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Combustion sources of particles: 1. Health relevance and source signatures

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Abstract

Combustion processes result in generation of a large number of particle and gaseous products that create health and environmental risks. Of particular importance are the very small particles that are emitted in large quantities from all the combustion sources, and that have been shown to be potentially more significant in terms of their impact on health than larger particles. To control and mitigate the particles with a view of health and environmental risk reduction, a good understanding is necessary of the relative and absolute contribution from the emission sources to the airborne concentrations. This understanding could only be achieved by developing source signature libraries through direct emission measurements from the sources on one hand, and by measuring particle concentrations in the air, and apportioning them to the specific local and distant sources using the signatures, on the other hand. This paper is a review of particle characteristics that are used as source signatures as well as their general advantages and limitations. The second part of the paper reviews source signatures of the most common combustion pollution sources.

Keywords: particulate matter, combustion, source signature, air pollution, emission source

1. Introduction

1.1 Combustion sources

Combustion sources could be classified into area or point sources, stationary or mobile sources, and outdoor or indoor sources. Outdoor combustion sources include stationary and mobile sources. Mobile sources are mainly motor vehicles, but also include aircraft and boats as well as small sources such as lawn mowers. Stationary sources are industrial plants, power plants, refineries, etc. The relative and absolute importance of these sources varies, and is a function of source strength, mixture of sources and population density in the vicinity of the sources.

Indoor combustion sources are related mainly to cooking, heating and tobacco smoking. The relative importance of these sources depends on the environment and lifestyle of the occupants. For example, there will be little contribution from indoor combustion sources in an indoor environment which does not require heating, where cooking is conducted using electric stoves, and where there are no smokers. On the other hand, environments with operating open fires or where cigarettes are smoked inside could have concentrations orders of magnitude higher than outdoor environments. Open fire burning presents a particularly severe problem in developing countries, where in many places it is the most affordable or the only available way of cooking. The impact of exposure due to indoor open fire burning is particularly high, as those who are most affected, are those who belong to susceptible groups (infants, sick, elderly), and at the same time those who spend a significant amount of time indoors.

The following combustion sources that have the most significant relative contribution to air pollution and result in exposures and risks to large populations will be discussed in this paper:

road transport, power plants and industrial combustion classified as industrial facilities, small combustion (domestic, commercial, public and agricultural combustion sources), environmental tobacco smoke and vegetation burning. Not considered here are sources which have small global contributions, or which are unique to specific local areas. Thus the sources not discussed include, for example, off-road transport, fire works displays or ritual or religious burning.

1.2 Emission products from the sources and their health relevance

Under ideal conditions, complete combustion of carbon would result only in generation of carbon dioxide (CO₂) and water vapour. Any products other than CO₂ are often called products of incomplete combustion and include particulate matter and gases. Particulate matter could be a mixture of solid particles and liquid droplets, which vary in concentration, composition (can contain various organic and inorganic compounds) and size distribution. A primary particle is a particle introduced from the source into the air in solid or liquid form, while a secondary particle is formed in the air by gas to particle conversion. An important characteristic of airborne particles is their size distribution as it strongly affects particle behavior and fate in atmospheric systems as well as deposition in the human respiratory tract, and determines the instrumentation to be used for particle detection. According to the most common definition, fine particles are those with an aerodynamic diameter smaller than 1 µm while ultra-fine particles are those below 0.1 µm. Accordingly, coarse particles are defined as being in the range above 1 µm (Willeke and Baron, 1993). The rationale behind this classification is, that one micrometer constitutes a natural division between particles which are emitted mainly from combustion processes and are smaller than particles which are generated from mechanical processes. Obviously this definition is still somewhat arbitrary, as nature itself does not provide a perfect division. The terminology that has

been used by the US Environmental Protection Agency (EPA) in the wording of the ambient air quality standards included $PM_{2.5}$ and PM_{10} mass concentrations. $PM_{2.5}$ refers to particles with aerodynamic diameters smaller than 2.5 μm , while PM_{10} refers to particles with aerodynamic diameters smaller than 10 μm (more precisely the definitions specify the inlet cut-offs for which 50% efficiency is obtained for these sizes). Fine particles (or $PM_{2.5}$ fraction) typically contain soot, acid condensates, sulfates and nitrates, as well as a major fraction of trace metals and other toxins present in the air (Wei et al., 1999). Fine particles are generated mainly from combustion processes and photochemical reactions followed by gas to particle conversion. Coarse particles are generated from mechanical processes including grinding, breaking and wear of crystalline material including dust re-suspension. Gaseous emissions from combustion sources include inorganic and organic gases and vapors. The main gaseous emissions include carbon monoxide (CO), carbon dioxide (CO_2), nitrogen oxides (NO_x), sulfur dioxide (SO_2), hydrocarbons (HC), and water vapor.

In recent years strong scientific evidence has been emerging that adverse health effects due to exposure to airborne particulate matter and specifically to fine particles could be more significant than due to exposure to many other airborne pollutants (Vedal, 1997). The first evidence of this came from the Harvard Six City Studies (Dockery et al., 1993) and since then many more studies have been initiated and completed to support these findings. Elevated levels of particle air pollution have been associated with decreased lung function, increased respiratory symptoms such as cough, shortness of breath, wheezing and asthma attacks, as well as chronic obstructive pulmonary disease, cardiovascular diseases and lung cancer. The size of airborne particles is significant, as this determines in which parts of the respiratory tract the particles are deposited, as

well as how rapidly and the manner in which they are cleared. Small airborne pollutant particles have small inertia and therefore are poorly impacted before entering the alveoli region of the lung; while in the alveoli, the probability of deposition is very high due to their high diffusion coefficient.

It is however not only the number of particles in the particular size range which is important, but also the composition of particles. The composition may determine in what way the respiratory tract reacts, or the body responds. Some particles can act as carriers of adsorbed chemicals or gases which can act as triggers for various health effects. Recent laboratory studies indicated that fine particles could be more significant; and particle number could be more significant than mass; and even non-toxic particles such as TiO_2 affect laboratory animals (Oberdorster et al., 1995).

1.3 Source apportionment and relative contributions to public exposure

Quantification of emissions from individual pollution sources and generation of emission inventories at local, regional and national levels is important for developing appropriate management and control strategies in relation to air quality. One aim of pollution concentration and emission measurements should thus be to provide relevant information that would enable a complete inventory time series to be compiled for all particle size ranges. To date not enough measurements have been conducted and there is very little data available to compile such inventories for places where deteriorated air quality, or potential for deterioration, requires control actions to be taken.

One example of a completed inventory is the assessment conducted by the Airborne Particles Expert Group on behalf of the Department of the Environment, Transport and the Regions, the Welsh Office, the Scottish Office and the Department of the Environment (Northern Ireland) (Airborne Particle Experts Group, 1999). An approach was taken such that inventories for $PM_{2.5}$, PM_1 and $PM_{0.1}$ were estimated based on PM_{10} monitoring data and from the mass fractions in these size ranges available for different emission sources and fuel types. While only 33 particle spectra were investigated, the report provides a comprehensive analysis of emission trends for the years 1970 to 1996. Analyzing the contributions of individual combustion sources to particle emission inventories it can be seen that in all size fractions motor vehicle emissions are the major contributor out of all other combustion and non-combustion sources in urban areas. With decreasing particle size the contribution of road transport to the total emissions increases and for $PM_{0.1}$ reaches 60%. Contributions from other combustion sources tend to decrease with decreasing particle size. One of the conclusions from the data presented in the report is, that there has been a significant decrease in emissions in the PM_{10} and $PM_{2.5}$ ranges during the period of time from 1970 to 1996, less in the PM_1 range and very little in the $PM_{0.1}$ range. This could be related to the increase in the number of vehicles used, as well as to the lack of strategies for decreasing emissions of the ultra fine fraction of particles.

2. Source signatures

2.1 General classifications of source signatures

A source signature or fingerprint consists of the physical and/or chemical characteristics of the emissions, which are specific and at best unique for that source. Availability of such signatures is essential for the determination of the contributions from specific sources, which in turn enables

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developing of emission inventories. The complexity related to source apportionment is that on one hand ambient air contains a dynamic mixture of pollutants emitted from various sources, a mixture which undergoes continuous change in time as the interactions between the pollutants take place and as the components of the mixture are removed from the air due to the presence of various sinks. On the other hand, it is only rarely that specific emission characteristics are unique to a particular source. More often emissions from some other sources display some of these characteristics as well. Source signatures include:

- specific size distribution of the particle phase
- specific source profile of organic compounds or elements
- specific ratios of compounds, elements or isotopes

In addition to the source signatures, certain elements or compounds have been used as markers of emissions from certain sources. A suitable marker should be: (1) unique or nearly unique to the emissions from the source under consideration, (2) similar in emission rates for a variety of the same type of fuels, (3) easily detected in air at low concentrations, and (4) present in consistent proportion to compounds that have effects on human health. Additionally, an ideal marker should also be easily (in real-time), accurately, and cost-effectively measurable.

2.2 Physical aspects of particle source signatures

Physical aspects of signatures are mainly the number or mass size distribution, density and shape of airborne particles. The characteristics that are most applicable as source signatures are number or mass size distribution. Particles generated by most sources have a lognormal size distribution that can be characterized for example, by count median diameter (CMD) and geometric standard

deviation. When a single pollution source is investigated and when it operates under steady state conditions (for example steady parameters of the combustion process), the size distribution obtained is likely to have one distinctive peak and sometimes additional, much smaller peaks. Those peaks are called modes of the distribution. In the case of a mixture of particles from various sources and of different size distributions, the measured size distribution may or may not display individual peaks from the contributing sources, and thus may or may not be used for source identification. In many cases, however, of the particle size distribution can be a very useful tool in source characterization.

Following formation, the highly dynamic mixture of combustion compounds undergoes a range of physico-chemical processes, which change their chemical composition, physical characteristics and concentration in the air. Particles measured away from the emission site, or particles generated indoors and measured some time after emission would have different characteristics to those displayed immediately after formation. The residence time of the combustion compounds in the air depends on the processes they are involved in and varies from seconds or minutes to days or weeks. Larger particles (of a micrometer size range in aerodynamic diameter and more) are removed from the atmosphere mainly through gravitational settling, while smaller particles by wash out or diffusional deposition. For example, at a distance of 20 km from an extensive fire, while the sub-micrometer particle concentration is significantly elevated above the background level, there is no increase in particles over one micrometer, indicating the coarse particles have been removed from the air plume, while travelling over this distance (WHO, 1999).

Particle distributions can be presented as number or mass distributions. In terms of number, the vast majority of airborne particles are in the ultra fine range. For example, in an urban environment where motor vehicle emissions are a dominant pollution source, over 80% of particulate matter in terms of number is in the ultra fine range (Morawska et al., 1998a). The total mass of these particles is, however, often insignificant in comparison with the mass of a small number of large particles with which most of the mass of airborne particles is associated. This relationship between particle number and mass is presented in Figure 1 using an example of a typical measured urban air particle size distribution (Morawska 2000).

Figures 2 and 3 present size distributions of emissions from diesel vehicles, spark ignition vehicles and environmental tobacco smoke (ETS) respectively. Analyzing the distributions in Figure 2 it can be concluded that the Count Median Diameter (CMD) of diesel emissions is about twice the size of those for gasoline emissions. The distributions presented are examples only, and other vehicles or other tobacco smoking situations will result in distributions that will vary from the ones presented here. This would depend on various aspects of the combustion process, engine characteristics, fuel used, smoking pattern, etc. The distributions presented illustrate the point that different emission sources are characterized by different size distributions that, however, are not unique to these particle sources alone. If, however, the source has been characterized in terms of its size distribution, this information can help identify its contribution to particle concentrations in ambient air.

2.3 Chemical aspects of signatures

Elemental signatures

Combustion of different types of fuels results in emissions of different trace elements, which are present in the fuel material. In most cases there is not just one specific element that is related to the combustion of a particular fuel, but a source profile of elements. Table 1 presents examples of the most common source profiles of elements related to specific combustion sources. For comparison, the crustal elements include Mg, Ca, Al, K, Sc, Fe and Mn.

Trace elements are often co-emitted with other pollutants, which can be more or less volatile, such as many hydrocarbons. Since most of the trace elements are non-volatile, associated with ultra fine particles and less prone to chemical transformations, they tend to undergo long range atmospheric transport and remain in the form they were emitted. To follow the trace elements back to their potential emission sources, air parcel movement in the form of calculated backward trajectories are combined with the measured concentrations using various modeling methods (e.g. Gao et al., 1996). Whether elemental signatures can provide meaningful qualitative and quantitative source apportionment will depend on how independent the regional signatures are, as well as on the variability and stability during long distance transport. Elemental concentrations could be highly variable, therefore the concentrations alone are not considered reliable regional tracers. Use of elemental signatures to apportion aerosols into major regional sources requires an understanding of the behavior of the trace element bearing aerosols during transport, and also seasonal variations of the signatures. While industrial outputs are not generally seasonally dependent, airborne concentrations of crustal material are greatly reduced during winter in areas covered with snow.

Elemental ratios

The effects of physical parameters can be minimized by using a normalization procedure for normalization of concentrations of the elements. The elements which are often used for normalization are: V* and Se (* denotes non-crustal component). For example, the Mn*/V* ratio could be a useful parameter for distinguishing between aerosols from oil burning and those from the coal burning. For aerosols from oil burning this ratio is $\ll 1$, while for aerosols from coal burning it is $\gg 1$ (Dutkiewicz et al., 1987). In general, any element/V* ratio can be used for this purpose and Se/V* ratios are particularly useful.

Characterization of chemical form

In some cases it is not just the presence of a specific element that provides information about its source, but the chemical form in which the element is present. Speciation is the process of identification of various chemical compositions of an element. Different chemical forms of an element have different physical and chemical properties. Processes such as environmental transport and bioavailability are species dependent. An example of this are lead compounds and in particular: lead from concentrate haulage as well as dust from smelter storage piles would be unaltered galena (PbS); concentrate roasting is likely to produce lead sulfates and oxides (PbSO₄, PbO); and blast furnace emissions could contain lead metal and oxides (Clevenger et al., 1991).

Selective extraction is one method currently being used to determine chemical forms. There are a few problems with this method: it is influenced by factors such as the choice of reagents, extraction sequence, time of extraction, and the ratio of the extractant to sample (Clevenger et al., 1991). There are also analytical problems such as selective readsorption and incomplete

distribution of a metal among various fractions. Therefore, a thorough validation of the extraction method is necessary for each sample type.

Isotope ratios

In some cases it is not the element itself, which could provide answers to source apportionment, but the isotope ratio(s) for this element. This can be illustrated on the example of characterization of lead sources using ratios of stable lead isotopes. Important combustion sources of lead are leaded gasoline, coal combustion and some industrial emissions.

The amount of ^{206}Pb , ^{207}Pb , and ^{208}Pb , in the earth's crust gradually changes with time due to the change in supply from the radioactive decay of ^{238}U , ^{235}U , and ^{232}Th , respectively. Therefore, each lead containing ore has different lead isotope ratios corresponding to when the ore was formed and its geological conditions. By using these differences, the origin of the lead found in environmental samples can be estimated (Mukul et al., 1993). The limitation of this method, however, is that any given isotope ratio measured in environmental samples can be constructed by the various types of mixing of more than two kinds of isotope ratios of lead sources.

Other isotope ratios used commonly and associated with similar advantages and limitations to the ones described above include $\text{C}^{14}/\text{C}^{12}$ and S isotope ratios.

Organic compounds

The most common, although not the only organic compounds emitted from combustion processes are hydrocarbons. Many investigations were conducted to determine concentration levels and speciation of organic compounds emitted by various types of sources. The reasons for

the interest in organic compounds are twofold: (1) some of the organic compounds are toxic or carcinogenic, such as benzene or 1,3-butadiene, and (2) they play an important role as precursors in photochemical process of ozone generation.

One class of compounds contained in the organic fraction of the fine particulate matter are polynuclear aromatic hydrocarbons (PAH), some of which are strongly carcinogenic. A compilation of the health effects of selected non-heterocyclic PAH has recently been published by WHO (1998). The PAHs considered included acenaphthene, acenaphthylene, anthracene, benzo[a]pyrene, benz[a]anthracene, dibenz[a,h]anthracene, fluoranthene, naphthalene, phenanthrene, and pyrene. The most studied PAH is benzo[a]pyrene (B[a]P) one of the best established human carcinogens. In low-oxygen environments, such as occurs inside the flame envelope in the fuel-rich region of the flame structure, PAH compounds are synthesized from carbon fragments into large molecular structures. If the temperature does not remain adequate sufficiently long to decompose compounds upon exiting from the flame zone, they are released into the free atmosphere and condense or are adsorbed onto the surface of particles. Many different combustion processes are known to produce PAH compounds.

Volatile and semi-volatile organic compounds can be used as markers of various combustion processes. As with the elemental markers, only very few organic markers are unique to specific combustion sources, while most of them are emitted in varied proportions from a number of combustion processes. Cass (1998) presented a review of different organic compounds as tracers for specific combustion sources. For example semi-volatile aliphatic hydrocarbons (ALIsv) present in ambient air are n-C₁₉ , n-C₂₀ , n-C₂₄ , n-C₂₅ , while particle related aliphatic

hydrocarbons (ALIp) are n-C₂₁, n-C₂₂, n-C₂₉, n-C₃₁, (Colombo et al., 1999). The aliphatic signal of diesel and gasoline engines consists of a narrow band of C₁₅₋₂₇ n-alkanes maximizing at C₂₀₋₂₁, and a very similar pattern to lubricating oils n-C₁₃₋₂₇, maximizing at C₁₉. The signal of diesel fuel has a broader spectrum extending to n-C₃₃, with a higher proportion of lower molecular weight components (n-C₁₀₋₂₂, maximizing at C₁₉) (Simoneit, 1985). Table 2 presents a summary of the most common organic compound emitted by a number of combustion sources. This table was compiled from the summary presented by Cass (1998).

Determination of the concentrations of the atmospheric hydrocarbons is conducted through a three-step process: (i) collection, (ii) speciation, and (iii) detection. The most important aspects of each of these steps are described by Westberg and Zimmerman (1993). In particular the most common method for speciation is gas chromatography, while detection is conducted using flame ionization technique, mass spectrometer (MS), atomic emission (AED-atomic emission detector) or special-purpose detectors, including ion mobility detector or mercuric oxide reduction detectors.

Methods used for chemical analyses

The most commonly used analytical techniques available for analyses of the composition of atmospheric particulate matter can be grouped into the following classes (Willeke and Baron, 1993):

- Elemental analyses by non-destructive techniques: X-ray Fluorescence Analysis, proton-induced X-ray Emission Analysis, and Instrumental Neutron Activation Analysis.

- Elemental analyses by destructive techniques: Inductively Coupled Plasma Emission Spectroscopy, Atomic Absorption Spectroscopy.
- Carbon determination: Combustion to CO₂ with several quantification options (total carbon), Selective pyrolysis (and/or combustion), light absorption for elemental carbon with organic carbon by difference.
- Water-extractable anion and cation analysis (ion chromatography) for: sulfate and nitrates, ammonium ions

Well established methods available for single particle analysis include: light microscopy; electron beam analysis; laser microscope mass spectrometry (LMMS); secondary-ion mass spectrometry (SIMS); Raman microprobe; infra-red (IR) microscopy. Principles of the operation, applications as well as limitations of the above methods are discussed in the literature (e.g. Willeke and Baron, 1993) and will not be further discussed here. The new developments in this area target real-time instrumentation that could be applied in field measurements. An example of this is an aerosols time-of-flight mass spectrometer that provides single particle size and composition measurements (Gard et al., 1997).

2.4 Relation between particle emissions and gaseous emissions

The relation between particle emissions and gaseous emissions can be used in some cases for identification of emission sources and their contributions to airborne pollutant concentrations. In general, ratios between ambient concentrations of particulate matter and gases such as CO, NO_x for example are variable, depicting contributions from various sources. When only one source is present the ratios are more uniform and, when regression analyses were conducted for

each monitoring site independently and for each season, a high degree of correlation was for example shown between PM_{10} and $PM_{2.5}$ as well as between NO_x and PM_{10} or $PM_{2.5}$ (Airborne Particle Experts Group, 1999).

There is also an indication that there is a scope for particle number to be used as a real time metric of local vehicle emissions. Comparison with existing PM_{10} data and CO and NO_2 gaseous concentrations may offer a route to further discriminate between diesel and gasoline emissions, as may more accurate particle size data (Airborne Particle Experts Group, 1999). However, there is not enough information about the long term temporal and spatial distributions of these emissions under varying weather conditions.

2.5 Signatures of specific sources

Road transport

Diesel emissions. Diesel exhaust particles are mostly submicrometer agglomerates of carbonaceous spherical particles with larger particles containing up to 4000 individual spherical particles clustered as agglomerates up to 30 μm (e.g. Kittelson et al., 1978). A significant proportion of diesel emission particles have aerodynamic diameters smaller than 0.1 μm . These particles are primarily elemental carbon, but also contain adsorbed or condensed hydrocarbons, hydrocarbon derivatives, sulfur compounds and other materials (Lipkea et al., 1979). Solvent extractable organic components of diesel aerosols represent 5 - 40% of the particle mass depending on the fuel and the operating conditions (engine speed, power, torque, temperature) of the vehicle (Hare et al., 1976). Associated with particles (especially fine and ultra fine) are many toxins, trace elements and also carcinogenic compounds. An example of these is 3-

nitrobenzanthrone, a nitrated polycyclic aromatic hydrocarbon (nitro-PAH), which produced the highest score ever reported in an Ames test, a standard measure of the cancer-causing potential of toxic chemicals.

Spark ignition emissions. The main gaseous emissions from spark ignition engines (unleaded gasoline or natural gas operated) include hydrocarbons (HC), CO, NO_x, CO₂, SO₂ and water vapour. The particles are mostly carbonaceous spherical submicrometer agglomerates smaller than diesel particles (Concawe Report, 1998), ranging from 0.01-0.08 µm, consisting of a carbon core with various associated organic compounds. Particles from CNG emissions range from 0.01-0.7 µm, with the majority being between 0.020 and 0.060 µm. (Ristovski et al., 1999). The main components of the particle phase include soot, ash, trace elements such as lead, iron, chlorine and bromine, organic compounds and low-to-medium boiling fraction of engine oil (Zinbo et al., 1995). Lubricating oil and other fuel hydrocarbons may also contribute to particle emissions. The sulfate particles present in gasoline engine emissions are mainly from catalyst equipped vehicles utilizing unleaded gasoline (Brodowicz et al., 1993). The common organic compounds are PAHs, such as pyrene, chrysene, benzo[a]pyrene. The semi-volatile fraction of the emissions can be found either in vapour or in particle phases.

Investigations of the elemental composition of particles emitted by a gasoline operated vehicle, as well as of engine oil used, were conducted by Ristovski et al., (1999). The study showed that the particles were clusters, made of spherical carbon particles of 0.02 µm diameter, observed in emissions for speeds up to 60 km.h⁻¹. For higher speeds formation of clusters was not observed.

Concentrations of the following trace elements were measured in gasoline engine emissions:

boron, calcium, titanium, chromium, manganese, iron, cobalt, nickel, copper, zinc, cadmium, barium, and lead. Iron particles were observed in very small size below 0.02 μm . Calcium and zinc, as the most abundant elements besides Fe, were observed in larger particle sizes around 0.1 μm . It is interesting to note that particles of pure Zn were rarely observed. Zn was usually in larger particles in a mixture with other elements. The most abundant elements were Fe, Ca, and Zn originating from the additives in lubricating oil. It is also interesting to note that although particle concentrations increased three orders of magnitude from 40 to 120 $\text{km}\cdot\text{h}^{-1}$, emissions of metals did not significantly increase. This would indicate that most of the particle emissions at higher loads come from the unburned fuel and consists mainly of carbon either in elemental or organic form.

Industrial facilities

A large variety of industrial facilities involve the combustion of fossil fuels or biomass. Examples of these combustion sources include steam/electric generating plants, industrial boilers, steel mills, and commercial and domestic combustion units. Coal, fuel oil, and natural gas are the major fossil fuels used by these sources. Liquefied petroleum gas (LPG) fuels are also used in relatively small quantities. Coal, oil, and natural gas currently supply about 95% of the total thermal energy consumed in the United States. Biomass power generation is receiving increasing attention because of its ability to fix carbon dioxide, a major greenhouse gas in the atmosphere. In some villages of China (and perhaps other developing countries as well), crop residues have been gradually used to synthesize producer gases and generate power, resulting from the fact that as farmers get more affluent, they are becoming less willing to directly burn dirty biomass residues for cooking and heating. The village-scale biomass-fired power plants and biomass gasification plants may become a significant emerging source of air pollution.

Power generation, process heating, and space heating are some of the largest fuel combustion sources of particulate emissions. Other industrial facilities generating particulate emissions include incinerators, chemical plants, metal smelters, petroleum refining plants, lime kilns, charcoal making kilns, paper mills.

Although the particles emitted from large-scale industrial combustion sources are all predominantly in the fine particle range, their chemical compositions varies substantially depending largely upon fuel types and boiler or furnace operating conditions. This can be illustrated using the fractional abundances of the elements and chemical compounds in the particulate emissions. Examples are shown in Table 3.

Industrial combustion sources are often found to be responsible for trace amounts of heavy metals and PAHs. Dozens of heavy metals have been identified in emissions of municipal waste incinerators, industrial waste sludge incinerators, oil-fired boilers, and coal-fired boilers (Buchholz and Landsberger, 1995; Miller et al., 1996; Ge et al., 2001). It is reported that metal emissions from incineration of solid wastes are impacted by compositions of feedstocks and that the chemical form of the metals depends on the operating conditions of the incinerator (Wey et al., 1999).

Since PAHs, present in the atmosphere in both gas and particulate phase, are produced by high temperature reactions such as incomplete combustion and pyrolysis of fossil fuels and other organic matters, it is not surprising to find PAHs in the emissions of all combustion sources. However, the following are relatively more important industrial combustion sources of PAHs.

(1) The petroleum industry: PAHs are produced mainly during the catalytic cracking process by which organic molecules in crude oil are broken down into lighter compounds used in the manufacture of gasoline, heating oil, aviation fuel or kerosene. (2) The carbon industry: PAHs are produced during the carbon black production process involving the high-temperature pyrolysis of aromatic liquid hydrocarbons. (Carbon black is a major industrial chemical used primarily as a reinforcing agent in rubber products such as tires.) (Nikolaou et al., 1984). (3) Coal-gas and coke plants. (4) ~~Aluminum plants.~~ (5) Refuse burning emissions: The intentional combustion of solid wastes as a method of disposal as well as accidental or naturally occurring combustion processes. PAHs were found in the stack gases and mostly in fly ash and solid residues of municipal and commercial incinerators as well as the burning of municipal and agricultural refuse and scrap automobile parts. Three PAHs, phenanthrene (PhA), fluoranthene (FluA), and pyrene (Pyr) were detected in great quantities in a laboratory simulation study of industrial waste incineration (Wei and Wu, 1997). (6) Oil- and coal-fired boilers (Miller et al., 1996).

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Compared to PAHs, other organic constituents of particles emitted from combustion sources are less known, and rarely measured. This is perhaps due to the better understood health relevance of PAHs as they are carcinogens and mutagens. A study of Ohio River Valley atmospheric aerosols indicates that coal-fired and oil-fired power plants were the principal source of carbonaceous aerosol (Huntzicker et al., 1986). Interestingly, a laboratory simulation study found that both carbon and heavy metals in the fly ash particles could greatly enhance the formation of PAHs. The suggested mechanism is that carbon enhances the adsorption capacity of the fly ash while the metals catalyze the formation of PAHs (Wey et al., 1998).

Small combustion devices

Small combustion devices such as household cooking stoves and space heaters are counted in billions throughout the world, providing the very basic household needs of heat. The types of fuels and stoves used, however, are very unevenly distributed between developed and developing countries and between rural and urban households. While a great number of households in developed countries have enjoyed for decades the convenient use of modern clean gas or liquid fuels or electricity, about half the world's population still cook and/or heat daily using dirty biomass fuels (e.g., animal dung, crop residue, wood, charcoal). The levels of particles, PAHs, CO, and other air pollutants found in the kitchens of developing-country villages are orders of magnitude above Western urban levels or relevant standards (Smith, 1986; Zhang et al., 2000; Zhang and Smith, 1996). In urban and rural areas of some developing countries such as China and South Africa, coal is one of the major household fuels. In general, because the household sources emit directly into the spaces and at the times of human occupancy, exposures to certain air pollutants derived from these small sources are often greater than those derived from large outdoor sources (Smith, 1993; Zhang et al., 1999, 2000; Saksena et al., 1992).

Raiyani et al. investigated emissions from burning several biomass fuels and coal in cooking stoves. The fuels tested included cattle dung, wood, crop residues, low-quality charcoals, and coal. The study revealed that 50-80% of total suspended particles (TSP) emissions from these cooking stoves were in a respirable fraction of $\leq 2\mu\text{m}$ size and that a large amount of the PAHs (>75%) were found in this fraction (Raiyani et al., 1993).

Since residential wood burning (for space heating or aesthetic purposes) is also common in the USA, a number of studies there have characterized the emissions from residential wood burning stoves. The studies reported that: (1) the particle mass distribution from wood (pine, oak, eucalyptus) combustion have a single mode at approximately 0.1 – 0.2 μm (Kleeman et al., 1999), (2) the particles are compact structures with fractal-like dimensions close to three and contained low mass fractions of volatile compounds (Hueglin et al., 1997), and (3) that operating conditions such as amount of air supply had a strong impact on the particle size distribution and the emission of particle-bound PAHs (Hueglin et al., 1997).

Particles from other small combustion sources are also in the sub-micrometer fraction. Natural gas, propane, and candle flames generated particles between 0.01 to 0.1 μm and meat charbroiling shows a major peak in the particle mass distribution at 0.1-0.2 μm with some material present at larger particle size but not larger than 1.0 μm (Kleeman et al., 1999). These aerosol particles initially generated through the combustion can grow hygroscopically 10% to 120%, depending on initial particle size and its origin (Li and Hopke, 1993).

The emissions from wood burning stoves were found to be acidic ($\text{pH} = 2.8\text{-}4.2$) (Burnet et al., 1986). Organic compounds were the dominant components of wood smoke and meat charbroiling smoke. Noticeable elemental carbon was found in wood smoke as well as measurable quantity of Na, K, Fe, Br, Cl, nitrate, sulfate, and ammonium. Statistically significant amounts of Na, Al, K, Sr, Ba, Cl, nitrate, sulfate were found in meat charbroiling emissions (Kleeman et al., 1999).

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High concentrations of PAHs have been found in soot generated from wood burning stoves and coal burning stoves (Mumford et al., 1987). Although PAHs have also been found in gasoline soot and diesel soot, the relative abundance of individual PAH species may be different for different types of soot. This makes it possible to use PAHs as source signatures in receptor modeling for residential wood and coal combustion (Li and Kamens, 1993). Guaiacol and its derivatives (e.g., 4-methylguaiacol, 4-ethylguaiacol), however, result solely from the pyrolysis of wood lignin. Guaiacol and most of its derivatives appear to be relatively stable in the atmosphere and therefore these compounds can serve as unique tracers of wood (Hawthorne et al., 1992).

Environmental tobacco smoke

Environmental tobacco smoke (ETS) is one of the most common indoor pollutants. ETS is a mixture of two components: mainstream smoke drawn through the tobacco, taken in and exhaled by the smoker, and sidestream smoke, which is emitted by the smoldering cigarette between puffs. Exposure by non-smokers - passive smoking - is of great concern as it is an involuntary risk, often incurred by the most susceptible members of society, unborn children, infants and young children. Over 4000 compounds have been identified in ETS, the most important of them being nicotine, acetone, benzene, phenol, toluene and B[a]P (Kleeman et al., 1999).

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A number of markers have been used in the past to represent ETS concentrations in both field and chamber studies. Nicotine, carbon monoxide (CO), 3-ethenylpyridine, nitrogen oxides, pyridine, aldehydes, acrolein, benzene, toluene and several other compounds have been used or have been suggested for use as markers for vapour phase constituents of ETS. Respirable

suspended particulate matter (RSP) (Leaderer and Hammond, 1991), solanesol, N-nitrosamines, cotinine, chromium, potassium are among the air contaminants used as markers for particle phase constituents of ETS. Most commonly, RSP, CO and nicotine are utilized as markers of ETS (Rando et al., 1992).

It is considered that the only markers used that may be related to actual exposure to ETS are nicotine and RSP concentrations. Both of these tracers, however, have potential problems. The use of nicotine as a marker of ETS is complicated by the fact that nicotine is found primarily in the gas phase (90%), making it a relatively poor particle marker (Eatough et al., 1989). Furthermore, gas phase nicotine is strongly basic and is removed from indoor environments at a faster rate than particle-phase nicotine or the particle portion of ETS. Thus, the concentration of gas-phase nicotine may underestimate exposure to the particle phase of ETS (Eatough et al., 1989). In addition, the fraction of nicotine in ETS varies with measurement conditions. For example, 5-10% of ETS nicotine was found in the particle phase in a controlled atmosphere, while 20% was found in field environments (Eatough et al., 1989). The problem associated with the use of RSP as a marker of ETS is that it is not unique to ETS. Thus, using RSP may overestimate ETS exposure. In many cases though, the elevated RSP level is significantly higher from ETS than from other sources.

3-Ethenylpyridine (3-EP) and solanesol are currently considered the best available ETS markers for the vapour and particulate phases, respectively (Ogden et al., 1996). However, 3-ethenylpyridine has been criticized as an ETS marker based on assertions that airborne concentrations do not increase with source strength (ie. with the number of cigarettes smoked)

and that the methods for 3-EP determination do not possess adequate sensitivity (Ogden et al., 1996). The utilization of solanesol as a marker of ETS is complicated by the fact that determination of solanesol is not simple. It involves extraction from a filter to a solution with a recovery of about 60-90% and samples are then analyzed by gas chromatography (GC) and supercritical fluid chromatography (Tang et al., 1990).

RSP, CO and NO_x are the only markers for which measurement can be performed on a real-time basis with existing commercial equipment. However, as was explained above, none of them is specific to ETS. The ratio of CO to RSP in ETS is about 0.2-0.3 mol CO/g RSP (Eatough et al., 1988). Yet even in environments where the major source of particulate matter is smoking, such as taverns, discos, bus terminals and restaurants, the ratio of CO to RSP is generally higher than that seen in controlled chamber experiments, varying from 0.4 to 1.5 and averaging 0.9 mol CO/g RSP (Eatough et al., 1989). Clearly, the majority of CO in all these environments comes from sources other than ETS. Similarly, the ratio of NO_x to RSP from values comparable to that found in ETS to ratios which are higher by factors of up to 10 (Eatough et al., 1989). These results show that CO and NO_x concentrations will significantly overestimate exposure to ETS.

Deleted: The problem associated with the use of RSP as a marker of ETS was discussed earlier in the text. The use of CO as an ETS marker has been criticised because it is non-specific to ETS. Comparison of the chemical composition of ETS in chamber experiments and the relationship between CO concentrations and other constituents of ETS in indoor environments suggests that the majority of CO in indoor environments comes from sources other than ETS.

Deleted: The same ratio of CO to RSP in a variety of homes, schools and offices where smoking occurred at modest levels, was showed to vary from 0.4 to 6 with an average of 2 (Eatough et al., 1989).

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Vegetation burning

Vegetation burning includes controlled burning, uncontrolled fires, as well as burning for the purpose of heating and cooking. It seriously affects many parts of the world: uncontrolled fires and prescribed burning occurs on regular basis in many parts of South Asia, Africa, South America and Australia (WHO, 1999). A large number of people are exposed to air pollution from the fires, and while the pollution from forest fires has episodic nature, its effects due to high

concentrations of pollutants could be quite serious. The most significant pollutants released in the process of vegetation combustion include particulate matter, semi-volatile and volatile organic compounds including polynuclear aromatic hydrocarbons, carbon monoxide, aldehydes and organic acids. From the health point of view, mainly the particles and also to some extent PAHs are considered to be important due the elevated concentrations at which they occur (WHO, 1999).

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The majority of particles emitted from biomass burning are ultra fine, with only a small fraction in the larger size range, while most of the mass is found in particles less than 2.5 μm in aerodynamic diameter. The size distribution of particles is usually bimodal with a fine-particle mode (mass median aerodynamic diameter (MMAD) 0.3 μm) and a coarse particle mode (MMAD 10 μm). Fine particles are produced during the combustion of organic material and larger particles are entrained into the smoke column as a result of the turbulence and buoyancy generated by the fire. The smaller fine particles consist of organic carbon (60 to 70 %) and graphitic carbon (2 to 15 %), and the remainder is inorganic ash material (Ward and Hardy, 1989).

Combustion conditions of wild fires are considered to be similar to those for prescribed fires. For low-intensity fires, the ratio of benzo[a]pyrene to particulate matter is higher by almost 2 orders of magnitude over that for high intensity fires (McMahon and Tsoukalas, 1978). This can be related to experiments conducted with wood stoves, in which a relationship was established between burning rate and PAH emission. Specifically, as the burning rate increased, total organic emissions decreased, but the proportion of PAH compounds increased. De Angelis et al. (1980)

found the PAH emission rate to be highest over a temperature range of 500 to 800°C that is consistent with the low- intensity backing fire.

Correlation of concentration of toxic air compounds to those of CO, CH₄, and PM_{2.5} has proved to be an effective way of estimating the release of a number of compounds (McKenzie et al., 1995). This method, however, has some shortcomings. For example, ratios of B[a]P to CO and/or to PM for different fuel types show a significant difference between flaming and smoldering combustion and fuel type. There is almost an order of magnitude difference between emission ratios of B[a]P to CO for flaming in comparison to smoldering ratios. An average weighted emission ratio can be calculated based on the percentage of fuel consumed by the respective phase of combustion producing the emissions. This can be done by assuming, for example, that the emissions along the fire line consist of 10% from vegetation consumed during the flaming phase, 70% for the first smoldering phase and 20% for the final smoldering phase. On the other hand, emissions released through flaming combustion are generally accompanied by the release of significant heat, which transports to higher altitudes the emissions through convection forces acting on the smoke plume. Most of the emissions near the surface may be produced through smoldering combustion. It is recommended that emission ratios for smoldering combustion are used for assessing exposure, except for those conditions where 75 to 80% or more of the fuel is consumed through flaming combustion.

2.6 Summary of current and future trends in source signature application

Particles that are emitted from combustion sources are in general very small, containing a large number of trace elements and compounds of organic and inorganic nature. In recent years

scientific evidence has been emerging that these very small particles could be more significant from the point of view of health than the larger particles or gaseous pollutants. To control and mitigate particle emissions with a view of health and environmental risk reduction, a good understanding is necessary of the relative and absolute contribution from various emission sources. This understanding could only be achieved by developing source signature libraries through direct emission measurements from the sources on one hand, and by measuring particle concentrations in the air, and apportioning them to the specific local and distant sources using the signatures, on the other hand. The latter is a particularly complex process as ambient air contains a dynamic mixture of pollutants emitted from various sources, undergoing continuous change in time due to the interactions taking place as well as the removal from the air due to the presence of various sinks. Current and future trends in source signature application could be summarized as follows:

- Only rarely specific emission characteristics are unique to a particular source. Usually emissions from other sources display some of these characteristics as well. Thus, a common practice is to take a holistic approach to source signatures, and to conduct source characterization based not only on one aspect of the signatures but on the whole body of information available on emission characteristics and the emission and post-emission processes.
- All the methods available for source signature measurements are complex and costly. Only a few of them provide information in real time (for example size distribution measurements of particles), most require lengthy laboratory analyses. It is unlikely that major simplifications in the methods used for measurements and analyses will take place, however new developments target real-time and portable measurement instruments.

- Despite the complexities involved, source signatures provide powerful tools for source identification and apportionment.
- Future directions in this area are (i) development of local source signature libraries, comprising of all the relevant aspects of the signatures, (ii) development of a better understanding of changes to the signature characteristics with time (taking transport and interaction processes into consideration), and (iii) development of simplified techniques applicable to at least certain, more common or significant pollution sources. For example remote sensing of vehicle emissions to enable emission rates to be determined for certain chemical components that can be used as surrogates of PM.

Deleted: <#>Source signatures are specific not only to some general classes of sources, but also depend on the factors that are locally specific. Thus application of any type of source signatures requires understanding of the signatures of the local emission sources.

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References

- Airborne Particles Expert Group, 1999. Source apportionment of airborne particulate matter in the United Kingdom. Report for the Department of the Environment, Transport and the Regions, the Welsh Office, the Scottish Office and the Department of the Environment (Northern Ireland).
- Brodowicz, P., Carrey, P., Cook, R., Somers, J., 1993. Motor Vehicle-Related Air Toxic Study. U.S. EPA Technical Support Branch, Emission Planning and Strategies Division, Office of Mobile Sources, Ann Arbor, Michigan.
- Buchholz, B.A., Landsberger, S., 1995. Leaching dynamics studies of municipal solid waste incinerator ash. *Journal of the Air and Waste Management Association* 45, 579-590.
- Burnet, P.G., Edmisten, N.G., Tiegs, P.E., Houck, J.E., Yoder, R.A., 1986. Particulate, carbon monoxide, and acid emission factors for residential wood burning stoves. *Journal of the Air Pollution Control Association* 36, 1012-1018.
- Cass, G.R., 1998. Organic molecular tracers for particulate air pollution sources. *Trends in Analytical Chemistry* 17, 356-366.
- Clevenger, T.E., Salwan, C., Kolrtyohann, S.R., 1991. Lead speciation of particles collected in the vicinity of a lead smelter. *Environmental Science and Technology* 25, 1128-1133.
- Colombo, J.C., Landoni, P., Bilos, C., 1999. Sources, distribution and variability of airborne particles and hydrocarbons in La Plata area, Argentina. *Environmental Pollution* 104, 305-314.
- Concawe Report 98/51, 1998. A Study of the Number, Size and Mass of Exhaust Particles Emitted from European Diesel and Gasoline Vehicles Under Steady-State and European Driving Cycle Conditions. Brussels.

- DeAngelis, D.D., Ruffin, R., Reznik, R., 1980. Preliminary characterization of emissions from wood-fired residential combustion equipment. Final Report to US Environmental Protection Agency, EPA - 600/7-80-040.
- Dockery, D.W., Pope, A., Xu, X., Spengler, J.D., Ware, J.H., Fay, M.E., Ferris, B.G., Speizer, F.E., 1993. An Association Between Air Pollution and Mortality in Six U.S. Cities. *New England Journal of Medicine* 329, 1753-1759.
- Dutkiewicz, V.A., Parekh, P.P., Husain, L., 1987. An evaluation of regional elemental signatures relevant to the Northeastern United States. *Atmospheric Environment* 21, 1033-1044.
- Eatough, D.J., Benner, C.K., Tang, H., Landon, V., Richards, G., Caka, F.M., Crawford, J., Lewis, E.A., Haasen, L.D., Eatough, N.L., 1989. The chemical composition of ETS III: identification of conservative tracers of ETS. *Environmental International* 15, 19-28.
- Eatough, D.J., Hansen, L.D., Lewis, E.A., 1988. Assessing Exposure to ETS. *Indoor and Ambient Air Quality*. Sepler Ltd, London, pp.131-140.
- Gao, N., Hopke, P.K., Reid, N.W., 1996. Possible sources for some trace elements found in airborne particles and precipitation in Dorset, Ontario. *Journal of the Air and Waste Management Association* 46, 1035-1047.
- Gard, E., Mayer, J.E., Morrical, B.D., Dienes, T., Fergenson, D.P., Prather, K.A., 1997. Real-time analysis of individual atmospheric aerosol particles: design and performance of a portable ATOFMS. *Analytical Chemistry* 69, 4083-4091.
- Ge, S., Liu, W., Bai, Z., Wang, T., Qing, S., Zhu, T., Zhang, J., 2001. The boiler briquette coal versus raw coal: 1. stack gas emissions. *Journal of Air and Waste Management Association* 51, 524-533.

- Hare, C.T., Springer, K.J., Bradow, R.L., 1976. Fuel and Additive Effects on Diesel Particulate Development and Demonstration of Methodology. Technical Paper, 760130, Society of Automotive Engineers.
- Hawthorne, S.B., Miller, D., Langenfeld, J.J., Keieger, M.S., 1992. PM₁₀ high volume collection and quantitation of semi- and non-volatile phenols, methoxylated phenols, alkanes, and polycyclic aromatic hydrocarbons from winter urban air and their relationship to wood smoke emissions. *Environmental Science and Technology* 26, 2251-2262
- Hueglin, C.H., Gaegauf, C.H., Kunzel, S., Burtscher, H., 1997. Characterization of wood combustion particles: morphology, mobility, and photoelectric activity. *Environmental Science and Technology* 31, 3439-3447.
- Huntzicker, J.J., Heyerdahl, E.K., Madow, S.R., Rau, J.A., Griest, W.H., MacDougall, C.S., 1986. Combustion as the principal source of carbonaceous aerosol in the Ohio River Valley. *Journal of the Air Pollution Control Association* 36, 705-709.
- Kittelson, D.B., Dolan, D.F., Verrant, J.A., 1978. Investigation of a Diesel Exhaust Aerosol. Technical Paper No. 780109, Society of Automotive Engineers.
- Kleeman, M.J., Schauer, J.J., Cass, G.R., 1999. Size and composition distribution of fine particulate matter emitted from wood burning, meat charbroiling, and cigarettes. *Environmental Science and Technology* 33, 3516-3523.
- Leaderer, B.P., Hammond, S.K., 1991. Evaluation of vapour-phase nicotine and respirable suspended particle mass as markers for environmental tobacco smoke. *Environmental Science and Technology* 25, 770-777.
- Li, C.K., Kamens, R.M., 1993. The use of polycyclic aromatic hydrocarbons as source signatures in receptor modeling. *Atmospheric Environment* 27A, 523-532.

- Li, W., Hopke, P.K., 1993. Initial size distribution and hygroscopicity of indoor combustion aerosol particles. *Aerosol Science and Technology* 19, 305-316.
- Lipkea, W.H., Johnson, J.H., Vuk, C.T., 1979. The Physical and Chemical Character of Diesel Particulate Emissions - Measurement Techniques and Fundamental Considerations. Technical Paper No. 791702, Society of Automotive Engineers.
- McKenzie, L.M., Hao, W.M., Richards, G.N., Ward, D.E., 1995. Measurement and modeling of air toxins from smouldering combustion of biomass. *Environmental Science and Technology* 29, 2047-2054.
- McMahon, C.K., Tsoukalas, S., 1978. Polynuclear aromatic hydrocarbons in forest fire smoke. In: Jones, P.W., Freudenthal, R.I. (Eds.), *Carcinogenesis*, Vol. 3: Polynuclear Aromatic Hydrocarbons. Raven Press, New York.
- Miller, C.A., Ryan, J.V., Lombardo, T., 1996. Characterization of air toxics from an oil-fired firetube boiler. *Journal of the Air and Waste Management Association* 46, 742-748.
- Morawska, L., Jamriska, M., Bofinger, N.D., 1997. Size characteristics and aging of the environmental tobacco smoke. *The Science of the Total Environment* 196, 43-55.
- Morawska, L., Thomas, S., Bofinger, N.D., Wainwright, D., Neale D., 1998a. Comprehensive characterization of aerosols in a subtropical urban atmosphere: particle size distribution and correlation with gaseous pollutants. *Atmospheric Environment* 32, 2461-2478.
- Morawska, L., Bofinger, N.D., Kosic, L., Nwankwoala, A., 1998b. Submicron and supermicron particles from diesel vehicle emissions. *Environmental Science and Technology* 32, 2033-2042.
- Morawska, L., 2000. Control of particles indoors – state of the art. In *Proceedings of Healthy Buildings 2000*, Espoo, Finland, 6–10 August 2000.

- Mukal, H., Furuta, N., Fujll, T., Ambe, Y., Sakamoto, K., Hashimoto, Y., 1993. Characterization of sources of lead in the urban air of Asia using ratios of stable lead isotopes. *Environmental Science and Technology* 27, 1347-1356.
- Mumford, J.L., Harris, D.B., Williams, K., Chuang, J.C., Cooke, M., 1987. Indoor air sampling and mutagenicity studies of emissions from unvented coal combustion. *Environmental Science and Technology* 21, 308-311.
- Nikolaou, K., Masclet, P., Mouvier, G., 1984. Sources and chemical reactivity of polynuclear aromatic hydrocarbons in the atmosphere – a critical review. *Science of the Total Environment* 32, 103-132.
- Oberdorster, O., Gelein, R.M., Ferin J., Weiss B., 1995. Association of particulate air pollution and acute mortality: involvement of ultrafine particles. *Inhalation Toxicology* 7, 111-124.
- Ogden, M., Heaven, D., Foster, T., Maiolo, K., Cash, S., Richardson, J., Martin, P., Simmons, P., Conrad, F., Nelson, P., 1996. Personal monitoring system for measuring ETS exposure. *Environmental Technology* 17, 239-250.
- Raiyani, C.V., Shah, S.H., Desai, N.M., Kenkaiah, K., Patel, J.S., Parikh, D.J., Kashyap, S.K., 1993. Characterization and problems of indoor pollution due to cooking stove smoke. *Atmospheric Environment* 27A, 1643-1655.
- Rando, R.J., Menon, P.K., Poovey, H.G., Lehrer, S.B., 1992. Assessment of multiple markers of environmental tobacco smoke in controlled, steady-state atmospheres in a dynamic test chamber. *American Industrial Hygiene Association Journal* 53, 699-704.

- Ristovski, Z., Agranovski, V., Bostrom, T., Thomas, S., Hitchins, J., Morawska, L., 1999. Elemental composition of combustion emissions from spark ignition vehicles. European Aerosol Conference, Prague.
- Ristovski, Z., Morawska, L., Bofinger, N.D., 1998. Submicrometer and supermicrometer particles from spark ignition vehicle emissions. *Environmental Science and Technology* 32, 3845-3852.
- Saksena, S., Prasad, R., Pal, R.C., Joshi, V., 1992. Patterns of daily exposure to TSP and CO in the Garhwal Himalaya. *Atmospheric Environment* 26A, 2125-2134.
- Simoneit, B.R.T., 1985. Application of molecular marker analysis to vehicular exhaust for source reconciliations. *International Journal of Analytical Chemistry* 22, 203-233.
- Smith, K.R., 1993. Fuel combustion, air pollution exposure, and health: the situation in developing countries. *Annual Review of Energy and the Environment* 18, 529-566.
- Smith, K.R., 1986. Biomass combustion and indoor air pollution: the bright and dark sides of small is beautiful. *Environmental Management* 10, 61-74.
- Tang, H., Richards, G., Benner, C., 1990. Solanesol: a tracer for environmental tobacco smoke particles. *Environmental Science and Technology* 24, 848-852.
- Vedal, S., 1997. Ambient particles and health: lines that divide. *Journal of the Air and Waste Management Association* 47, 551-581.
- Ward, D.E., Hardy, C., 1989. Organic and elemental profiles for smoke from prescribed fires. In: Watson, J.G. (Ed.). *Receptor Models in Air Resources Management: Transactions of an International Specialty Conference of the Air and Waste Management Association*; San Francisco, CA. Pittsburgh, PA, pp. 299-321.

- Wei, F., Teng, E., Wu, G., Hu, W., Wilson, W.E., Chapman, R.S., Pau, J.C., Zhang, J., 1999. Ambient concentrations and elemental compositions of PM₁₀ and PM_{2.5} in four Chinese cities. *Environmental Science and Technology* 33, 4188-4193.
- Wei, Y., Wu, C., 1997. PAH emissions from the fluidized-bed incineration of an industrial sludge. *Journal of the Air and Waste Management Association* 47, 953-960.
- Westberg, H., Zimmerman, P., 1993. Analytical methods used to identify nonmethane organic compounds in ambient atmospheres. In: Newman, L. (Ed.). *Advances in Chemistry Series 232: Measurement Challenges in Atmospheric Chemistry*. The American Chemical Society, Washington D.C. pp. 275-290.
- Wey, M.Y., Su, J.L., Chen, J.C., 1999. Influence of operating conditions on the formation of heavy metal compounds during incineration. *Journal of the Air and Waste Management Association* 49, 444-453.
- Wey, M., Chao, C., Chen, J., Yu, L., 1998. The relationship between the quantity of heavy metal and PAHs in fly ash. *Journal of the Air and Waste Management Association* 48, 750-756.
- Willeke, K., Baron, P.A., 1993. *Aerosol Measurement: Principles, Techniques and Applications*. Van Nostrand Reinhold, New York.
- World Health Organization (WHO), 1998. Selected heterocyclic polycyclic aromatic hydrocarbons, *Environmental Health Criteria 202*, World Health Organization, Geneva, Switzerland.
- World Health Organization (WHO), 1999. *World Health Organization Health Guidelines for Vegetation Fire Events*. World Health Organization, Geneva, Switzerland.

- Zhang, J., Smith, K.R., 1996. Hydrocarbon emissions and health risks from cookstoves in developing countries. *Journal of Exposure Analysis and Environmental Epidemiology* 6, 147-161.
- Zhang, J., Smith, K.R., Ma, Y., Ye, S., Jiang, F., Qi, W., Liu, P., Khalil, M.A.K., Rasmussen, R.A., Thorneloe, S.A., 2000. Greenhouse gases and other pollutants from household stoves in China: a database for emission factors. *Atmospheric Environment* 34, 4537-4549.
- Zhang, J., Smith, K.R., Uma, R., Ma, Y., Kishore, V.V.N., Lata, K., Khalil, M.A.K., Rasmussen, R.A., Thorneloe, S.T., 1999. Carbon monoxide from cookstoves in developing countries: 2. potential chronic exposures. *Chemosphere: Global Change Science* 1, 367-375.
- Zinbo, M., Korniski, T.J., Weir, J.E., 1995. Relationship between the composition of engine particulate emissions and emission control system performance. *Industrial Engineering Chemistry Research* 34, 619-625.

Table 1. Characteristic elements emitted from various combustion sources.

Emission Source	Characteristic Elements Emitted
Oil fired power plants	V, Ni
Motor vehicle emissions	Br, Pb, Ba
Refuse incineration	Zn, Sb, Cu, Cd, Hg
Coal combustion	Se, As, Cr, Co, Cu Al
Refineries	V
Nonferrous metal smelters	As, In (Ni smelting), Cu
Use of pesticides	As
Iron and steel mills	Mn
Plant producing Mn metal and Mn chemicals	Mn
Copper refinery	Cu

Table 2. Summary of the most common organic compound emitted by a number of combustion sources (Cass, 1998).

Emission Source	Emitted Components
Cigarette smoke	nicotine, iso-alkanes, anteiso-alkanes (anteiso-trioacontane, anteiso-hentriacontane, anteiso-dotriacontane, iso-tritriacontane),
Motor vehicle emissions	hopanes and steranes (present in lubricating oil for diesel and gasoline vehicles, and in diesel) black elemental carbon (present in a higher fraction in diesel emissions) high molecular PAHs: coronene and benzo[ghi]perylene (less specific)
Wood combustion	Retene, phytosterols, lignans, phenolic compounds from lignins, diterpenoids from resins
Meat charbroiling	cholesterol, supplemented by fatty acids
Vegetative detritus	High molecular weight n-alkanes ranging from C ₂₇ – C ₃₄ (high concentration of odd number n-alkanes)
Tire dust	styrene/butadiene copolymer, very high molecular weight even number n-alkanes, benzothiazole
Natural gas combustion Natural gas fired home appliances Motor vehicles	benz[a]anthracene some PAHs and oxyPAHs

Table 3. Typical chemical abundances in source emissions.

Source	Dominant particle size	Chemical abundance (mass fractions)			
		> 10%	1 -10%	0.1 - 1%	< 0.1%
Coal-fired boiler	Fine	Si	SO ₄ ²⁻ , OC, EC, S, Ca, Fe, Al	NH ₄ ⁺ , P, K, Ti, V, Ni, Zn, Sr, Ba, Pb	Cl, Cr, Mn, Ga, As, Se, Br, Rb, Zr
Incinerator	Fine	NH ₄ ⁺ , Cl, SO ₄ ²⁻ , OC	NO ₃ ⁻ , Na, EC, Si, S, Ca, Fe, Br, Pb	K, Al, Ti, Zn, Hg	V, Mn, Cu, Ag, Sn
Residual oil boiler	Fine	S, SO ₄ ²⁻	Ni, OC, EC, V	NH ₄ ⁺ , Na, Zn, Fe, Si	K, OC, Cl, Ti, Cr, Co, Ga, Se
Wood waste boiler	Fine	K	Na, Fe, Mn,	Zn, Br, Cl, Rb,	Cr, Cu, Co, Ni, Se, Cd, Ar, Cr, Pb

key: OC=organic carbon, EC=elemental carbon.

Figure captions:

Figure 1. Typical measured urban air particle number size distribution (upper diagram), and mass distribution (lower diagram) calculated from the number distribution (Morawska 2000).

Figure 2. Size distribution spectra measured for a vehicle run on (a) unleaded gasoline, (b) diesel
(c) LPG (Morawska et al., 1998b, Ristovski et al., 1998).

Figure 3. Size distribution of side stream smoke (SS) produced by a human smoker. The measurements were performed independently by two different instruments in the submicrometer and supermicrometer ranges (Morawska et al., 1997).

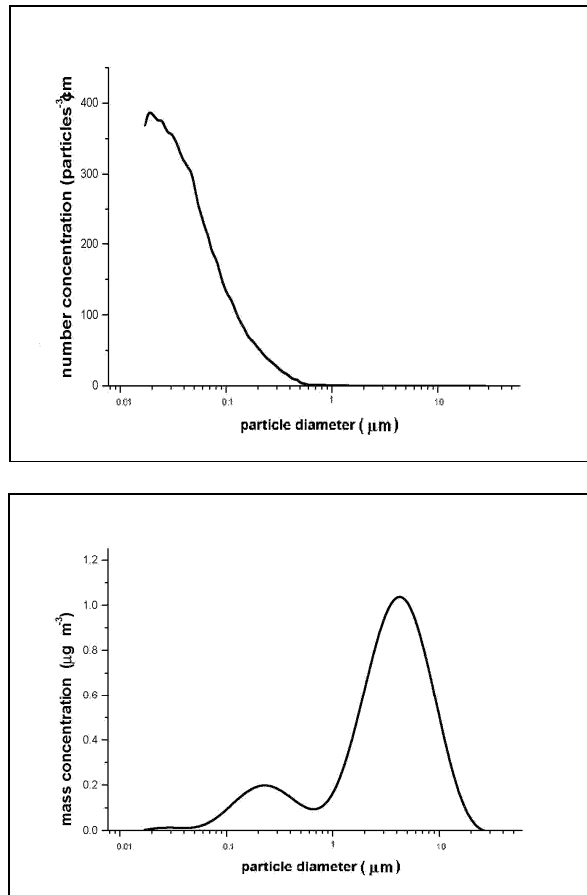


Figure 1. Typical measured urban air particle number size distribution (upper diagram), and mass distribution (lower diagram) calculated from the number distribution (Morawska 2000).

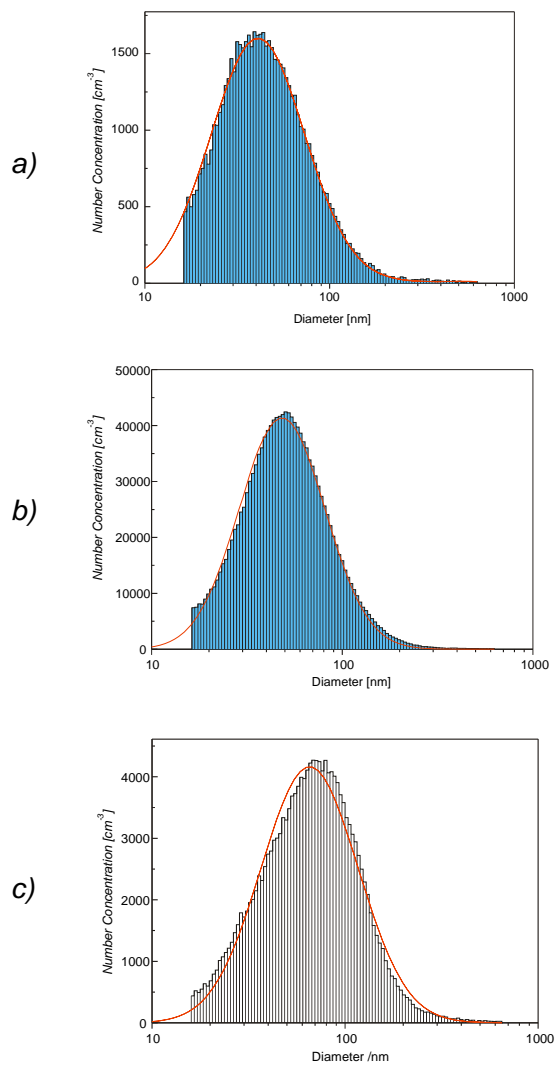


Figure 2. Size distribution spectra measured for a vehicle run on (a) unleaded gasoline, (b) diesel (c) LPG (Morawska et al., 1998b, Ristovski et al., 1998).

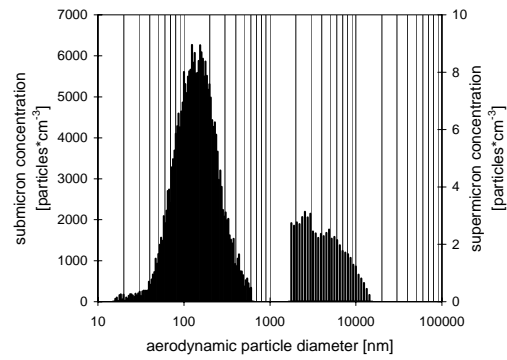


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