, comparing emission rates found in other studies with the AP-42 factors provides an indirect means of estimating what emissions would be if alternative emission rates were utilized.

For paved roads, the current emission factor (in lbs/VMT) can range between 0.000109-6.56. This is based on the range of acceptable values listed for silt loading and vehicle weight. The listed range for silt loading is 0.02-400 g/m2 while the range for vehicle weight is 2-42 tons.

The emission factor equation in the final chapter version is:

$$E = k \times (sL/2)^{0.65} \times (W/3)^{1.5}$$

where:

E = emission rate (in lb/VMT, g/VMT or kg/VMT depending on the value of k used
$k_{(1)}$ = particle size multiplier for particle size range and units of interest
sL = road surface silt loading (grams per square meter) (g/m2), and
W = average weight (tons) of the vehicles traveling the road.

(1) For PM2.5, the values for "k" are 1.1g/VKT; 1.8g/VMT; and 0.0040lb/VMT

These emission rates are based on the current final version of chapter 13.2.1. However, the emission rates in that chapter include tailpipe, tire and brake wear emissions as well as re-entrained dust. EPA has recently released a draft version of chapter 13.2.1 which attempts to account for the tailpipe, tire and brake wear emissions. In that chapter, a correction is added to the emission factor equation to account for tailpipe, tire and brake wear values from 1980s vehicles (the age of vehicles when the emission factor was developed). The new equation is:

$$E = k \times (sL/2)^{0.65} \times (W/3)^{1.5} - C$$

Where:

C = emission factor for 1980's vehicle fleet exhaust, brake wear and tire wear.

The value given for C for PM2.5 (in lb/VMT) is 0.00036. If this value is used with the minimum silt loading and minimum vehicle weights listed above, a negative emission value is obtained. U.S. EPA is aware of this possibility and has determined that emissions should be set to zero should that circumstance arise.

Using typical values for silt loading (from Table 13.2.1-2 of AP-42) and a value for the fleet vehicle weight of 3 tons produces an emission factor of 0.00057 lb/VMT for a high ADTV roadway (> 5000 vehicles per day) and 0.001405 for low ADTV roadways (< 5000 vehicles per day). These emission factors would represent a fleet that was cars only.

Two recent studies have looked at emission rates from paved roads. Abu-Allaban et. al. (2003, in press) in a paper submitted to Atmospheric Environment determined fugitive PM10 and PM2.5 emission rates from paved roads using roadside measurements. Their approach was to use a multi-lag regression approach to determine the emission rates of on-road tailpipe, brake wear, tire wear, and resuspended (re-entrained) fugitive road dust. Measurements were made in Reno, NV and in Research Triangle Park, NC. Their emission rates (shown in Table 3-5) were determined for these source types by vehicle type (cars, trucks, and buses). They used CMB to apportion the total emission rates determined by the multi-lag regression to the various source components (e.g., tailpipe, brake wear, etc.). The CMB analysis failed to find any contribution from tire wear in the measured concentrations.

Interestingly their findings found that tailpipe emissions dominated the PM2.5 emissions with fugitive road dust contributing a lesser fraction. This is directly opposite most emission inventory based studies which show significantly higher levels from re-entrained fugitive dust. The emission rates found in this study for cars can be directly compared with the ranges provided above for AP-42 minimum values since the fleet vehicle weight used to calculate that value was 2 tons (similar to a car’s weight). The emission rates for cars for fugitive PM2.5 in this study are approximately a factor of three below those for the *minimum* value for the AP-42 emission factor.

Table 3-5. Emission rates (lb/VMT) and uncertainties for PM10 and PM2.5 from paved roads in Reno, NV and Research Triangle Park, NC.

Vehicle Type	**Size**	**Tailpipe**			**Road Dust**			**Brake wear**		
Cars	PM10	0.000192	±	0.000035	0.000781	±	0.000060	0.000039	±	0.000013
Cars	PM2.5	0.000050	±	0.000008	0.000043	±	0.000007	0.000004	±	0.000001
LD Trucks	PM10	0.000312	±	0.000060	0.001100	±	0.000092	0.000096	±	0.000031
LD Trucks	PM2.5	0.000067	±	0.000012	0.000060	±	0.000010	0.000005	±	0.000001
HDD Trucks	PM10	0.005678	±	0.001277	0.004968	±	0.000426	0.000568	±	0.000185
HDD Trucks	PM2.5	0.000958	±	0.000192	0.000224	±	0.000043	0.000011	±	0.000003
Buses	PM10	0.001419	±	0.000295	0.001952	±	0.000174	0.000053	±	0.000015
Buses	PM2.5	0.000461	±	0.000085	0.000085	±	0.000011	0.000009	±	0.000002
Average		**0.001142**			**0.001151**			**0.000098**		

A second study to determine fugitive dust emission rates from paved roads was conducted in California as part of a contract with the California Air Resources Board (CARB). In that study (Fitz, 2001), the investigators attempted to determine emission rates from paved roads in two different ways. First they tried to establish a long-term upwind-downwind monitoring program to measure fugitive PM concentrations on both sides of an arterial road. Upwind-downwind sampling is a common method for determining emission rates. The method uses sampling on the upwind and downwind sides of a source couple with dispersion equations to back calculate the source emission rate from the measured ambient concentrations. The upwind site is used to subtract out the background concentration from the concentration measured at the downwind source, leaving only the contribution from the source itself. That value is then used (along with appropriate meteorology data) to back calculate the emission rate from the source. One important component of the method is that the winds must be within 45 degrees of perpendicular in order for the dispersion equation to yield reliable results.

The second method used in this study was to measure fugitive PM concentrations directly in the vehicle wake using a trailer towed behind the vehicle. The investigators evaluated several different locations and heights for the sampler inlet and also looked at the emission rates from several different roadway functional classes (local, collector, arterial, and freeway). The measurements were made with a DustTrak particle size measurement device and converted to mass using calibration against particles of known size and density.

The results from the two methods were mixed. Despite measuring for two months in the upwind-downwind configuration and focusing on periods of time when the winds were perpendicular to the roadway, the downwind fugitive PM10 concentrations were only slightly above those of the upwind (on average) and no attempt was made to measure PM2.5 since the concentration difference between upwind and downwind samplers would be expected to be much smaller (and consequently more uncertain). As the investigators stated "further analysis of the data and application of dispersion models would not likely produce emission factors with high confidences levels." They attribute the lack of available data and the inability to determine emission factors using this approach to the very small and diffuse source strength of the paved roadway.

Using their second method they were able to develop emission factors from the measurements. The emission factors that they developed were calculated by assuming that the vehicle swept out a volume based on the frontal area of the vehicle and that the PM measurements in the plume behind the vehicle were representative of the mean concentrations within the wake. The calculated fugitive dust emission rates ranged from 0.00023 lb/VMT for a collector road to 0.000465 lbs/VMT for an arterial road. While these factors are not as low as those found by Abu-Allaban et. al., they are still somewhat lower than values calculated using AP-42 (without the tailpipe, brake and tire wear correction). No attempt was made in this study to eliminate the tailpipe, brake and tire wear components from the measurements.

The author of this study does raise a couple of questions concerning the AP-42 emission factors. With regard to AP-42's dependence on silt loading they say "The AP-42 document states that traffic rapidly develops an equilibrium silt loading and that new deposits are needed for continual PM production. Therefore, it is difficult to understand the dependency between silt loading and the PM emission rate."

They also point out that in an earlier study that they had performed (Venkatram and Fitz, 1998) to look at only fugitive PM10 from paved roads, they had found no correlation between silt loading and emission factors. They further indicate that silt loading values are likely to equilibrate at a low level (without a replenishment mechanism) due to the "vacuuming" effect that the vehicle movement creates and cited a study by Nicholson and Branson (1990) that observed rapid attainment of equilibrium for particles tagged with fluorescent dye and deposited on a road and monitored.

They also point out that emission factors calculated using the AP-42 emission factor equation (uncorrected for tailpipe, tire and brake wear) tend to be higher than that measured and that all studies of urban roads have found the measured concentration differential of fugitive PM between upwind and downwind to be very close to the measurement uncertainty (as was the case in their study). They attribute this to the fact that the paved road emission factor equation in AP-42 was initially developed using industrial roadways where the PM emissions were much higher due to the higher rate of deposition of surface materials than on public roadways.

Thus for fugitive dust from paved roads, the newer emission rate studies indicate that the values for emission rates are approximately 1/2 to 1/3 (or more) lower than those found using AP-42. Since emissions are linearly related to the emission rate (according to AP-42), it can be inferred that emissions (and thus the mobile source contribution to emissions) would be reduced by an equivalent amount based on these alternative emission rates.

Unpaved Roads

For unpaved roads, the current emission factor (in lbs/VMT) for public roads can range between 0.04104-0.49139. This is based on the range of acceptable values listed for silt content, vehicle speed, and surface moisture content and using the equation for public roadways. The listed range for silt content is 1.8-35 percent, 10-43 mph for speed, and 0.03-13 percent for surface moisture.

The emission factor equation used to calculate these emission factors is found in the draft AP-42 chapter (prepared in Oct., 2001) and is as follows:

$$E = (k \times (s/12)^{a} \times (S/30)^{d})/(M/0.5)^{c}$$

where and:

E = emission rate (in lb/VMT, g/VMT or kg/VMT depending on the value of k used
k = particle size multiplier for particle size range and units of interest
s = surface material silt content (percent),
S = mean vehicle speed of the vehicles traveling the road,
M = surface material moisture content (percent) and

a, c and d are empirical constants (with values of 1, 0.2, and 0.5 respectively for PM2.5). The size fraction value (k) for PM2.5 is 0.27.

These emission rates include emissions from tailpipe, brake and tire wear. Unlike paved roads, no correction term has been developed to date for the unpaved road emission factor. However because of the way that the correction term was developed for paved roads (using MOBILE6 with a 1980 vehicle population) it would be fairly safe to apply the correction term to this equation if an accounting of that component was desired.

Researchers in the western U.S. have performed studies recently related to determining the fugitive dust emission rates from unpaved roads however these studies have been oriented towards PM10 rather than PM2.5. For example, Gilles et. al. (2003) found that emission factors measured using DustTraks (also used in the UC Riverside paved road studies) at Ft. Bliss, TX were less than corresponding AP-42 emission factors for a vehicle mix of civilian and military vehicles of varying weights and shapes. If one assumes that the k value for the AP-42 emission factor held for each study, that would also mean that PM2.5 emissions were higher from unpaved roads at Ft. Bliss than AP-42 values would predict.

These researchers did find that vehicle speed was an important factor with respect to roadway PM10 emissions for the tested vehicles. The effect of speed on emissions was found to be linear and relatively invariant with vehicle type. Regardless of test vehicle type the emissions from the roadway increased at a constant rate with increasing speed. The AP-42 emission factor equation shows the effect of speed to be a power function rather than linear, with speed raised to a power typically between 1 and 1.5. This suggests that physical characteristics of the vehicles such as shape and number of tires do not have a great influence on the emissions as vehicles change their speed.

These researchers did notice a discernable effect of vehicle weight on the fugitive emissions from the unpaved road. Their data showed that for every increase in unit weight there is an increase in the emission factor (as a function of speed) by approximately a factor of two. In earlier AP-42 emission factor estimation methodologies the affect of vehicle weight on fugitive PM10 emissions was treated as a power function with the weight being raised to the 0.74 or 0.454 power. The Ft. Bliss data shows a strong linear relationship between weight and emissions. The effect of vehicle undercarriage area and the number of wheels on the vehicles had weak and no discernable affect, respectively on emission factors.

In comparing the measured emission factors from the vehicles tested at Ft. Bliss with the AP-42 emission factor, they found several differences were clear. The AP-42 emission factor under-predicts the Ft. Bliss emissions when the road has a silt content of 4%. For a 7% silt content, which was measured at Ft. Bliss in the later stages of testing, the AP-42 emission factor under-predicts for vehicles exceeding 10 km/hr. This relationship of underprediction up to a certain speed is related to the difference between the Ft. Bliss and AP-42 relationship between emissions and vehicle speed (linear for Ft. Bliss and a power function for AP-42).

Little additional work on unpaved road fugitive dust emission rates has been performed other than that associated with minor updates to AP-42. Virtually no work has been performed in the east, southeast, northeast or midwest on unpaved or paved road emission rates in the last few years. The majority of new investigations has been in the western U.S.

Estimates of Re-entrained dust contributions based on Receptor Modeling/Source Apportionment Studies

The third method of determining the contribution of re-entrained road dust from on-road mobile sources is to use receptor modeling/source apportionment techniques. Source apportionment modeling techniques typically use information about the chemical composition of particulate or gaseous phase pollutants in ambient air samples to attribute the relative amounts of pollutants to their respective sources. The relative contributions from each source are estimated based on knowledge of the characteristic chemical species emitted from the sources and the quantities measured in the ambient samples. This approach is sometimes referred as the "top-down" approach as opposed to the "bottom-up" or emission inventory approach that estimates relative contributions to ambient levels based upon estimated emission rates, activity levels of emission sources, and dispersion from the sources. Source apportionment models range from the relatively simple, in the case of the material balance approach to the complex mathematical treatments of multivariate receptor models.

Using a simple material balance approach, chemical analyses of particulate samples collected at a receptor are used to attribute the components of the total mass to broad categories of aerosol types. Typical categories include, but are not limited to, carbonaceous components (from combustion sources), geological material (from fugitive dust emissions), and nitrates and sulfates (which are secondary aerosols).

More detailed source apportionment is normally accomplished through the application of receptor models that utilize measurements of total and speciated mass concentrations of gases and particulate matter in the ambient air in combination with representative chemically-speciated source profiles for specific emission source categories. These receptor models can provide estimates of contributions to more specific sources than the general categories of the material balance method. For example, the contribution of PM from different combustion sources, such as motor vehicles and wood smoke, can be estimated using receptor models by specifying species composition for each source type. These sources would be grouped into the carbonaceous particle category using the material balance approach. Receptor models attempt to apportion atmospheric pollutants to sources by relating chemical and physical properties of the source material to the properties observed at a receptor site. There are two main approaches to receptor modeling, chemical mass balance (CMB) and multivariate models. The U.S. EPA sanctions the CMB model version 7.0 as its reference method for source apportionment.

Gertler et.al. (2000) have recently published an overview of mobile source contributions to PM10 and PM2.5 that focuses on source receptor contributions. However, the majority of the paper is devoted to tailpipe emission attribution, and provides little information on direct attribution of PM2.5 from re-entrained fugitive dust. This report does indicate that re-entrained road dust (from both paved and unpaved roads) contributes approximately 4 percent of the PM2.5 carbon in the Northern Front Range Air Quality Study (NFRAQS). The NFRAQS study itself (Lawson and Smith, 1998) found that "dust and debris" (which would include re-entrained road dust) contributes 20-30 percent of measured PM2.5. This provides an upper range to the potential contribution of re-entrained fugitive road dust to ambient levels. Of course there are likely to be several additional sources (construction, agriculture, etc.) to the "dust and debris" component of PM2.5.

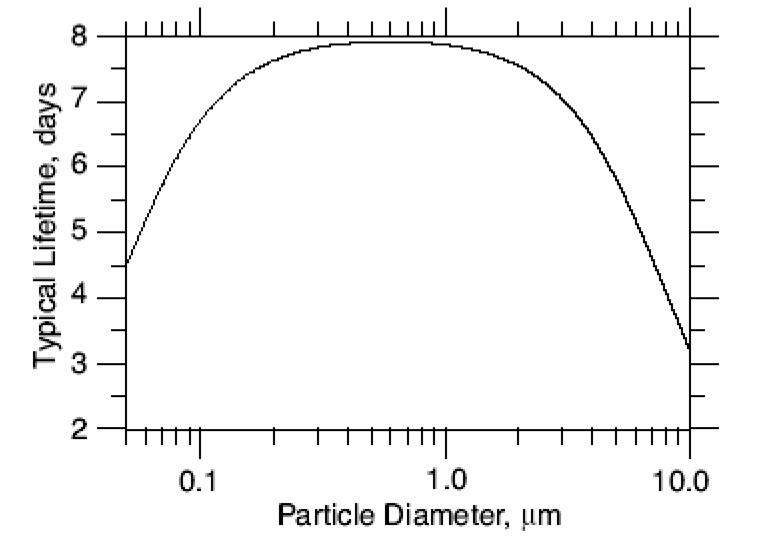
Table 2-3 of this report showed that Road Dust/Soil Dust contributed between 1.1 and 14 percent to ambient concentration levels. That information represents an upper limit in those areas since it cannot be completely specified whether or not that is totally paved road dust, unpaved road dust or activities such as construction or agricultural tilling. Most of those sources would have similar chemical profiles (the “co-linearity” issue with CMB modeling).

One of the more interesting receptor modeling approaches presented recently is that of Sattler and Liljestrand (2003). In their study, they use a modified version of the CMB model that takes chemical reactions and differential deposition or fractionation between source and receptor into account. Their work was performed in the Los Angeles area (Claremont and Long Beach). They showed improvements between nitrate apportioned from 5-6 percent to slightly over 80 percent after deposition and fractionation were included. They also calculated depletion factors in order to use the CMB model to account for long range pollutant transport. Their apportionment was made using both fractionated and unfractionated profiles including one for fugitive dust from paved roads. Using unfractionated profiles, they found that paved roads attributed between 1.9 to 2.8 percent of all mobile source emissions of PM2.5. Using fractionated profiles these values fell to 0.3 to 0.8 percent of all mobile source PM2.5. The depletion factors that they determined were calculated for 16-hour transport times. Minimum and maximum values were presented for various meteorological stability classes. These values ranged from 0.976 to 0.402 (stability classes A-F minimum values) and from 0.990 to 0.641 (stability classes A-F maximum values).

One of the most interesting things about these calculated depletion factors is that estimating depletion of fine PM (both PM10 and PM2.5) has received a significant amount of attention lately. In recent years several individuals and groups have noticed the apparent overestimate of fugitive dust emissions that is contained in the EPA’s National Emissions Inventory. Efforts to reconcile air quality model estimates of dust concentrations with ambient estimates of the crustal component of PM-10 and PM-2.5 have been unsuccessful. In most cases, modelers have resorted to arbitrarily scaling back emissions by a factor of four and in some cases, even this has not been enough reconcile the model with ambient measurements. A workshop at Desert Research Institute in 2000 (Watson and Chow, 2000) began to explore the reasons for this apparent disparity. This was followed by the convening of an expert panel by the Western Regional Air Partnership (WRAP) to further discuss the issue (Countess et. al., 2001). Several papers have been presented or circulated and several field studies have been completed in an attempt to reconcile the discrepancy. Out of these studies and discussions, the concept of a transport fraction was developed. The transport fraction can be defined as the portion of the original emissions that remains airborne and potentially transportable from the vicinity of the source. The transport fraction is a function of both the release height of the source and of removal mechanisms (such as impaction) by buildings and vegetation located close to the emissions source. The transport fraction varies from county to county due to differences in the vegetative cover and degree of urbanization.

Researchers have long known that removal of particles occurs as a result of both deposition and other removal mechanisms such as impaction on surfaces. Figure 3-6 shows the typical lifetime of a particle based on its particle size. As can be seen from this figure, a PM2.5 particle has an average lifetime of approximately 8 days. However this figure represents ideal conditions for dispersion.

Figure 3-6. Expected lifetime of a particle based on particle diameter.



However, most fugitive dust sources (such as re-entrained dust from paved and unpaved roads) has a release point that is only a few meters above the ground and is typically in a regime where removal by impaction could be substantial. As a consequence EPA (and others) has developed the transport fraction. The transport fraction has typically been based on information on the vegetation types found in a county along with the percentage of urbanized area. Calculation of the transport fraction is based on depletion values for different land types (or an urban area) coupled with a determination of what fraction of each land type is found in a region (typically for inventory purposes a county). Figure 3-7 shows county level transport fractions based on land use data. The values presented in Figure 3-7 (Pace and Cowherd, 2003) are based on weighted values where the transport fraction of each component is multiplied by the fraction of that land use in each county. The raw values for transport fractions are:

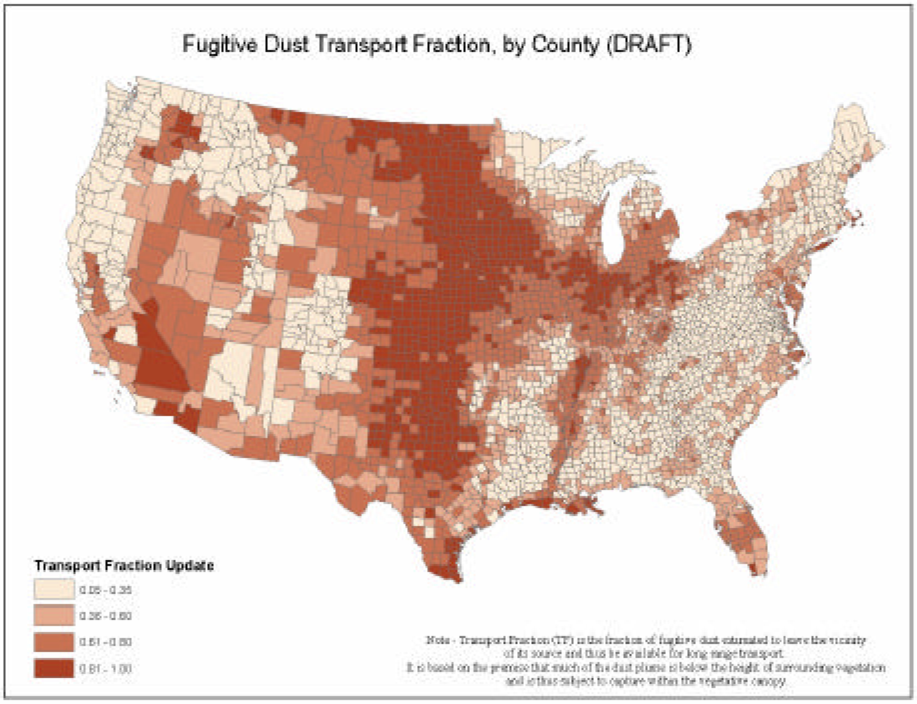
barren land and water = 0.97
agricultural = 0.85
grasses = 0.7
scrub and sparsely wooded = 0.6
urban = 0.3
forested = 0.05

Thus for emissions in forested areas, only 5 percent of the emissions would be considered transportable. County by county values for the transport fraction are available on the EPA website at http://www.epa.gov/ttn/chief/emch/invent/index.html.

It is interesting to compare these values to those found in the Sattler and Liljestrand paper for depletion factors. The range for their work showed depletion factors ranging from 0.4 to 0.99 depending upon stability class. Since their work was performed in the Los Angeles area, it would be considered urban. Figure 3-7 shows that Los Angeles County would have a transport fraction of 0.35-0.50. This would be equivalent to a depletion fraction of 0.5-0.65. While this value is on the low side for the Los Angeles study, it does fall between the minimum and maximum values found for that study.

To date, these transport fractions have only been applied to fugitive dust sources. They have not been applied to tailpipe, tire or brake wear components of emissions. However the removal mechanisms should be the same and an argument could be made that the transport fraction should be applied to all ground or low level emission sources. It will be interesting to see if the transport fraction is applied in that manner in future emission inventory efforts.

Figure 3-7. Fugitive dust transport fractions by county.



Note - Transport Fraction (TF) is the fraction of fugitive dust estimated to leave the vicinity of its source and thus be available for long range transport.
It is based on the premise that much of the dust plume is below the height of surrounding vegetation and is thus subject to capture within the vegetative canopy.

4. CONCLUSIONS

One focus of this report has been to identify, review, and discuss current scientific literature to provide a consensus on the contribution of PM2.5 precursor compounds from on-road mobile sources. Similarly, we researched the contribution of the re-entrained dust component of on-road emissions to PM2.5 concentrations.

As shown in Section 2 of this report, on-road mobile sources are responsible for between 16 and 33% of the VOC, and 26 to 45% of the NOx emitted annually depending on the region of the United States. Of course, this information alone says nothing about how much of these components react to form PM2.5. The subset of VOC from on-road mobile sources that contributes to PM2.5 formation is primarily PAHs and hydrocarbons with more than 10 carbon atoms. This is due to the lower volatility of these compounds and their ability to join with other compounds and form particles. The contribution of this subset of VOC toward total PM2.5 formation is highly variable with some studies showing that VOC contributes to between 20 and 80% of the PM2.5. The NOx and SOx contribution toward PM2.5 formation is also highly variable depending on atmospheric conditions including moisture, temperature and other factors as discussed in Section 2. The overall results are inconclusive regarding the formation of PM2.5 from on-road mobile source PM2.5 precursor compounds as evidenced by the differing results from the studies that were included in this research. In large part, this is due to the variability of conditions that result in the formation of PM2.5.

The re-entrained dust component of PM2.5 was discussed in Section 3 of this report. Re-entrained dust is generated from pavement wear (or silt/soil in the case of unpaved roads), tire fragments, and other loose material that has been deposited on the road surface. Historically, inventories have showed that fugitive dust sources contribute approximately 70% or more to primary particulate emissions, but the results from receptor sites show a much smaller contribution. Limitations in the studies that were used to derive the EPA's calculation methods for re-entrained dust which are used in inventory preparation were caused by a use of only western States to determine silt loading for paved and unpaved roads. Additionally, industrial roads, which are not necessarily the same as public roads were used in the determination of silt loading values for unpaved roads. Use of alternative silt loading values and other variables generated from more recent studies shows a decrease in the predicted values, which in turn are more in line with the monitored values. Air quality modeling studies have also struggled to arrive at calculated values that resemble ambient air measurements. The answer to this problem has been a study of the transportable fraction of PM2.5, which is significantly less than the amount of PM2.5 initially re-entrained. Factors have been developed to represent various fractions of transportable PM2.5 depending on several variables. County-level values have been developed for all counties in the US to assist in air quality modeling of re-entrained PM2.5 emissions. These values assist in more accurately predicting the re-entrained dust component of PM2.5. Depending on the region of the country, it appears that re-entrained fugitive dust from paved roads contributes between 3 and 6% to the overall PM2.5 inventory, and unpaved roads contribute between 9 and 22% to the inventory.

REFERENCES

Abu-Allaban, M., J.A. Gillies, and A.W. Gertler, 2003. “Application of a Multi-Lag Regression Approach to Determine On-Road PM10 and PM2.5 Emission Rates”. Atmos. Environ., in press.

Abu-Allaban, M., J.A., Gillies, A.W. Gertler, R. Clayton, and D. Proffitt, 2003. “Tailpipe, Resuspended Road Dust, and Brake-Wear Emission Factors from On-Road Vehicles”. Atmos. Environ., in press.

Baldauf, R.W.; Bailey, C.R.; Fulper, C.R.; Somers, J.H. *The Contribution of Gasoline and Diesel Vehicles to Particulate Matter Emission Inventories*. A&WMA conference paper.

Cabada, J.C.; Pandis, S.N.; Robinson, A.L. *Sources of Atmospheric Carbonaceous Particulate Matter in Pittsburgh, Pennsylvania*. JAWMA v.52:732-741.

Choi, Y.; Ehrman, S.H.; Calabrese, R.V. *Source Apportionment of Volatile Organic Carbon at a Suburban Mid-Atlantic Site.* A&WMA conference paper.

Countess, R., W.R. Barnard, C. Claiborn, D. Gillette, D. Latimer, T. Pace, and J. Watson, 2001. “Methodology for Estimating Fugitive Windblown and Mechanically Resuspended Road Dust Emissions Applicable for Regional Scale Air Quality Modeling”. Final Report prepared for Western Governor’s Association, Electronically published at http://www.wrapair.org/reports/Fugitive Dust Final.doc.

Countess, R.J., 2003a. “Reconciling Fugitive Dust Emission Inventories with Ambient Measurements”, paper presented at the 12th Annual EPA Emission Inventory Conference San Diego, CA, April 29 – May 1, 2003.

Countess, R.J. and S.J. Countess, 2003. “Fugitive Dust Concentrations in the San Joaquin Valley”, Paper # 69319, 96th Annual Conference and Exhibition, Air and Waste Management Association, San Diego, CA, June 2003.

EPA. “Control of Emissions of Hazardous Air Pollutants from Motor Vehicles and Motor Vehicle Fuels”, December, 2000.

Fitz, D.R., 2001. “Measurements of PM10 and PM2.5 Emission Factors from Paved Roads in California”, Final Report, Contract No. 98-723, California Air Resources Board, Monitoring and Laboratory Division, Sacramento CA.

Gertler, A.W., J.A.Gillies, and W. R. Pierson, 2000. “An Assessment of the Mobile Source Contribution to PM10 and PM2.5 in the United States”, Water, Air, and Soil Pollution, 123, p. 203-214.

Gertler, A.W., December, 2003. Personal communication with Bill Barnard.

Gillies, J.A, H. Kuhns, V.Etyemezian, D. Nikolic, and D.Gillette, 2003. "Effect of Vehicle Characteristics on Unpaved Road Dust Emissions", Paper #69658, 96th Annual Conference and Exhibition, Air and Waste Management Association, San Diego, CA, June 2003.

Grosjean, D.; Seinfeld, J.H. *Parameterization of the Formation Potential of Secondary Organic Aerosols*. Atmos. Environ., 1989 v.23:1733-1747.

Kourtidis, K.; Ziomas, I. *Estimation of Secondary Organic Aerosol (SOA) Production from Traffic Emissions in the City of Athens*. Global Nest: the Int. J. Vol 1, No 1 pp 33-39: 1999.

Lawson, D.R. and R.E. Smith, 1998. "The Northern Front Range Air Quality Study – A Report to the Governor and General Assembly".

Lewis, C.W.; Norris, G.A.; Conner, T.L. *Source Apportionment of Phoenix PM2.5 Aerosol with the Unmix Receptor Model*. JAWMA March, 2003 v.53:325-338.

Mendoza-Dominguez, A.; Russell, A.G. *Emission Strength Validation Using Four-Dimensional Data Assimilation: Application to Primary Aerosol and Precursors to Ozone and Secondary Aerosol*. JAWMA November, 2001 v.51:1538-1550.

Nicholson, K.W. and J.R. Branson, 1990. "Factors affecting resuspension by road traffic", Sci. Tot. Environ., 93, 349-358.

Nett Technologies webpage: http://168.143.83.57/faq_diesel.html.

Pace, T.G. and C. Cowherd, Jr., 2003. "Estimating PM-2.5 Transport Fraction Using Acreage-weighted County Land Cover Characteristics –Example of Concept", Paper No. 70445, 96th Annual Conference and Exhibition, Air and Waste Management Association, San Diego, CA, June 2003.

Particulate Matter Science for Policy Makers - A NARSTO Assessment. Parts 1 and 2. NARSTO Management Office. February 2003.

Sattler, M.L. and H.M. Liljestrand, 2003. "Chemical Mass Balance Model with Fractionation: Source Apportionment of PM2.5", Paper #68936, 96th Annual Conference and Exhibition, Air and Waste Management Association, San Diego, CA, June 2003.

Schewe G. J. and M. Kellar, 2002. "PM10 and Precursor Emission Inventory for Modeling the Portneuf Valley, Idaho Non-attainment Area", Paper No. 43531, 95th Annual Conference and Exhibition, Air and Waste Management Association, Baltimore, MD, June 2002.

Schewe G. J. and J.A.Wagner, 2003. "Using the Portneuf Valley, Idaho PM10 and Precursor Emission Inventory for CALPUFF and Rollback Modeling", Paper No. 69347, 96th Annual Conference and Exhibition, Air and Waste Management Association, San Diego, CA, June 2003.

Tran, C. A. Pollack, and I.Yu, 2003. "Revised Approach to Unpaved Road Dust Emissions Estimation – Results from Application in 13 Western States", Paper # 69832, 96th Annual Conference and Exhibition, Air and Waste Management Association, San Diego, CA, June 2003.

U.S. Environmental Protection Agency, 1995. "Compilation of Air Pollutant Emission Factors, Volume I: Stationary Point and Area Sources", AP-42, Fifth Edition, (Chapter 13: Miscellaneous Sources [available on the EPA website at http://www.epa.gov/ttn/chief/ap42/ch13/index.html])

Venkatram, A. and D.R. Fitz, 1998. "Measurement and modeling of PM10 and PM2.5 Emissions from Paved Roads in California", Final Report, Contract No. 94-336, California Air Resources Board, Monitoring and Laboratory Division, Sacramento CA.

Watson, J. G., and J. C. Chow, 2000. "Reconciling Urban Fugitive Dust Emissions Inventory and Ambient Source Contribution Estimates: Summary of Current Knowledge and Current Research", Report No. 6110.4D2 prepared for U.S. Environmental Protection Agency, Research Triangle Park, N.C., by Desert Research Institute, Reno, NV.

BIBLIOGRAPHY

Abu-Allaban, M.; Coulomb, W.; Gertler, A.W.; Pierson, W.R.; Rogers, C.F.; Sagebiel, J.C.; Tarnay, L. *Exhaust Particle Size Distribution Measurements at the Tuscarora Mountain Tunnel*. Aerosol Science and Technology, 2002; v.36:771-789.

Abu-Allaban, M.; Gillies, J.A.; Gertler, A.W.; Clayton, R.; Proffitt, D. *Determination of On-Road PM10 and PM2.5 Emission Rates Using Roadside Measurements.*

Austin, J. *Day-of-Week Patterns in Toxic Air Contaminants in Southern California*. JAWMA July, 2003 v.53:889-896.

Baum, M.M.; Kiyomiya, E.S.; Kumar, S.; Lappas, A.M.; Lord, H.C. *Multicomponent Remote Sensing of Vehicle Exhaust by Dispersive Adsorbtion Spectroscopy – Effect of Fuel Type and Catalyst Performance*. Env. Science & Technology, 2000, v.34:2851.

Baum, M.M.; Kiyomiya, E.S.; Kumar, S.; Lappas, A.M.; Kapinus, V.A.; Lord, H.C. *Multicomponent Remote Sensing of Vehicle Exhaust by Dispersive Adsorbtion Spectroscopy – Direct On-Road Ammonia Measurements.* Env. Science & Technology, 2000, v.34:2851.

Blanchard, C.L.; and Tanenbaum, S.J. *Differences Between Weekday and Weekend Air Pollutant Levels in Southern California*. JAWMA July, 2003 v.53:816-828.

Brewer, P.; Hornback, J. *VISTAS Analyses of Regional Haze in the Southeastern United States*. A&WMA conference paper.

Chen, L.-W.A.; Chow, J.C.; Doddridge, B.G.; Dickerson, R.R.; Ryan, W.F.; Mueller, P.K. *Analysis of a Summertime PM2.5 and Haze Episode in the Mid-Atlantic Region*.

Chinkin, L.R.; Coe, D.L.; Funk, T.H.; Hafner, H.R.; Roberts, P.T.; Ryan, P.A. *Weekday versus Weekend Activity Patterns for Ozone Precursor Emissions in California's South Coast Air Basin.* JAWMA July, 2003 v.53:829-843.

Chow, J.C. *Introduction to the A&WMA 2002 Critical Review Visibility: Science and Regulation*. JAWMA June, 2002 v.52:626-713.

Cowherd, C.; Gebhart, D.L. *Vegetative Capture of Dust from Unpaved Roads*. A&WMA conference paper.

Dittenhoefer, A.C.; Ellis, H.M.; Yousuf, A.A.; Hydari, N.H.; Bent, A.; Roy, S.; Hidy, G. *Projected Attainment Status of Each County in the U.S. with the PM2.5 National Ambient Air Quality Standards Based on 1999-2001 Monitoring Data and Strategies for Dealing with Nonattainment Designations*. A&WMA conference paper.

Durbin, T.D.; Wilson, R.D.; Norbeck, J.M.; Miller, J.W.; Huai, T.; Rhee, S.H. *Estimates of the Emission Rates of Ammonia from Light-duty Vehicles Using Standard Chassis Dynamometer Test Cycles*. Atmos. Environ., 2000 v.36:1475.

Durbin, T.D.; Smith, M.R.; Norbeck, J.M.; Truex, T.J. *Population Density, Particulate Emissions Characterization, and Impact on the Particulate Inventory of Smoking Vehicles in the South Coast Air Quality Management District*. JAWMA January, 1999 v.49:28-38.

Eisinger, D.S; Nanzetta, M.K.; Kear, T.P.; Niemeier, D.A.; O'Loughlin, R.M.; Brady, M.J. *Particulate Matter and Transportation Projects, and Analysis Protocol*. A&WMA conference paper.

Environment Canada, *Precursor Contributions to Ambient Fine Particulate Matter in Canada.*

Etyemezian, V.; Kuhn, H.; Gillies, J.; Green, M.; Pitchford, M.; Watson, J. *Vehicle-based Road Dust Emission Measurement – Part I: Methods and Calibration*. To be published in Atmos. Environ.

Etyemezian, V.; Gillies, J.; Kuhns, H.; Nikolic, D.; Gillette, D.; Seshadri, G.; Veranth, J.M. *Estimating Near-Field Removal of Fugitive Dust: The Regionally-Transporatble Fraction of PM10 Emissions from Unpaved Roads*. A&WMA conference paper.

Etyemezian, V.; Kuhn, H.; Gillies, J.; Chow, J.; Hendrickson, K.; McGown, M.; Pitchford, M. *Vehicle-based Road Dust Emission Measurement (III): Effect of Speed, Traffic Volume, Location, and Season on PM10 Road Dust Emissions in the Treasure Valley, ID.* To be published in Atmos. Environ.

Fraser, M.P.; Cass, G.R. *Detection of Excess Ammonia Emissions from In-use Vehicles and the Implications for Fine Particle Control*. Env. Science & Technology, 1998; v.32:1053.

Fujita, E.M.; Stockwell, W.R.; Campbell, D.E.; Keislar, R.E.; Lawson, D.R. *Evolution of the Magnitude and Spatial Extent of the Weekend Ozone Effect in California's South Coast Air Basin, 1981-2000*. JAWMA July, 2003 v.53:802-815.

Fujita, E.M.; Campbell, D.E.; Zielinska, B; Sagebiel, J.C.; Bowen, J.L.; Goliff, W.S.; Stockwell, W.R.; Lawson, D.R. *Diurnal and Weekday Variations in the Source Contributions of Ozone Precursor in California's South Coast Air Basin*. JAWMA July, 2003 v.53:844-863.

Gertler, A.W.; Gillies, J.A.; Pierson, W.R.; Rogers, C.F.; Sagebiel, J.C.; Abu-Allaban, M.; Coulombe, W.; Tarnay, L.; Cahill, T.A.; Grosjean, D. Grosjean, E. *Emissions from Diesel and Gasoline Engines Measured in Highway Tunnels*. Health Effects Institute No. 107, Jan. 2002. *Preprint Version*.

Gertler, A.W.; Gillies, J.A.; Pierson, W.R. *An Assessment of the Mobile Source Contribution to PM10 and PM2.5 in the United States*. Water, Air, and Soil Pollution, 2000; v.123:201-214.

Gertler, A.W. *Diesel vs. Gasoline Emissions: Does PM from Diesel or Gasoline Vehicles Dominate in the U.S.?* Draft Paper: DRI.

Gillies, J.A; Etyemezian, V.; Kuhns, H.; Nikolic, D.; Gillette, D.A. *Effect of Vehicle Characteristics on Unpaved Road Dust Emissions*; to be published.

Gillies, J.A; Gertler, A.W. *Comparison and Evaluation of Chemically Speciated Mobile Source PM2.5 Particulate Matter Profiles*. JAWMA August, 2000 v.50:1459-1480.
Gulf Coast Aerosol Research and Characterization Program (Houston Supersite) EPA Contract: R-82806201.

Ho, C. Jensen, G. *Transportation Conformity – 10 Years of Implementation Experience*. A&WMA conference paper.

Huess, J.M.; Kahlbaum, D.F.; Wolff, G.T. *Weekday/Weekend Ozone Differences: What Can We Learn From Them?* JAWMA July, 2003 v.53:772-788.

Kean, A.J.; Harley, R.A.; Littlejohn, D.; Kendall, G. *On-Road Measurement of Ammonia and Other Motor Vehicle Exhaust Emissions*. Env. Science & Technology, 2000; v.34:3535.

Kinney, P.L.; Aggarwal, M.; Northridge, M.E.; Janssen, N.A.H.; Shepard, P. *Airborne Concentrations of PM2.5 and Diesel Exhaust Particles on Harlem Sidewalks: A Community Based Pilot Study*. Environ. Health Perspectives v.108 no.3, March, 2000.

Kuhns, H.; Etyemezian, V.; Gillies, J.; Nicolic, D.; Ahonen, S.; Durham, C. *Spatial Variability of Unpaved Road Dust Emission Factors near El Paso, Texas*. A&WMA conference paper.

Labban, R.; Veranth, J.M.; Pardyjak, E.; Yin, F. Etyemezian, V. *Dust Emission from Unpaved Roads*. A&WMA conference paper.

Mangelson, N.F.; Lewis, L.; Joseph, J.M.; Wenxuan, C.; Machir, J.; Eatough, D.J.; Rees, L.B.; Wilkerson, T.; Jensen, D.J. *The Contribution of Sulfate and Nitrate to Atmospheric Fine Particles During Winter Inversion Fogs in Cache Valley, Utah*. JAWMA February, 1997 v. 47:167-175.

Matallebi, N.; Tran, H.; Croes, B.E.; Larsen, L.C. *Day-of-Week Patterns of Particulate Matter and Its Chemical Components at Selected Sites in California*. JAWMA July, 2003 v.53:876-888.

Odum, J.R.; Jungcamp, T.P.W.; Griffin, R.J.; Flagan, R.C.; Seinfeld, J.H. *The Atmospheric Aerosol-Forming Potential of Whole Gasoline Vapor*. Science, April, 1997 v.276:96-99.

Pace, T.G.; Cowherd, C. Estimating PM2.5 Transport Fraction Using Acreage-Weighted County Land Cover Characteristics – Example of Concept. A&WMA conference paper.

Pollack, Alison. *On-Road and Off-Road Mobile Source Emission Inventories for Regional Haze Modeling*. A&WMA conference paper.

Pun, B.K.; Seigneur, C. *Day-of-Week Behavior of Atmospheric Ozone in Three U.S. Cities.* JAWMA July, 2003 v.53:789-801.

Singh, R.B.; Huber, A.H. *Application of a Microscale Emission Factor Model for Particulate Matter (MicroFacPM) in Conjunction with CALINE4 Model*. A&WMA conference paper.

Winebrake, J.J.; Wang, M.Q.; He, D. *Toxic Emissions from Mobile Sources: A Total Fuel-Cycle Analysis for Conventional and Alternative Fuel Vehicles*. JAWMA July, 2001 v.51:1073-1086.

Yarwood, G.; Stoeckenius, T.E.; Heiken, J.G.; Dunker, A.L. *Modeling Weekday/Weekend Ozone Differences in the Los Angeles Region for 1997*. JAWMA July, 2003 v.53:864-875.

Key Words: PM2.5, secondary PM2.5, primary PM2.5, PM2.5 precursor compounds, mobile sources