Appendix – Properties of Diesel Emissions

A fact sheet prepared by ToxProbe

Diesel exhaust is a complex mixture of gases and fine particles that are emitted by internal combustion engines using diesel oil as fuel. The gaseous component of diesel exhaust is similar to the combustion products of other fuels. Although the adverse effects of diesel emissions are due both to the gaseous and particulate components, the toxicity of diesel exhaust is often expressed in relation to its particulate component. Several agencies have classified diesel exhaust as a carcinogen.

In North America, the diesel engine is used mainly in trucks, buses, agricultural and other off-road equipment, locomotives, and ships. The chief advantages of the diesel engine over the gasoline engine are its fuel economy and durability. Diesel engines, however, emit more particulate matter per mile driven compared with gasoline engines of a similar weight class. Over the past decade, modifications of diesel engine components have substantially reduced particle emissions.

Appendix A refers to diesel exhaust only, and not to diesel fuel oil, which also needs to be considered when estimating the risk from the use of diesel vehicles and other diesel engines.

Physico-Chemical Properties

Complete and incomplete combustion of fuel in diesel engines results in a complex mixture of gases and particles composed of hundreds of organic and inorganic compounds. The physical and chemical characteristics of diesel exhaust are dependent on many factors such as the composition of the fuel, the characteristics of the engine and the conditions under which the diesel is burned. This section provides an overview of the different components of diesel exhaust. Table A1 lists the major constituents of diesel exhaust.

There are several toxic gaseous components in diesel exhaust. The primary one is formaldehyde, which makes up 65%-80% of the aldehyde emissions. The other main aldehydes present are acetaldehyde and acrolein. The gaseous portion also includes benzene, 1,3-butadiene, carbon monoxide, polyaromatic hydrocarbons (PAHs), and nitro-PAHs. Dioxin compounds have also been detected in trace quantities. Dioxins from diesel exhaust account for 1.2% of total annual dioxin emissions in the US.

Diesel particulate matter (DPM) is the particle-phase of substances emitted in diesel exhaust. It refers to both the primary emissions and the secondary particles that are formed by atmospheric processes. Primary diesel particles are considered fresh after being emitted and undergo ageing (oxidation, nitration, or other chemical and physical changes) in the atmosphere.

Table A1. Percent Composition (by weight) of light-duty diesel engine exhaust (IPCS, 1996)

Pollutant	*Percent Composition*
Carbon dioxide	*7.1*
Water vapour	*2.6*
Oxygen	*15.0*
Nitrogen	*75.2*
Carbon monoxide	*0.03*
Hydrocarbons	*0.0007*
Nitrogen oxides	*0.03*
Hydrogen	*0.002*
Sulphur dioxide	*0.01*
Sulphates	*0.00016*
Aldehydes	*0.0014*
Ammonia	*0.00005*
Particles	*0.006*

Diesel exhaust particles are aggregates of primary spherical particles that consist of solid carbonaceous material and ash with associated adsorbed material. The particle portion of diesel exhaust contains elemental carbon (EC), organic carbon (OC), and small amounts of sulphate, nitrate, metals, trace elements, water, and other unidentified compounds. Elemental carbon usually makes up 50%-75% of the particles. Organic carbon makes up 19%-43% of the exhaust. It is composed of unburned fuel, engine oil, and small amounts of partial combustion and pyrolysis products. Polyaromatic hydrocarbons make up less than 1% of diesel exhaust particle mass.

Carbonaceous matter refers to all carbon-containing compounds in diesel particles, and includes the elemental and organic carbon. Organic carbon is made up of compounds containing carbon and hydrogen. The soluble organic fraction (SOF) is the portion of diesel particulate matter that can be extracted into solution. About one quarter of SOF is unburned fuel and three quarters is unburned engine lubrication oil. Partial combustion and pyrolysis products represent a very small fraction of the mass of SOF. Soot is the insoluble portion of diesel particle matter formed by clusters of elemental carbon and organic carbon particles.

The soluble organic fraction of diesel exhaust varies with many factors but has generally decreased since 1975. At present, exhaust particles from light-duty diesel engines have a higher proportion of soluble organic fraction than particles from heavy-duty engines. However, even with newer engines, some driving modes may produce a soluble organic fraction as high as 50% of the particulate matter.

A large number of elements and metals have been detected in diesel exhaust. They include barium, calcium, chlorine, chromium, copper, iron, lead, manganese, mercury, nickel, phosphorus, sodium, silicon, and zinc. These make up less than 1% of particle mass.

Most of the sulphur in the fuel is oxidized to sulphur dioxide (SO_2), but about 1-4% is oxidized and then converted to sulphate and sulphuric acid in the exhaust. The amount of SO_2 emitted is related to the sulphur content of the fuel. Non-road equipment uses fuel containing more sulphur than on-road diesel engines. The maximum allowable sulphur content in diesel is being reduced. Vehicles tested using low-sulphur fuel were found to have a sulphate content of only about 1%. Water content is about 1.3 times the amount of sulphate.

About 1-20% of total particle mass in diesel exhaust is in the ultra-fine size range ($PM_{2.5}$). The majority of these ultra-fine particles have an average size of 0.02 microns (range of 0.005-0.05 microns). They account for 50%-90% of the total number of particles. These very small particles are largely composed of sulphate and/or sulphate with condensed organic carbon. The composition of the ultra-fine particle component in the eastern United States differs from that in the west. In the east it is mostly composed of sulfates, and in the west, of nitrate, ammonium or organic carbon.

Approximately 80%-95% of the mass of particles in diesel exhaust is made up of fine particles (PM_{10}) with an average diameter of about 0.2 microns size range (range from 0.05-1.0 microns). The particles in this range are composed of spherical elemental carbon cores on which are adsorbed organic compounds, sulphate, nitrate and trace elements. Their large surface area makes them excellent carriers for the adsorbed compounds, which can effectively reach the lowest parts of the lung.

PAH and nitro-PAH make up about 1% of the particulate component of diesel exhaust. Differences in engine type and make, general engine condition, fuel composition and test conditions can influence the emissions levels of PAH. Increasing the aromatic content of the fuel may also increase PAH emissions.

The chemical composition of diesel particles to which people are currently exposed is a product of old and new technology and on-road and non-road engines. Although it is not possible to accurately characterize the mix, available data indicate that toxicologically significant organic components of diesel exhaust (e.g., PAHs, PAH derivatives, nitro-PAHs) that were present in the 1970s are still present.

Environmental Fate

The effects of diesel exhaust in the environment are similar to the effects of emissions from burning other fossil fuels. Diesel exhaust contributes to acid deposition (acid rain), the formation of ground-level ozone and global warming. Knowledge concerning the products of chemical transformation of diesel exhaust in the air is still limited. Secondary aerosols such as nitoarenes, nitrates and sulphates from diesel exhaust may also exhibit different biological reactivity than the primary particles. There is evidence that reaction of PAH in the exhaust with nitrogen oxides will form nitroarenes that are often more mutagenic than their precursors. A recent study has suggested that reaction with ground-level ozone increases the inflammatory effect of diesel particles in the lung of the rat.

After being emitted, diesel particles undergo ageing (oxidation, nitration or other chemical and physical changes) in the atmosphere. The atmospheric lifetime of the various compounds found in diesel exhaust varies and ranges from hours to days. Particles that are smaller than 1 micron can remain in the atmosphere for up to 15 days.

Primary diesel emissions are a complex mixture containing hundreds of organic and inorganic constituents in the gas and particle phases. The more reactive compounds with short atmospheric lifetimes will undergo rapid transformation in the presence of the appropriate reactants, whereas more stable pollutants can be transported over greater distances.

The particulate portion of diesel exhaust can be either primary (emitted directly) or secondary (formed from the transformation of the gaseous component). There is little or no hygroscopic growth of primary diesel particles, however products of oxidation are more hygroscopic. Since the products of oxidation are more soluble they are more readily removed from the air. Particles are removed from the atmosphere through accretion of the particles and dry or wet deposition. Particles of small diameter (<1 µm) are removed less efficiently and thus have longer atmospheric residence times. Because of their small size, diesel exhaust particles have residence times in air of several days, and they may be transported over long distances. Ultimately, they may be removed by wet deposition if they serve as condensation nuclei for water vapour deposition or are scavenged by precipitation in or below cloud.

Atmospheric lifetimes for several gas-phase components of diesel exhaust are on the order of hours or days, during which time atmospheric turbulence and advection can disperse these pollutants widely. Inorganic species such as sulphur dioxide (SO_2) and nitric acid have relatively fast deposition rates and remain in the air for less time than the organic components. Dry deposition of organic species is typically on the order of weeks to months.

Gaseous diesel exhaust will primarily react with sunlight, the hydroxyl (OH) radical, ozone, the hydroperoxyl (HO_2) radical, various nitrogen oxides and sulphuric acid. Reaction with the OH radical is the major removal route for PAHs in the gas phase and occurs within a few hours in daylight. In the presence of nitrogen oxides, this oxidation reaction can lead to the formation of nitroarenes or nitro-PAHs.

Oxides of nitrogen (primarily NO) that are emitted in diesel exhaust are also oxidized in the atmosphere to form nitrogen dioxide (NO_2) and particulate nitrate.

About 98% of sulphur emitted from diesel engines is in the form of SO_2. This is readily oxidized by the OH radical in the atmosphere and then rapidly transformed into sulphuric acid aerosols (H_2SO_4) through the reaction of the HO_2 radical and HSO_3 with water. Because SO_2 is soluble in water, it is scavenged by fog, cloud water and raindrops.

The particle matter of diesel exhaust is primarily composed of carbonaceous material (organic and elemental carbon) with a very small fraction composed of inorganic compounds and metals. The elemental carbon component of diesel exhaust is inert to atmospheric degradation.

High-molecular-weight PAHs in particulate matter are generally more resistant to atmospheric reactions than PAHs in the gas phase, leading to an anticipated half-life of 1 or more days. PAHs undergo photolysis, nitration, and oxidation. They react with sunlight, ozone, hydroxyl radicals, nitrogen oxides, nitrates and sulphates.

Ultra-fine particles emitted by diesel engines undergo nucleation, coagulation and condensation to form fine particles.

Toxicokinetics

Absorption

The primary route of human exposure to diesel exhaust is through inhalation. The properties and composition of an individual particle influence the biological fate of the various components of diesel exhaust. About 10% of diesel particles are deposited in the alveolar region of the lung. The half-time for clearance of particles in the alveolar region in humans is several months. Particles that are not cleared are absorbed by macrophages.

Distribution

The lung is the major target organ for diesel exhaust. Diesel particles absorbed by macrophages remain mostly in the lung. Elevated levels of DNA adducts in the lymphocytes of workers, and the presence of radio-labelled organic compounds in biological tissue and fluids of animals exposed by inhalation, suggest that some components of diesel exhaust are bioavailable.

Metabolism

The metabolism of diesel exhaust particles is similar to that of other insoluble foreign bodies. The particles are taken in by macrophages. This is followed by inflammation, cell death, impaired clearance and eventually deposition of collagen.

Excretion

Lung clearance mechanisms will remove diesel particles. At high concentrations, an overload of the removal mechanisms can occur. Macrophages that are laden with particles show decreased movement and lessened removal ability.

Human Health Effects

The main target organ of diesel exhaust is the lung. Available evidence indicates that current exposure levels are high enough to lead to adverse health effects. Diesel exhaust may cause cancer and may affect the immune system.

Death

Diesel exhaust is of low acute toxicity, however exposure can result in death from carbon monoxide, a component of diesel exhaust.

Respiratory effects
Acute exposure to diesel exhaust has been associated with irritation of the eye, nose, and throat, and with respiratory symptoms such as cough and phlegm. Diesel exhaust is known to contain various irritants in both the gaseous phase and particulate phase (for example, sulphur oxides (SO_x), nitrogen oxides (NO_x) and aldehydes). The evidence for potential chronic non-cancer health effects of diesel exhaust is based primarily on findings from chronic animal inhalation studies showing chronic inflammation and tissue changes in the lung in rats, mice, hamsters and monkeys. A few studies of workers have noted some respiratory symptoms, but overall, available studies have not shown significant chronic non-cancer health effects associated with diesel exhaust exposure in humans. Several epidemiological studies have demonstrated an association between air pollution and day-to-day changes in mortality, hospital emergency visits, and changes in lung function. The specific contribution of diesel exhausts to these effects is not known, however.

Immunological effects
Some studies in animals have shown decreased immune function after exposure to diesel exhaust, but others have not. Recent human and animal studies have shown that short exposures to diesel exhaust can produce allergic reactions and exacerbate symptoms to other allergens. Given the increases in allergic hypersensitivity in the U.S. population, the USEPA has indicated that this endpoint is of potential public health concern.

Neurological effects
Some reports of individuals in the workplace and in clinical studies exposed acutely to high concentrations of diesel exhaust have shown neurophysiological symptoms such as headache, light-headedness, nausea, vomiting, and numbness or tingling of the extremities. There has been some evidence from animal studies indicating possible neurological and behavioural effects. However, these have been observed at exposures higher than those have that caused respiratory effects.

Developmental and reproductive effects
There have been a few studies in animals showing sperm abnormalities, neurobehavioural effects in pups and other effects on reproduction.

Genotoxic effects and cancer
Diesel particulate matter and extracts of its organic components have induced gene mutations and chromosomal changes in a variety of bacterial and mammalian cell test systems. Both the particle core and the associated organic compounds have demonstrated carcinogenic properties. The particle component appears to contribute the most to carcinogenic effects, at least at high exposure levels. It is possible that the absorbed organic compounds, such as PAHs, play a more important role at lower exposure levels. The role of the gaseous components is still unclear.

The mechanism by which diesel exhaust causes tumours is not well understood. The carcinogenic effects may be related to the small size of diesel exhaust particles. It has been suggested that this could be the result of the genotoxicity of the compounds that condense on *the particles. Others suggest the exhaust causes DNA damage or that the particles cause an inflammation that then leads to increased cell multiplication.*

Many studies in both humans and animals have shown the potential for diesel exhaust to cause or contribute to the development of cancer in the lung. The evidence linking diesel exposure to bladder cancer is weak. Increased lung cancer risk has been observed in railroad workers, truck drivers, heavy equipment operators, and professional drivers. Several well-conducted studies in the rat have demonstrated that chronic inhalation exposure produced dose-related increases in lung tumours (benign and malignant). However, in other species the evidence is less clear. The consistent findings of carcinogenic activity by the organic extracts of diesel particle matter in non-inhalation studies (intratracheal instillation, lung implantation and skin painting) further contribute to the overall animal evidence.

It is biologically plausible for the mutagenic and carcinogenic components of diesel exhaust to increase the risk of lung cancer. This supports a causal relation between the association observed between exposures and cancers. Overall, the human evidence that diesel exhaust is carcinogenic is judged to be strong but not sufficient to consider diesel exhaust a human carcinogen. There is a lack of consensus about whether the effects of smoking have been adequately accounted for in various studies. The USEPA has concluded that chronic inhalation exposure to diesel exhaust has the potential to induce lung cancer in humans and has classed diesel exhaust particles in Group B1 – probable human carcinogen. In the 9th Report on Carcinogens (2000), diesel exhaust particles were listed as reasonably anticipated to be a human carcinogen. The International Agency for Research on Cancer (IARC, 1989) classified diesel exhaust in group 2A – probably carcinogenic to humans. There is insufficient information for an evaluation of the potential cancer hazard posed by the oral or dermal route of exposure.

References

Brightwell, J. et al., 1986. Neoplastic and functional changes in rodents after chronic inhalation of engine exhaust emissions. In Ishinishi, N. et al. (eds.) Carcinogenic and mutagenic effects of diesel engine exhaust. Elsevier, Amsterdam: 471-485. (As cited in IPCS, 1996)

CalEPA, 1998. Initial statement of reasons for rulemaking, staff report: proposed identification of diesel exhaust as a toxic air contaminant. California Environmental Protection Agency, Air Resources Board and Office of Environmental Health Hazard Assessment.

Creutzenberg, O. et al., 1990. Clearance and retention of inhaled diesel exhaust particles, carbon black, and titanium dioxide in rat lung overload conditions. J. Aerosol Sci (21): 455-458. (As cited in IPCS, 1996)

Garshick, E. et al., 1987.A case-control study of lung cancer and diesel exhaust exposure in railroad workers. Am Rev Respir Dis (135): 1242-8. (As cited in OEHHA, 1998)

Garshick, E. et al., 1988. A retrospective cohort study of lung cancer and diesel exhaust exposure in railroad workers. Am Rev Respir Dis (137): 820-5. (As cited in OEHHA, 1998)

Harris, J.E., 1983. Diesel emissions and lung cancer. Risk Anal (3/2): 83-100. (As cited in OEHHA, 1998)

Heinrich, U. et al., 1995. Chronic inhalation exposure of Wistar rats and two different strains of mice to diesel engine exhaust, carbon black, and titanium dioxide. Inhal Toxicol (7): 533-556. (As cited in IPCS, 1996; USEPA, 2000)

IPCS, 1996. Diesel and fuel exhaust emissions. World Health Organisation for the International Programme on Chemical Safety, Geneva. (Environmental Health Criteria, 171)

Ishinishi, N. et al., 1986. Long-term inhalation studies on effects of exhaust from heavy and light duty diesel engines on F344 rats. In Ishinishi, N. et al. (eds.) Carcinogenic and mutagenic effects of diesel engine exhaust. Elsevier, Amsterdam: 329-348. (As cited in IPCS, 1996)

Ishinishi, N. et al., 1988. Long-term inhalation experiments on DE. In: DE and health risks: results of the HERP studies. Tsukuba, Ibaraki, Japan: Japan Automobile Research Institute, Inc., Research 34 Committee for HERP Studies: 11-84. (As cited in IPCS, 1996; USEPA, 1993, 2000)

Mauderly, J.L. et al., 1987. DE is a pulmonary carcinogen in rats exposed chronically by inhalation. Fundam. Appl. Toxicol. (9): 208-221. (As cited in IPCS, 1996; USEPA, 2000)

Mauderly, J.L. et al., 1987. Effects of inhaled nitrogen dioxide and DE on developing lung. Cambridge, MA: Health Effects Institute; research report no. 8. (As cited in USEPA, 2000)

Nikula, K.J. et al., 1995. Comparative pulmonary toxicities and carcinogenicities of chronically inhaled DE and carbon black in F344 rats. Fundam Appl Toxicol (25): 80-94. (As cited in USEPA, 2000)

OEHHA, 1998. Health risk assessment for diesel exhaust. For the "Proposed identification of diesel exhaust as a toxic air contaminant. California Environmental Protection Agency, Berkeley, CA.

OEHHA, 1999. Toxicity criteria database: Cancer potency information. California Environmental Protection Agency, Berkeley, CA. http://www.oehha.org/risk/chemicalDB/

Smith, A.H., 1998. Direct simplified estimation of diesel exhaust cancer risk with linear extrapolation.
Presented at SRP meeting, 11 March 1998. (As cited in OEHHA, 1998)

USEPA, 1993. Integrated risk information system (IRIS): Diesel engine emissions. US Environmental Protection Agency, Washington, D.C. File on-line 06/01/1993. http://www.epa.gov/iris/subst/0642.htm

*USEPA, 2000. Health Assessment Document for Diesel Exhaust (SAB Review Draft). U.S. Environmental Protection Agency National Center for Environmental Assessment and Office of Research and Development
Washington, D.C. (EPA/600/8-90/057E)*

US NTP, 2000. 9th Report on carcinogens. US Dept. of Health and Human Services, National Toxicology Program.

WHO, 1989. IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Humans, vol. 46: Diesel and gasoline engine exhausts and some nitroarenes. International Agency for Research on Cancer, Lyon.

Yu, C.P. et al., 1991. Retention modeling of diesel exhaust particles in rats and humans. J Aerosol Med (4/2): 79-115. (As cited in USEPA 2000)