Environmental Aerosol Physics

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Assignment-papers for:
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part II
Application of optical particle counting technique to environmental sampling and monitoring
handed in:
Pierre Madl

University of Salzburg
Department of Biophysics
Environmental Aerosol Physics

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Assignment-paper:

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**Introduction**: Definition and effects of an Aerosol

**Aerosol**:

An aerosol is a multiphasic system in a gas in which dispersely distributed particles of solid or liquid nature are suspended. Such airborne particles (or collection of particles) can be smoke, salt, fog, which includes even the products of spray cans.

The health effects of an aerosol depends upon its inhalability: larger aerosols remain trapped in the nasopharyngeal cavity, while the smallest ones are capable to penetrate the alveolar section of the lungs. Even though the exhalable fraction gradually increases with decreasing particle size, the "smaller" aerosols are considered the most dangerous.

Biological relevance have been assigned to particles in the sub-ultrafine region (<20nm), as they are capable to penetrate the interstitial cellular space of the alveolar lining by expressing their potentially toxic effect. It is generally agreed upon that aerosols account for lung tumors, fibroses, allergies, and even for irritating or chemo-toxical effects. Accommodation, transportation (clearance, via the bronchial cilia and mucus or incorporation by phagocytes in the lymphatic tissue in alveoli), and deposition in the respiratory tract determine the potential effects of an inhaled particle.

Consequently, the effect of an aerosol depends on:

- on type and site of the deposit; this again is defined by the size, shape, and surface structure, the chemical composition, bio stability and hygroscopic properties of the particle (the more hydroscopic the particle, the deeper it can penetrate into the lungs);
- furthermore, in very small particles, the solubility and absorptive characteristics by the target cell, where it may then fully develop its toxicological effects, play a crucial role.

**Definitions**

Fig. 2: Aerosol fractions as a function of the aerodynamic diameter; medically relevant deposited aerosol fractions according to the industrial standards are underlined; the framed proportions relevant for the measuring techniques contain also their respective exhalable portions.

**Separation Curves**

Fig. 3: The separate fractions for the inhalable, thoracic and alveolar portions of airborne dust within the respiratory tract; because of the logarithmic representation an aerodynamic diameter "zero " is not representable; for which a separation rate of 100%.
The common instruments for atmospheric particle size classification include:

- optical particle counters
- electrostatic classifiers (not further described in this paper)
- diffusion batteries (not further described in this paper)

**Optical Particle Counting Technique:**

Optical particle counters (OPCs) can be used to determine the size-dependence of the aerosol light scattering coefficient in spite of uncertainties about particle shape and refractive index. These measurements are made in units of particles per cubic centimeter (pt/cm³) versus traditional aerosol Measurements of milligrams per cubic meter (mg/m³) made by photometers.

**Advantages** of optical direct-reading particle counting techniques:

- rapid response
- continuous (in-situ) measurements
- non-destructive detection

High resolution size distribution measurements over a size range typically from 0.5 to 30µm can be accomplished; since the instruments usually combine a PC for data processing, presentation of the results in graphical and tabular format is straightforward.

**Disadvantage:** the amount of light scattered may not be directly related to the property which needs to be investigated.

**Solution:** combination of optical detection techniques with the manipulation of other particle parameters (for example motion, mass, diameter, chemical properties, etc.)

**Basic concept of a conventional OPC** (refer also to fig.1):

A light source (typically a plasma laser or laser diode) is collimated to illuminate a sample volume of aerosol flowing out of a nozzle. As shown in fig.4, a photo-detector, rotatable and off-axis from the light beam, measures the amount of light scattered from single particles by refraction, reflection and diffraction. Both the size and the number of particles are measured simultaneously. The size of the particle is deduced from the intensity of the scattered light.

Typically, the wavelength of light used in OPCs ranges from about 0.6 to 0.8µm. As particles become smaller than a wavelength, the amount of light they scatter into the detector collection optics drops off rapidly. For example, to upgrade the sensitivity of a counter from 0.2 to 0.1µm requires about a 17-fold increase in light power focused into the view volume. To achieve a sensitivity approaching 0.1µm requires a well-designed laser/optical system with a narrow optical bandwidth in order to develop high light intensity in the view volume. Making the optical bandwidth too narrow in order to achieve high sensitivity can actually lead to calibration instability (in the presence of mild shock or vibration) with the attendant loss of sensitivity.

**Basic concept of a Ultrafine OPC** (refer also to fig.1):

An Ultrafine Optical Particle Counter (UOPC) measures ultrafine particle (0.05-1µm) concentrations in real-time.

Particles are drawn through the sampler using a built-in pump. Upon entering the instrument, particles pass through a saturator tube where they mix with an alcohol vapor. The particle/alcohol mixture then passes into a condenser tube where alcohol condenses onto the particles, causing them to grow into a larger droplet. The droplets then pass through a focused laser beam, producing flashes of light which are sensed by a photo-detector. The particle concentration is determined by counting the light flashes. If the particles were not "grown" into larger droplets, they would not produce enough light (scatter) to be detected.

The UOPC uses the same fundamental technology behind condensation particle counters (CPCs), that are used in research and industrial applications to track and record particle sources (for details regarding CPC’s refer to lecture paper – Morawska).
Optical Physics and OPC:

As the exponential relationship changes inversely with particle size, some fundamental aspects should be briefly highlighted.

In the Rayleigh-region, where particles are smaller than the light wavelength, light is scattered equally in all directions (isotropically) from the particle. Its intensity varies as a function of the 6th power of particle size in this region (exp = 6).

In the Mie-region, where particles are nearly the same size as the light wavelength, the light pattern surrounding the particle becomes "scalloped" (refracted). The forward lobe (pointing in the same direction as the laser beam) becomes larger as the particle size increases.

In the Geometric-region where particles are much larger than a wavelength, classical optical theory takes over.

Light scattering from a particle can be calculated from the physical effects of diffraction, reflection, refraction, and absorption.

Coincidence Effect:

Ideally, if the particles go through the sensing zone one by one, it is possible to count the total number detected in the sensing zone. However, simultaneous occupancy of the sensing zone by more than one particle often occurs. This phenomenon is called "coincidence" and the resulting count error is known as the coincidence error. When more than 2 particles are located in the view window (aperture or sensing zone), coincidence phenomena are observed (see fig.6) particle 1 and particle 2 are detected as a single, somewhat distorted, large pulse; therefore, one of the cells is not counted (coincidence loss). The degree of coincidence loss depends on the concentration. The magnitude of the coincidence error increases with the concentration of particles. By using measurements from samples of different concentrations, the coincidence correction formula can be established. This correction formula may be integrated into the analyzer’s computer and the coincidence-corrected result reported.

Two simple models of coincidence are illustrated in fig.7 and help to analyze coincidence phenomena. In the case of horizontal interaction (a) one wide M-shaped pulse is produced; in the case of vertical interaction (b) one large pulse is observed (valid for electrostatic counters only); optical counters are not able to discriminate them as separate particles, once particle B hides behind particle A (in reference to the pathway of the laser light). Conversely, it is not always possible to identify the existence of two particles in the viewing window from the observed pulse.

Selected Parameters: Counting Efficiency, Sensitivity and Resolution; referring to the Particle Size vs. Energy Curve illustrated in fig.8, the detected light energy falls off exponentially with decreasing particle size. In conventional OPCs the detected energy drops off at 0.3µm as a function of about the 4th power of particle size; at 0.1µm the detected light energy drops off as a function of about the 5th to 6th power of particle size.

- **Accuracy** - the "correctness" of the size measurement; expressed as a percentage (fig.8): A = (Dm - Dt) / 100 / Dt [%]
  where Dm is the measured diameter and Dt is the true diameter;

- **Resolution** - the smallest detectable particle size difference. It is the ratio of the standard deviation (s) to the diameter (Dm) expressed as a percentage (fig.8): R = s / 100 / Dm [%]
  Resolution is a function of the width of the bell-shaped curve. It is also referred to as "coefficient of variation, relative precision and relative standard deviation".

- **Precision** - the standard deviation (σ) of repeated measurements of the same size monodispersed spheres:
  \[ \sigma = \sqrt{\frac{\sum (D_n - D)^2}{N-1}} \] [m]
  where: D_n = the n^th measurement of particle diameter (arithmetic mean of N measures)
  N = total number of measurements
- **Reproducibility** (also called repeatability and calibration stability) - the extent to which an OPC will give the same sizing and counting response to the same diameter PSL spheres over a long period of use.
- **Sensitivity** - the smallest size particle an OPC can detect at a specified counting efficiency, e.g. conventional OPCs detect 0.3µm particles at 50% counting efficiency.
- **Counting efficiency** - the detected particle concentration divided by the true concentration (as measured by a hypothetically perfect instrument); this curve provides useful information regarding the sensitivity and resolution of the instrument.
- **False count rate** - the counts per unit volume using perfectly filtered air at a specified flowrate.
- **Signal** - the magnitude of the sensed scattered light produced only by the passing of a particle through the view volume. Size is deduced from the signal magnitude. Noise is the opposite of signal in that it is produced by anything but a particle in the view volume. A high signal-to-noise ratio implies low false count rate.

Selecting an optical particle counter (OPC) appears deceptively simple. Typically, the specification focuses on sensitivity, flow rate, size range and coincidence loss. Secondary requirements are number of channels, the sample/hold periods, and alarm limits. For example:

- Specifying sensitivity without considering the counting efficiency curve could mean good sensitivity (ability to sense small particles) but extremely poor resolution (ability to detect small differences in particle size). Poor resolution can cause large errors in the particle count.
- Relying exclusively on sensitivity or counting efficiency measurements based on ideal (transparent and spherical) test particles can result in wrong answers when counting particles in the real world. These particles occur in a wide variety of shapes and refractive indices, causing large errors in particle sizing.
- Failure to recognize the difference between a "highly tuned" lab instrument (which can easily slip out of calibration with normal handling) and a "ruggedized" field instrument (which holds its calibration month after month) can be costly. Poor calibration stability causes sizing drift, non-repeatability, random spikes and ultimately, loss of user confidence.

**Calibration of an OPC**: As an aid to arrive at a definition of counting efficiency, let us assume the presence of an ideal reference particle counter (fig.10). This counter can "see" every particle passing through the view volume to a diameter much lower than the lowest detection limit of the OPC under test. Typically, this instrument is a condensation nucleus counter (CNC or an OPC with a verified counting efficiency of 100% at the lower detection limit of the OPC under test). However, a CNC only counts particles above a given size corresponding to a preset threshold (e.g. 0.01µm); it cannot size particles. A reference CNC must be used with an electrostatic classifier to analyze particles by controlled deflection in an electrostatic field (see also lecture paper – Morawska).

An aerosol carrying mono-dispersed polystyrene latex (PSL) spheres is generated by the atomizer (fig.10). The aerosol is mixed with filtered air in the mixing chamber. The OPC under test and the reference counter simultaneously sample the mono-dispersed spheres at the same concentration. As smaller mono-dispersed spheres are introduced, there is a point where the OPC under test fails to detect all the particles that the reference instrument is sensing. Further reduction in particle size results in the eventual loss of particle detection. Therefore, counting efficiency is expressed as follows:

\[ \eta_C = \frac{N_m}{N_t} \cdot 100 \quad \text{[\%]} \]

where \(N_m\) is the measured concentration and \(N_t\) is the true concentration as measured by the reference instrument. Thus, measurements with ideal (PSL) spheres represent a powerful tool for assessing the sensitivity, accuracy, resolution and false count level of a counter. This calibration technique serves two purposes:

1) Gives comparative evaluations of a wide variety of counters,
2) Provides a measure of how well a counter maintains its calibration (reproducibility).
Particles in the Real World versus the Lab World:

In the field of optical particle counting one generally specifies sensitivity and counting efficiency on the basis of ideal test particles that are transparent and spherical. Most often, PSL spheres are used for testing. In the particle counting industry, there is a tendency to emphasize PSL sphere sensitivity and skirt the issue of OPC sizing accuracy and sensitivity with particles found in the real world. Unfortunately, real world particles come in a wide variety of shapes and refractive indices, leading to a significant degradation of sensitivity, resolution and accuracy. For convenience, OPC measurements are based on the introduction of aerosol with suspended PSL particles of highly mono-dispersed sizes over the range of approximately 0.1 to 3µm. OPCs are calibrated with “ideal” particles having a refractive index between 1.5 and 1.6. The size measured by the OPC is then an “equivalent PSL diameter”, depending on the calibrating aerosol used.

At particle diameters of 0.1µm, optical scattering is strongly dependent on the particle’s shape, color and electromagnetic characteristics which reinforces the fact that significant error exists in sizing real world particles. Particle sizing errors due to changes in refractive index encountered with particles that are highly reflective while others absorb most of the incident light energy.

Current UOPC-Technology based on the TSI-model 3320:

The model described in fig.11 (Thermo-Systems Inc. - sketch depicted below) accelerates the aerosol sample flow through an accelerating orifice. The aerodynamic size of a particle determines its rate of acceleration, with larger particles accelerating more slowly due to increased inertia. As particles exit the nozzle, they cross through two partially overlapping laser beams in the detection area (fig.11 - lower left inlet). Light is scattered as each particle crosses through the overlapping beams. The optical arrangement that brings about the translation uses an elliptical mirror (fig.11 - lower right inlet). This gives much improved light collection. The elliptical mirror, placed at 90 degrees to the laser beam axis, collects the light and focuses it via an extra lens onto an avalanche photo-detector (APD). The APD then converts the light pulses into electrical pulses. The configuration of the detection area improves particle detection and minimizes Mie- scattering oscillations in the light-scattering-intensity measurements.

The use of two partially overlapping laser beams results in each particle generating a single two-crested signal. Peak-to-peak time-of-flight is measured with 4-nanosecond resolution for aerodynamic sizing. The amplitude of the signal is logged for light-scattering intensity. The smallest particles may have only one detectable crest and are binned separately. In uncorrelated mode, small particles are displayed in the smallest size channel (less than 0.5µm). Particles with more than two crests, indicative of coincidence, are also binned separately but are not used to build aerodynamic-size or light-scattering distributions.

Fig.11: Sketch of the UOPC Model 3320 (TSI)
Field-applications of OPC:
Applications where optical particle counting and sizing would typically include those cases when only a small quantity of sample is available, identification of trace amounts of contamination, the analysis of mixed particle systems, and when an exact end point is required.
State authorities and industry’s alike can use particle sizing techniques for the following applications:
Abrasives - Absorption and adsorption of heavy metal vapor; on the other hand, polishing and lapping compounds must be produced to very strict tolerances. Too many large particles can produce surface defects in the polishing process; e.g. in the reduction of corrosion and fouling of the gas turbine blades or the surfaces of the heat exchangers in the boiler furnaces.
Powder sizing - powder production and surface coating process (sintering); there is an optimum particle size for toners and powders, too large and image quality will degrade, too small will effect transfer properties and will clog equipment and degrade image quality or homogeneity of the coating layer respectively. Particle count data can identify excessive amounts of either large or small particles.
Biological application - counting of cells is a common task, sizing information enables checks to be made to ensure that the correct particles are counted. Applications would include evaluating effect of pesticides, food additives, drug development, cell cultures, yeast viability, etc.
Biohazard detection - in military applications, biological warfare relies heavily on particle counters to monitor the spread and effectiveness of the modified bacterial and viral strains.
Polymers - the production of materials to high tolerances for large scale industrial applications; e.g. chromatography column packing, electronic displays, etc. rely on particle counters whenever surfaces are coated.
Workplace monitoring – in a corn or grain mill, for example, the dust (flour) concentration requires strict monitoring. Likewise in the wood industry; processing and manipulation of wood products may lead to a substantial dust freight in the ambient air of the workplace. The field measurements show that the instrument enables a more comprehensive and more realistic characterization of the individual dust burden of workers exposed to health-endangering aerosol concentrations than was previously possible.
Spray technology - to boost combustion efficiencies in the motor industry, nebulization is crucial to optimize the allower efficiency in the turnover of the fuel input and the output obtained as work; other applications regard the performance evaluations i.e. not only are alternative means of aerosol generators studied but can also be referred to existing particle generators as used in measurement equipment (e.g. electrothermal AAS, nebulizers in ICPs, etc).
Filter and air-cleaner testing - contamination control and fluid clarification are key processes in a wide range of industries including the pharmaceutical, food and drink manufacture, biotechnological GM-production, semiconductors, chemicals, hydraulics and aerospace applications where small particles and trace quantities of contamination must be removed from ultra-high purity process streams which rely on highly efficient filtration systems.
Indoor air-quality monitoring - cleanroom design and micro-contamination control in semiconductor and micro-machine industries, as well as optical and ceramic materials processing The OPC has two basic functions in the cleanroom. The first is to certify the cleanroom to meet standards. The second function is to support a quality maintenance program in the cleanroom. The goal is to eliminate "killer defect" particles which can destroy product yield.
Ambient air monitoring - examples of the applications in environmental protection and monitoring involves the control of generation and removal of particulate pollutants (PMt, PM2.5, PM10, etc.) contained in the air. Especially soot sampling enables precise allocation, correlation, and removal of diesel emission. Gaseous pollutants like SOX, NOX, PAH, PCDD, PCDF, etc. readily adsorb on particulate matter by increasing the potential toxic effects of the aerosols in ambient air.
Atmospheric research - heterogeneous processes on stratospheric aerosols and polar stratospheric clouds (PSC) play an important role in the activation and passivation of reservoir gases such as ClONO2, HCl, BrONO2, HBr and N2O5. Knowledge of the growth of aerosol particles and their phase transitions upon cooling as well as their influence on the chemistry of the polar stratosphere are important for an improved understanding of these stratospheric processes.
Drug delivery studies - medical inhalation therapies often encounter restricted efficiency in supplying an aerosol to the target tissue in the lungs. Usually therapeutic aerosols are deposited far off the intended site; till now, medical staff just counteracted this problem by increasing the dose rather than the aerosol properties.
Inhalation toxicology - distribution studies of monodisperse aerosols within the respiratory tract, enhance the understanding and allow predictions to be made of the inhalation of toxic polydisperse particles.
Characterization of test aerosols used in particle instrument calibration - UOPCs are used for the calibration of conventional OPCs.
Basic research - in basic aerosol science UOPCs are used to study the generation, distribution, and deposition of suspended particulate matter.
Conclusion:
Simple OPCs are powerful tools to monitor aerosol concentrations in terms of particles per cubic meter \([\text{pt/m}^3]\). As their lower detection range is somewhat restricted by the wavelength of the laser source used, the more complex UOPCs are capable of detecting particles as small as 20 nm. As UOPCs employ condensation chambers to count particles, additional equipment is needed to size the particle according to its aerodynamic diameter. Sensitivity is a problem in any OPC; sensitivity fluctuates considerably along the detection spectrum of each particle counter and are quite poor in the smaller particle size class (Rayleigh- and Mie-region) compared to the larger size class (Geometric region). Vertical interaction of particles can not be discriminated when talking about coincidence in OPC, while electrostatic classifiers may easily detect them.

Stability must be considered at least as important as sensitivity. It is extremely important that the counter maintain its calibration over the long term, otherwise, particle concentration baselines become meaningless. Instead of an absolute particle sizer and counter, the OPC can be used more effectively as an early warning trend indicator or burst detector. This will allow authorities and production quality supervisors to shut down or interfere with a process if the concentration level or parameters exceeds a preset threshold. Thus the OPC can function both as a process tool in quality assurance program and as an environmental tool in public health services.

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Introduction:

Diesel vehicles like trucks together with diesel engines used in various industrial applications, such as power generation, irrigation in agriculture, construction, shipping, port activities, oil drilling, mining in general, and railroads; they all expel diesel exhaust into the air we breathe, especially in cities. Therefore, diesel exhaust is a feature of everyday life - even in fireplaces, BBQ-food, burnt potatoes, etc.

Diesel exhaust emissions are mixtures of particles and gases containing hundreds of chemical compounds. Water and Carbon Dioxide (CO₂) make up about 99% of the emissions. The other 1% contains unburned carbon particles (soot), oxides of nitrogen, sulfur oxides, carbon monoxide and hydrocarbons (PAHs).

Diesel exhaust is also a major contributor to various types of air pollution, including smog-forming oxides of nitrogen (NOₓ) and fine particles (PM₂.₅). In California, an estimated 26 percent of particles (PM₁₀) from fuel combustion sources in outdoor air come from diesel engines.

Physical and chemical characteristics of diesel:

Diesel fuel is heavier and oilier. It evaporates more slowly than gasoline, its boiling point is higher than the boiling point of water. Diesel fuel contains more carbon atoms in longer chains than gasoline does (gasoline is typically C₉H₂₀ while Diesel fuel is typically C₁₄H₃₀). It takes less refining to create Diesel fuel, which is another reason why it is cheaper than gasoline. Diesel fuel has a higher energy density than gasoline. On average, a gallon of Diesel fuel contains approximately 155⋅10⁶ joules, while a gallon of gasoline contains 132⋅10⁶ joules. This, combined with the improved efficiency of Diesel engines, explains why diesel engines get better mileage than equivalent gasoline engines.

Gaseous and particle emissions from diesel vehicles

The amount and type of emissions from diesel exhaust is dependent on the type of diesel engine used, the grade of diesel fuel used, engine speed, engine loading, the condition of the engine, etc. Diesel engines run with more air than they need and therefore combustion can usually be more efficient than gasoline engines. They tend to produce considerably less Carbon Monoxide than gasoline engines.

Total particulate, particulate organics and inert material emissions are significantly higher in diesel exhaust emissions than normally found in gasoline engine exhaust emissions.

Inert material consists primarily of elemental carbon (soot). These carbon particles are small enough that they do not get absorbed by the mucous lining of the upper respiratory tract and get drawn deep into the lungs where they can damage the ciliar lining of the bronchial tube. This damages the lungs defense and clearance mechanism.

Diesel exhaust particles (DEP): are an important constituent of PM₂.₅. DEP consists of chain aggregates of roughly spherical nuclei composed largely of elemental carbon (EC). DEPs have large surface areas, ranging from 30 to 100 m²/g, on which a wide range of organic compounds are adsorbed. Nearly all DEPs fall within the PM₂.₅ size range, with mass median diameters ranging from 0.05 to 0.3 μm.
DIESEL engines also produce nearly 20% of the total nitrogen oxides and nearly two-thirds of all particulate pollution emitted by all on-road vehicles.

Ultra-fine particles, The small particles which come from diesel exhaust are particularly dangerous because they are coated with a mixture of chemicals such as polycyclic aromatic hydrocarbons (PAHs), nitro-aromatics, benzene, dioxins, and other toxicants. The particles act like a special delivery system which places these toxic chemicals deep within our lungs. Some asthma medications use the principle of delivering a beneficial drug in a fine inhaled aerosol. The particles are retained in the body along with the toxic chemical hitchhikers which would otherwise be quickly eliminated. Thus the particles lengthen our exposures to the toxicants in diesel exhaust.

Carbon monoxide and hydrocarbons are products of incomplete combustion of fuel. Hydrocarbons are fuel molecules which are not totally burned and they are responsible for the diesel exhaust odor. They attach themselves to the sticky (hydrophobic) carbon particles; i.e., hydrocarbons such as PAHs are produced as pyrolytic (the carbon atoms are striped off their hydrogens) products during the carbon exhaust, also known as soot.

Diesel engines also produce nearly 20% of the total nitrogen oxides (NOx) in outdoor air and 26 percent of the total NOx from on-road sources. Nitrogen oxides are a major contributor to ozone production and smog.

Sulfur oxides are compounds of sulfur and oxygen (sulfur dioxide SO2 and sulfur trioxide SO3). SO2 combines with moisture at the tailpipe to form sulfuric acid (H2SO4, H2SO3). Nitrogen oxides and sulfur also cause respiratory problems.

Nitrogen oxides occur in diesel exhaust as compounds of nitrogen and oxygen (nitric oxide NO, and nitrogen dioxide NO2). NO2 is produced when the NO present in the exhaust gases react with oxygen.

Nitrogen Dioxide (NO2) is an odorless and colorless gas, that cannot be detected by the human nose. This makes it even more dangerous. As mentioned above, any odor that is associated with diesel exhaust is the unburned hydrocarbon fuel particulates and any "smoke" seen is the soot particulates. NO2 is heavier than air and will eventually settle. However, it is usually a good idea to mount NO2 sensors in the "Breathing Zone", approximately 120 to 180 cm from the floor. This is the area of air where most people breath when standing.

Nitrogen dioxide and other toxic hydrocarbons are carried deep into the lungs when inhaled, because they attach themselves to the carbon particles (soot).
Many components of diesel exhaust, such as benzene, arsenic, dioxins, and formaldehyde, are also known carcinogens in California. Other components, such as toluene and dioxins, are known as reproductive toxicants.

For the same load and engine conditions, diesel engines spew out 100 times more sooty particles than gasoline engines. As a result, diesel engines account for an estimated 26 percent of the total hazardous particulate pollution (PM$_{10}$) from fuel combustion sources in our air, and 66 percent of the particulate pollution from on-road sources. 10 over 40 chemicals in diesel exhaust are considered toxic air contaminants by the State of California (see Table 1).

**Table 1: Substances in Diesel Exhaust listed by Cal EPA as Toxic Air Contaminants**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Inorganic lead</th>
<th>Manganese compounds</th>
<th>Mercury compounds</th>
<th>Methyl ethyl ketone</th>
<th>Naphthalene</th>
<th>Nickel</th>
<th>4-nitrophenyl</th>
<th>Phenol</th>
<th>Phosphorus</th>
<th>Polycyclic organic matter, including polycyclic aromatic hydrocarbons (PAHs) and their derivatives</th>
<th>Propanaldehyde</th>
<th>Selenium compounds</th>
<th>Styrene</th>
<th>Toluene</th>
<th>Xylene isomers and mixtures</th>
<th>o-Xylenes</th>
<th>m-Xylenes</th>
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**Note:** California Health and Safety Code section 39655 defines a "toxic air contaminant" as "an air pollutant which may cause or contribute to an increase in mortality or in serious illness, or which may pose a present or potential hazard to human health."

Diesel buses and trucks are also important contributors to smog (ground-level ozone) and, as mentioned above, also fine toxic soot, two pollutants that have recently come under increased scrutiny because of their important public health impacts.
Soot Chemistry

Diffusion flames have a tendency to emit soot with the most complex chemical system because the fuel spends a considerable time at high temperatures in the absence of oxygen. Fuel rich pockets may form in diesel engines within a few microseconds, in gas turbine combustors and in furnaces as a result of incomplete mixing i.e., the non-premixed nature of the flames in these devices. Soot is a form from thousands of carbon atoms. It may also contain small amounts of hydrogen and some oxygen. The particles are usually emitted from combustion systems as long chain-like agglomerates. The individual particles in the agglomerates are spheres with typical diameters of 20 to 100 nm.

![Fig. 7. Representation of the different processes involved in soot formation](image)

![Fig. 8. Soot particle micrograph from Hess and Herd (1993).](image)

The gas-phase is modeled using a reaction system containing more than 1000 chemical reactions and over 100 species. The first aromatic rings, e.g. benzene and small PAHs, are formed in the gas phase. Acetylene molecules can react with these small PAHs and polymerize to larger PAHs. This process is modeled by the method of linear lumping. The first soot particles are formed when two PAHs collide and form a 3-D particle (particle inception). The soot particles formed can interact with the gas-phase by the addition of acetylene to their surfaces (surface growth) and by the reaction with molecular oxygen and the hydroxyl-radical (oxidation). Another process which increases the soot mass is the collision of a PAH with a soot particle.

However, soot particles are generally an aggregation of primary spheres (see figure 8) with diameters less than about 60 nm which can be described by fractal theories. The aggregates may vary in size from a few primary particles to equivalent diameters of 0.5 mm.

The nature of flames also create new solid materials like soot in their highest-temperature regions (as shown in the photomicrograph from figure 9). The mechanisms that produce soot in flames are among the most important unknowns of combustion science because soot affects contemporary life in many ways. Diesel soot is treated as non-reactive but forces the transformation of NO₂ and HNO₃ according to the following equations:

\[
\text{NO}_2 + \text{diesel soot} \rightarrow \text{NO} \\
\text{HNO}_3 + \text{diesel soot} \rightarrow \text{NO}_2.
\]

The calculated chemical life-times of NO₂ and HNO₃ due to heterogeneous reactions amount between 1 and 1½ hours.
Soot and Particulate Generation Mechanisms

The formation mechanisms for particles provide both insights on the factors that are important for health effects (such as the enrichment of surface layers in toxic compounds) and the details of the particle characteristics that can be used for source attribution. The formation mechanisms for particles from oil, coal, and waste combustion are shown in figure 9.

Larger particles are produced by the coking of the carbonaceous content of the fuel or the fusion or sintering of the inorganic particles and are in the size range of 1 to 100 µm. The shape and composition of these particles are strongly related to that of the parent fuel or waste.

In addition, a small fraction of the inorganic content of the fuel will vaporize and condense to form either a submicron aerosol or a surface coating on the larger particles. A fraction of the organic vapors will also be converted to soot.

- The distribution of particle sizes is primarily bimodal, with the order of 1% of the ash as submicron particles and the residual in the 1 to 20 µm range. The vaporization of the mineral matter can be modeled for both the refractory oxides and the trace toxic metals.
- The submicron ash is enriched in volatile elements relative to the larger particles. The enrichment is due to either condensation or reaction of the trace, sometimes toxic, elements with the particle surfaces.
- The surfaces of the larger particles are also enriched in volatile elements relative to their core.
- The submicron particles consist of aggregates of primary particles of 10–30 nm, similar to soot, whereas the larger particles consist of spherical particles including cenospheres and plerospheres.
- The particles that penetrate air pollution control devices are primarily in the 0.1 to 0.3 µm range, so that the submicron particles form a large fraction of the particles.

**Vaporization - Nucleation - Condensation - Coagulation Pathway**

![Diagram of particle formation mechanisms](image)

Fig. 9. Particle formation mechanisms (adapted from Huffman et al).
Soot behavior:

Upon liberation into the atmosphere, the dominant cooling mechanism for the particle becomes conduction to the surrounding gas. During the conduction phase, the difference between the particle surface temperature and the ambient gas temperature decays steadily in an exponential manner and these particles tend to increase their masses size with time.

Since the heat transfer by conduction depends on the temperature difference between the particle surface and the ambient gas, the gas temperature must also be known. The gas temperature may be determined from thermocouple measurements or other means. The relationship between particle size and the characteristic time of the exponential decay is shown in figure 10 for a range of sizes expected for primary particles.

Projected images of typical aggregates constructed using the present simulation are illustrated in figure 11 for N = 16, 64, and 256, which cover the range of mean aggregate sizes observed in non-premixed flames. The appearance of the aggregates varies considerably with the direction of projection, and from aggregate to aggregate within a population of given size. Nevertheless, the simulated aggregates are qualitatively similar to both past experimental observations of soot aggregates.
Instrumentation for Soot-Measurements (and for particles in general):

To develop processes and techniques for limiting the emission of soot, we must first possess suitable means for reliably measuring various soot-related parameters. These methods must have adequate dynamic range in order to be able to monitor and characterize the pollutant emissions over a very wide range of concentrations and must operate under a range of environmental conditions from in situ exhaust to atmospheric monitoring. In the case of particulate matter, information on the particle mass, size, and volume fraction is needed. The lack of availability of suitable diagnostics has resulted in a degree of uncertainty in the correlation of the particulate loading with health effects. Improvements in the instrumentation are needed to help in developing the test protocols, standards and regulations that will preserve the environment and limit risks to health.

Currently, the Scanning Mobility Particle Sizer (SMPS) is the method considered to be appropriate for measuring the particle size distribution in vehicle emissions. Unfortunately, the method requires extraction and sampling of the exhaust, dilution of the sample, and its operation is repeatable and reliable only under steady-state conditions.

Condensation nucleus counters (CNCs) which are similar to the Differential mobility particle sizers (DMPS) - the difference between the two is a more advanced software of the SMPS, but the hardware is virtually the same. It is equipped with pre-impactors and used to make coarse estimates of the size of particles above and below a set size (e.g. 0.3 mm). This method also requires sampling and a significant dilution of the sample (on the order of 1000:1) which can lead to errors in the measurements. In this device, the particles are charged using an electric field and separated by size. The particles separated into classes are then counted using a CNC to produce a number-weighted size distribution. Another related approach for measuring particles in the size range of 0.05 to 10 mm is the Electrical low-pressure impactor (ELPI). With this instrument, the particles are first charged and then passed through a Cascade impactor (CI) to segregate them into bins or size classes. The current deposited on each stage of the impactor may be related to the particle concentrations in the various size classes. These methods are useful but leave a degree of uncertainty due to the sampling process and transport of the particle samples to the device.

Gravimetric techniques are considered to be acceptable methods for characterizing the total particle loading. However, the methods do not provide information on the size distribution, require significant sampling times at low particle concentrations, are very time consuming, and are often unreliable because filters do not discriminate particulate matter from other condensed material. Laser-induced incandescence (LII) measurement is an emerging technology that promises to be a reliable means for spatially and temporally measuring the soot volume fraction and primary soot particle size.

Other analytical techniques to be used and the information they will provide are briefly summarized below and are shown schematically in the next page.

- **XAFS spectroscopy** (X-ray absorption fine structure): molecular structure of both major and trace elements, particularly metals and sulfur.

- **CCSEM** (Computer controlled scanning electron microscopy): Particle size distributions (PSD), particle morphology, and chemical composition ranges using binary and ternary diagrams.

- **TEM** (Transmission electron microscopy): can be used to investigate particles larger than 0.1µm structure as well as PSD of particles <0.1 micron in diameter.

- **Mössbauer spectroscopy**: quantitative iron phase distributions.

- **High-resolution ICP-MS** (Induction-coupled plasma mass spectrometry): measurement of sulfur isotopic ratios to determine the percentage of ammonium sulfate in and as well as outside PM2.5 fraction, derived from different fossil fuels.

- **XRF** (X-ray fluorescence spectrometric radiation detector) and **INAA** (Instrumental neutron activation analysis): major, minor and trace element concentrations.

- **TD-GC/MS** (Thermo-desorption gas chromatograph / mass spectrometry): volatile organic structure.

- **$^{13}$C NMR** (Nuclear magnetic resonance): molecular and skeletal structure of carbon.
Soot Clearance: (Non-Thermal Plasma Treatment of Soot - just one of many existing solutions)
The following tool relates to a new reactor configuration based on dielectric barrier discharge (DBD), which combines both plasma and filter techniques.

The system for the treatment of soot comprises a reactor based on DBD. The special DBD-configuration consists of two electrodes, one of which is a porous and gas-permeable (Fig. 14).
The DBD arrangement achieves more than 95 % of the soot particles can be removed from the diesel engine exhaust. The degree of soot reduction depends on the pore size distribution of the porous electrode (ceramics) mainly.

Fig. 13. Schematic showing relationship of the particle types, analytical techniques, and types of data to be produced by the proposed study (adapted from Huffman et al.).

Fig. 14. Schematic of the DBD-configuration
Existing Air Quality Standards:

The Clean Air act (an US national standard) was last amended in 1990, requires EPA to set National Ambient Air Quality Standards for pollutants considered harmful to public health and the environment. The Clean Air Act established two types of national air quality standards. **Primary standards** set limits to protect public health, including the health of "sensitive" populations such as asthmatics, children, and the elderly. **Secondary standards** set limits to protect public welfare, including protection against decreased visibility, damage to animals, crops, vegetation, and buildings.

The EPA office of Air Quality Planning and Standards (OAQPS) has set National Ambient Air Quality Standards for six principal pollutants, which are called "criteria" pollutants. Units of measure for the standards are parts per million (ppm) by volume, milligrams per cubic meter of air (mg/m$^3$), and parts per million (ppb) by volume, micrograms per cubic meter of air (µg/m$^3$).

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<tr>
<th>Pollutant</th>
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<tbody>
<tr>
<td><strong>Carbon Monoxide (CO)</strong></td>
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<tr>
<td>8-hour Average</td>
<td>9 ppm (10 mg/m$^3$) Primary</td>
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<tr>
<td>1-hour Average</td>
<td>35 ppm (40 mg/m$^3$) Primary</td>
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<tr>
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<tr>
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<td><strong>Ozone (O$_3$)</strong></td>
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<tr>
<td>1-hour Average</td>
<td>0.12 ppm (235 mg/m$^3$) Primary &amp; Secondary</td>
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<tr>
<td>8-hour Average**</td>
<td>0.08 ppm (157 mg/m$^3$) Primary &amp; Secondary</td>
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<td><strong>Lead (Pb)</strong></td>
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<td>Quarterly Average</td>
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<td><strong>Particulate (PM 10)</strong></td>
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<td><strong>Particulate (PM 2.5)</strong></td>
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<td>24-hour Average**</td>
<td>65 µg/m$^3$ Primary &amp; Secondary</td>
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<td><strong>Sulfur Dioxide (SO$_2$)</strong></td>
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<tr>
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<td>0.03 ppm (80 µg/m$^3$) Primary</td>
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<td>24-hour Average</td>
<td>0.03 ppm (365 µg/m$^3$) Primary</td>
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<td>3-hour Average</td>
<td>0.50 ppm (1300 µg/m$^3$) Secondary</td>
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* Parenthetical value is an approximately equivalent concentration
** The ozone 8-hour standard and the PM 2.5 standards are included for information only.
The 1990 Clean Air Act Amendments established a Heavy-Duty Clean Fuel and Low-Emission Vehicle (combined nonmethane hydrocarbon NMHC plus NO) standard from 3.15 grams per kilowatt-hour (g/kWh) implemented in the 1998 model year was down to 2.8 g/kWh because it determined that the "emission standard of 2.35 g/kWh is infeasible for clean diesel-fueled engines..."

Standards: US EPA 2004 Proposal:
The emissions standards for the more common identified gases found in diesel exhaust are 0.007 g/kWh for particulate matter (PM), 0.15 g/kWh for nitrogen oxides (NOx), and 0.1 g/kWh for NMHC. Nitrogen dioxide, sulfur oxides and hydrocarbons attached themselves to the carbon particles. For comparison, today's PM standard is 0.07 g/kWh for truck engines and 0.04 g/kWh for urban buses. Today's standards for NOx and NMHC are 3.0 g/kWh and 1.0 g/kWh, respectively, and the year 2004 combined NOX + NMHC standard is 1.8 g/kWh. The EPA estimates that this proposal, once fully implemented, would reduce 2.8 million tons of smog-causing nitrogen oxides emissions per year. Emissions of soot would be reduced by 110,000 tons each year.

Standards: US EPA 2007 Proposal:
The EPA is proposing a particulate matter (PM) emission standard for new heavy-duty engines of 0.01 g/kWh, to take full effect in the 2007 heavy-duty engine (HDE) model year. The proposed standards for oxides of nitrogen (NOx) and nonmethane hydrocarbons (NMHC) are 0.15 g/kWh and 0.10 g/kWh, respectively. These NOx and NMHC standards would be phased in together between 2007 and 2010, for diesel engines. Gasoline fueled heavy-duty engines would be also subject to these standards, effective 2007. The EPA is also proposing formaldehyde emission standards and new requirements for crankcase emissions control on turbocharged diesel engines.

Exhaust after treatment technologies that are expected to be required to meet the new standards are not tolerant to sulfur. Therefore, as a "technology enabler" the regulation establishes a maximum sulfur level in highway diesel at 15 ppm (by weight), down from today's 500 ppm. A phase-in schedule that has been adopted requires 80% of all highways fuel meeting the 15 ppm sulfur specification by Sept 2006, and nationwide availability by 2010. The emissions standards are tailored to force the use of diesel particulate filters on new heavy-duty engines.

Alternatives to diesel, such as natural gas and electric vehicles, are currently available for many applications. Many companies have successfully used alternative fuel trucks and buses, but more must be done to accelerate the transition to make these engines more available and economically viable. There is strong support from environmental groups that the state and the federal government provide incentives programs to help with the finance and assistance for owners of diesel vehicles and equipment who seek to switch to cleaner alternative fuels.

Cleaner alternatives to diesel engines include electric, liquefied natural gas (LNG) or compressed natural gas (CNG) in buses and trucks, fuel cells, etc. Biodiesel made from renewable resources such as vegetable oil or animal fat and even from used cooking oil, etc.

Although initial purchase prices may be higher for alternative fuel buses and trucks, federal, state, and local funds are available to offset these higher costs. These funds are specifically earmarked for clean technologies and would not otherwise be available for these purchases.
Health effects:

Diesel exhaust contains hundreds of constituent chemicals, dozens of which are recognized human toxicants, carcinogens, reproductive hazards, or endocrine disruptors.

In the past decade there have been numerous scientific studies evaluating the relationship between airborne particle pollution and human health effects. Since 1988, human exposure studies have evaluated acute effects of particle exposures. Almost all of these studies showed short-term impairment of respiratory function in healthy individuals and greater effects in people with asthma to increased hospital admissions for respiratory diseases, chronic obstructive pulmonary diseases (COPD), pneumonia, heart disease, and death. Most of the epidemiological studies published between 1988 and 1996 found a significant association between ambient levels of particles in the air and deaths from cardiac and respiratory problems.

In urban areas, exposure to low levels and short-term peak levels of diesel has the potential to cause more than 500 cancer cases per million persons. Two classes of possible health effects are:
1. Nonmalignant respiratory effects
2. Carcinogenic effects.

The EPA confirmed that the non-cancer effects of ambient PM can increase mortality and morbidity. The recommended chronic exposure level without appreciable hazard (inhalation reference concentration, RfC) for diesel particulates has been at 5 \( \mu \text{g/m}^3 \).

A number of conclusions has been drawn on the cancer effects of diesel exhaust particulates, as follows:

- Diesel exhaust is classified as "likely to be carcinogenic." Epidemiological studies suggest that occupational exposures to diesel exhaust particulates cause a small increase in the risk of lung cancer, in the range of about 20-50%. The EPA believes the cancer hazard is also applicable to ambient (i.e. environmental) exposures, even though none of the studies examined by the EPA show that lung cancer hazard is indeed present at environmental levels of exposure.

- Animal (rat) cancer studies are not clear for human hazard prediction and unsuitable for environmental exposure risk estimate. Quantitative statements on human risk cancer should be based on human epidemiological studies. However, the currently available data, due to a number of uncertainties, is deemed unsuitable for quantitative risk assessment.

- As a result, no specific cancer unit risk estimate for diesel exhaust is adopted or recommended in the EPA assessment.

According to experts estimate, lifetime exposure to diesel exhaust at the outdoor average concentration (2.2 \( \mu \text{g/m}^3 \)) may result in about one in every 2,000 people developing cancer due to this exposure. This estimate increases to as many as one in every 1,200 at levels found in the South Coast Air Basin in Southern California (3.6 \( \mu \text{g/m}^3 \)), and to even higher risks for those living near freeways or in highly polluted urban communities.

Further, a study published by the Health Effects Institute reports that more than 98 percent of the total number of particles in diesel exhaust are less than 1 \( \mu \text{m} \) in size. Small particles, such as those in diesel exhaust; and due to their hydrophobic properties, are particularly hazardous because they penetrate deeper into the recesses of the lungs, and tend to remain in there and in the surrounding lymph nodes rather than being cleared efficiently from the body.

The task of studying exposure to diesel exhaust is further complicated by the fact that there is no standard methodology for measurement of exposure, and there is uncertainty about which component or components of diesel exhaust may be most significant in inducing disease. Despite these difficulties, the occupational studies consistently demonstrate that exposure to diesel exhaust for ten years or more does significantly increase the human incidence of lung cancer, and possibly of bladder cancers.
Among a million people exposed chronically to 1 µg/m³ of diesel exhaust, it is estimated that 90 percent confidence range indicates that 34 to 650 people might be expected to develop lung cancer. The average estimate is 230 per million people are so exposed. In fact, the California Air Resources Board estimates that the average total exposure for Californians who spend most of their time indoors is 1.54 µg/m³ of diesel exhaust, while the average outdoor air concentration of diesel exhaust in California in 1995 is 2.2 µg/m³. These estimates were arrived at by averaging levels in both rural and urban areas. Estimates of diesel exhaust exposure levels in urban areas range as high as 23 µg/m³. Chronic exposure at these levels would potentially result in many more lung cancer cases. We expect exposure levels in rural and urban areas throughout the country to be similar to those found in California.

Scientific evidence suggests that non-cancer lung damage (such as reduced lung function and increased sensitivity to asthma) can occur when long-term ambient diesel particle levels are greater than 5 µg/m³. Although this is higher than the average concentration of diesel particles in California's air, people can be exposed to diesel-particle concentrations greater than 5 µg/m³ near truck stops, busy freeways, and other places where multiple diesel engines are in operation.

The International Agency for Research on Cancer concluded in 1989 that diesel engine exhaust "is probably carcinogenic to humans". In 1990, the State of California administratively listed diesel exhaust under Proposition 65 as a chemical known to the State to cause cancer. The National Toxicology Program in 2000 listed diesel particles as being "reasonably anticipated to be a human carcinogen."
The health risk from diesel exposure is greater for children, the elderly, people who have respiratory problems or who smoke, people who regularly strenuously exercise in diesel-polluted areas, and people who work or live near diesel exhaust sources.

Conclusions as to the state of knowledge in this area:

The worlds dependence on diesel fuel must be reassessed in light of growing scientific evidence that diesel exhaust poses a major health hazard, particularly to children, the elderly and people with weak immune systems. Diesel emissions are comprised of a witch's brew of potent carcinogens, reproductive toxicants, irritants, and other hazardous chemicals. This complex mixture of fine particles and toxic chemicals has been linked to cancer, asthma and other respiratory complications, and premature death. Fortunately, alternatives such as electric, natural gas, and other less polluting fuels are technologically feasible and, in some cases, economically advantageous. Another probably cheaper option for lowering the emissions from diesel combustion in addition to the recommended, which is turning to different fuels. This option improves vehicle combustion technologies. Application of new technologies in relation to diesel combustion result in significantly lower emissions, almost at the level of emissions from alternative fuels. For example a combination of ultra low sulfur fuel with particle traps and catalytic converts, results in extremely low emissions. One of the problems is that particle traps have not been developed yet to the level that it would be possible to use them on routine bases. Reduction of sulfur content in the fuel, while still expensive and not affordable for many countries, is becoming more and more commonly introduced. In the long term, the move away from diesel to clean alternatives will take a concerted effort by public and private operators and continued pressure from the people most affected by the health impacts of diesel exhaust.

Soot Summary

Aerosol black carbon "soot"

• Formed in all combustion of carbon fuels
• Small particle size ( < 1 µm)
• Graphitic microstructure is black (10 m²/gram)
• Inert: not destroyed by in- atmosphere processes: removed from the atmosphere only by deposition
• Surface may be highly porous and covered with chemically- active functional groups and/ or toxic compounds

Black carbon (BC) source emissions

• BC emission factors vary enormously (10⁶): depends on quality of combustion
• BC not automatically related to CO₂ emission
• BC emissions can not be predicted: must be measured
• BC particles from different sources can have different characteristics that produce different effects in the atmosphere (Coal/ Diesel, USA/ China/ Europe, etc.).
Dispersion scales
- Local: 10 km: public health, aesthetics
- Regional: 100 km: “haze”, environmental impact
- Continental: 1000 km: albedo, cloud modification
- Global: 10000 km: climate forcing, Global circulation models (GCM) tracing.

Ambient concentrations near sources
- Local concentration = Emission / Dispersion
- Strongly influenced by meteorology: storm vs. stagnation can result in 1000:1 change in BC
- Removal (dry deposition, precipitation) is slow
- Typical plume ~ 1000 km
- Local “smog”, regional haze

Continental-scale dispersion
- Removal by precipitation is dominant
- Strongly influenced by surface chemistry: hygroscopic vs. Hydrophobic
- Participation in heterogeneous chemistry
- Modification of cloud microphysics and albedo
- Mixed throughout troposphere
- “European Brown Cloud”

Long-range transport and dispersion
- Arctic Haze (1000 ng/ m³ at Barrow, AK)
- Asia Plume (100 ng/ m³ at Mauna Loa, HI)
- Antarctica (0.1 - 10 ng/ m³ at South Pole)
- In-transit survival depends on surface chemistry
- Stratosphere: aircraft exhaust: 1 - 10 ng/ m³

Direct optical effects
- Strong absorption, low albedo
- Tropospheric column optical depth >0.1 over Arctic

Indirect optical effects
- Deposition to snow and ice, modify surface albedo: Greenland ice cores
- May promote premature thawing
- *(Spy satellite pix of USSR)*

Heterogeneous-process effects - hygroscopic particles may
- participate in atmospheric chemistry (SO₂, SO₄)
- grow optically larger
- modify cloud nucleation and droplet size
- influence precipitation (“Weekend rainfall”)

Mitigation
- Improvement of combustion efficiency can drastically reduce emissions.
  Better diesel engine injectors, etc.
- Emissions standards for diesel vehicles (*esp.* Europe)
- Filtration and scrubbing at large point sources, reduce smokestack releases.
- Substitute electricity, gas or liquid fuels for domestic coal and wood use in developing countries.
Literature review of diesel emissions contributions either/or in terms of emission factors and airborne concentration levels:

**Literature:**
- Morawska L., 1999; *Lecturing Script for Environmental Aerosol Physics*; Dept. of Physics; QUT, Brisbane - AUS
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- Lutgens, F., Tarbuck, E.; 1998; *The Atmosphere*; 7th Edition; Prentice Hall; NI, USA

**Diesel / Soot Web-Sites:**
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  - http://www.epa.gov/otaq/regs/fuels/diesel/diesel.htm
  - http://www.epa.gov/otaq/id-hwy.htm
  - http://www.arb.ca.gov/newsrel/nr992800.htm
  - http://www.arb.ca.gov/toxics/diesel/diesel.htm
- Diesel exhaust:
  - http://www.epa.gov/nea/dieslehem.htm
  - http://www.state.nj.us/health/ohr/peosshweb/diesel.htm
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  - http://www.arb.ca.gov/toxics/diesel/tac/de-fnds.htm
  - http://www.nrdc.org/air/transportation/ebd/chap2.asp
- Diesel exhaust standards:
  - http://www.epa.gov/airs/criteria.html
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  - http://www.beatcs/sandfms.org/html/CheckForHg.html
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  - http://www.epa.vic.gov.au
  - http://www.epa.gov/OWOW/watershed/Procedeed/armstron.html
- Particulate matter:
- Soot-sites
  - http://members.nbci.com/LNellis/soot.html
  - http://www.chemie.tu-muenchen.de/wasser/aerosol/seite1.htm
  - http://www.mniprg.org/enviro/diesel/
  - http://microgravity.grc.nasa.gov/combination/lsp/lsp1_results.htm
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- Diesel soot purifier:
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- Soot chemistry: