

Diesel Exhaust Particulates

CAS No.: none assigned

Reasonably anticipated to be a human carcinogen

First listed in the *Ninth Report on Carcinogens* (2000)

Carcinogenicity

Exposure to diesel exhaust particulates is *reasonably anticipated to be a human carcinogen*, based on limited evidence of carcinogenicity from studies in humans and supporting evidence from studies in experimental animals and mechanistic studies.

Cancer Studies in Humans

There is limited evidence for the carcinogenicity of diesel exhaust from studies in humans. Occupational exposure to diesel exhaust particulates was associated with elevated lung-cancer rates in the majority of studies, principally in transportation or construction workers exposed to diesel exhaust (IARC 1989, Cohen and Higgins 1995, Bhatia *et al.* 1998). Meta-analyses by Cohen and Higgins (1995) and Bhatia *et al.* (1998) suggested an overall relative risk of approximately 1.3 to 1.5 for lung cancer; some studies found higher risks in more heavily exposed subgroups. The increased risk was not readily explained by confounding from smoking or exposure to asbestos. However, only some studies used quantitative or semi-quantitative assessments of exposure, and many studies used inadequate measures of exposure.

Since diesel exhaust particulates were listed in the *Ninth Report on Carcinogens*, additional epidemiological studies have been identified. A meta-analysis reported that exposure to diesel exhaust increased the relative risk for lung cancer (Lipsett and Campleman 1999), and additional cohort and case-control studies reported relative risks in the range of 1.2 to 2.21 (Bruske-Hohlfeld *et al.* 2000, Gustavsson *et al.* 2000, Larkin *et al.* 2000, Järnholm and Silverman 2003, Kaupinen *et al.* 2003, Garshick *et al.* 2004, 2006, 2008, Laden *et al.* 2006, Parent *et al.* 2007, Neumeyer-Gromen *et al.* 2009). In the majority of studies in which adjustments were made for smoking or other exposures, the increase in risk was not substantially altered; however, as in earlier studies, residual confounding or interactions could not be ruled out. Some studies found higher risk estimates among individuals with higher cumulative exposure (Neumeyer-Gromen *et al.* 2009) or duration of exposure (Laden *et al.* 2006, Garshick *et al.* 2008). Some studies have also reported increased risks of cancer at other tissue sites, particularly the urinary bladder, but the evidence is generally less consistent than that for lung cancer (Boffetta and Silverman 2001, Boffetta 2004).

Cancer Studies in Experimental Animals

Exposure to diesel exhaust caused tumors in two rodent species, at two different tissue sites, and by several different routes of administration. In numerous studies, inhalation of whole diesel exhaust caused benign or malignant lung tumors (mainly adenoma, squamous-cell carcinoma, or adenocarcinoma) in rats of both sexes (IARC 1989, Brightwell *et al.* 1989, Nikula *et al.* 1995, Heinrich *et al.* 1995). Carcinogenicity appeared to be due to the particulate component of the exhaust, because the filtered vapor phase of exhaust did not cause lung tumors (Brightwell *et al.* 1989, Heinrich *et al.* 1995). Dermal exposure to solvent extracts of diesel exhaust particles caused benign and malignant skin tumors in mice of both sexes, and implantation of wax pellets containing the extracts into the lungs of female rats caused benign and malignant lung tumors (bronchiolar/alveolar adenoma and carcinoma and squamous-cell carcinoma) (IARC 1989).

Studies on Mechanisms of Carcinogenesis

Diesel exhaust contains known mutagens and carcinogens both in the vapor phase and associated with respirable particles (NTP 2000). Diesel exhaust particles are considered likely to account for the human lung cancer findings, because (1) they are almost all small enough to penetrate to the alveolar region in human lungs and (2) mutagenic and carcinogenic chemicals, including polyaromatic hydrocarbons (PAHs) and nitroarenes, have been extracted from these particles with organic solvents or with a lipid component of mammalian lung surfactant. In addition, only diesel exhaust that was not filtered to remove particles caused lung tumors in rats (Brightwell *et al.* 1989, Heinrich *et al.* 1995).

Although exposure to diesel exhaust particulates caused lung cancer in rats, the relevance of this finding for predicting carcinogenicity in humans has been questioned (NTP 2000). Exposure to diesel exhaust particulates caused a spectrum of inflammatory and neoplastic pulmonary responses in rats that are characteristic of responses also seen with other inhaled particles of varying toxicity. These responses apparently are little influenced by the chemical constituents of the particles. The precise bioavailability of chemical mutagens and carcinogens from inhaled diesel particulates is not known; however, DNA adducts were found in the lungs of rats exposed to diesel exhaust particulates (IARC 1989, NTP 2000). Furthermore, more DNA adducts were found in lymphocytes from workers occupationally exposed to diesel exhaust than in those from workers exposed at lower or ambient levels (Hou *et al.* 1995, Nielsen *et al.* 1996). However, diesel exhaust exposure was not quantified in these studies, and exposure to used motor oil may have contributed to the adducts observed in one study.

Properties

Diesel exhaust is a complex mixture of combustion products of diesel fuel; the exact composition of the mixture depends on the nature of the engine, operating conditions, lubricating oil, additives, emission control system, and fuel composition (Obert 1973, Ullman 1989). Diesel engines typically are classified by their service requirements, and the operating conditions for light- and heavy-duty diesel engines differ with respect to engine speed, expected load, fuel composition, and engine emission controls. Light-duty vehicles, such as automobiles and light trucks, typically operate at higher speeds than do heavy-duty vehicles, such as trucks. Depending on operating conditions, fuel composition, and engine-control technology, light- and heavy-duty diesel engines, respectively, can emit 50 to 80 times and 100 to 200 times as much particulate mass as typical catalyst-equipped gasoline engines (McClellan 1986).

Most diesel exhaust particles have aerodynamic diameters falling within a range of 0.1 to 0.25 μm (Groblicki 1979, Dolan *et al.* 1980, NRC 1982, Williams 1982). The particle size distribution of diesel exhaust is bimodal, with a nuclei mode of 0.0075 to 0.042 μm (for particles formed by nucleation) and an accumulation mode of 0.042 to 1.0 μm (for particles formed by agglomeration of nuclei particles) (Baumgard and Johnson 1996). Approximately 92% of the particles emitted from diesel engines are less than 1.0 μm in diameter (CARB 1997).

Diesel emissions consist of a nonpolar fraction (57%), a moderately polar fraction (9%), and a polar fraction (32%) (Schuetzle and Perez 1983, Schuetzle *et al.* 1985); the remainder is unrecoverable. The inorganic fraction of the particulate emissions consists primarily of small elemental carbon particles, ranging from 0.01 to 0.08 μm in diameter. Organic and elemental carbon account for approximately 80% of the total particulate matter mass. The remaining 20% is composed of sulfate (mainly sulfuric acid) (Pierson and Brachaczek 1983).

and some inorganic additives and components of fuel and motor oil. In general, the organic compounds identified in diesel exhaust emissions contain hydrocarbons, such as alkanes and alkenes, hydrocarbon derivatives, aldehydes, PAHs, PAH derivatives, multifunctional derivatives of PAHs, heterocyclic compounds, heterocyclic derivatives, and multifunctional derivatives of heterocyclic compounds (Schuetzle 1988).

Because of their large surface area, diesel exhaust particulates can adsorb relatively large amounts of organic material coming from unburned fuel, lubricating oil, and pyrosynthesis during fuel combustion. A variety of mutagens and carcinogens, such as PAHs and nitro-PAHs, are adsorbed by the particulates (NRC 1982, Tokiwa and Ohnishi 1986, IPCS 1996). The organic-extractable fraction of diesel exhaust particulates is typically in the 20% to 30% range, but it may be as high as 90% (Williams *et al.* 1989), depending upon vehicle type and operating conditions. In general, incomplete combustion in diesel engines operating under low-load conditions produces relatively low particle concentrations and a higher proportion of organic material associated with the particles (Dutcher *et al.* 1984). Particulate matter produced at low exhaust-gas temperatures has more adsorbed soluble organics than does particulate matter produced at high exhaust-gas temperatures (Kishi *et al.* 1992).

Use

Diesel exhaust particulates have no known uses.

Production

Internal combustion engines have been used in cars, trucks, locomotives, and other motorized machinery for about 100 years (IARC 1989). Diesel exhaust has three major groups of sources: mobile sources (on-road vehicles and other mobile sources), stationary area sources (e.g., oil- and gas-production facilities, stationary engines, repair yards, and shipyards), and stationary point sources (e.g., chemical-manufacturing facilities and electric utilities). As discussed above, the composition and quantity of the emissions depend mainly on the type and condition of the engine, fuel composition and additives, operating conditions, and emission-control devices.

Diesel engines operate with excess air (~25 to 30 parts air to 1 part fuel) (Lassiter and Milby 1978). The gas-phase fraction of emissions is composed primarily of typical combustion gases such as nitrogen, oxygen, carbon dioxide, and water vapor. As a result of incomplete combustion, the gaseous fraction also contains pollutants such as carbon monoxide, sulfur oxides, nitrogen oxides, volatile hydrocarbons, and low-molecular-weight PAHs and their derivatives. The total particulate emission concentration from light-duty diesel engines is much smaller than that from heavy-duty diesel engines. In general, newer heavy-duty trucks emit diesel particulates at a rate 20 times that of catalyst-equipped gasoline-fueled vehicles (IPCS 1996).

Exposure

Occupational exposure to diesel exhaust particulates has been studied among railroad workers, mine workers (who use diesel-powered equipment), bus-garage workers, trucking-company workers, forklift truck operators, firefighters, lumberjacks, toll-booth and parking-garage attendants, and workers in many occupations involved in servicing or handling automobiles (e.g., car mechanics and professional drivers). The National Institute for Occupational Safety and Health estimated that 1.35 million workers were occupationally exposed to diesel exhaust particulates in 80,000 U.S. workplaces (MMWR 1989).

Railroad workers' potential for exposure has increased since 1959, when almost all of the U.S. railroad system (95%) converted to diesel

engines. In studies conducted between 1996 and 2002, occupational exposure to elemental carbon was reported to be 4 to 20 $\mu\text{g}/\text{m}^3$ for train crews and 3 to 39 $\mu\text{g}/\text{m}^3$ for maintenance crews (Pronk 2009). Exposure to respirable particulate matter ranged from 17 $\mu\text{g}/\text{m}^3$ for clerks to 134 $\mu\text{g}/\text{m}^3$ for locomotive shop workers (Woskie *et al.* 1988). More recently, the U.S. Environmental Protection Agency reported that exposure of locomotive workers to respirable particulate matter ranged from 39 to 191 $\mu\text{g}/\text{m}^3$ (EPA 2002). In a railway repair facility in England, mean personal exposure to respirable particulate matter was 250 $\mu\text{g}/\text{m}^3$, and the concentration in ambient air was 163 $\mu\text{g}/\text{m}^3$ (Groves and Cain 2000).

Diesel engines have been, and continue to be, commonly used in U.S. mines since their first introduction in the early 1950s. Exposure occurs from activities that use diesel-fueled heavy machinery, such as blasting. From 1997 to 2004, occupational exposure to respirable elemental carbon in U.S. underground mining operations ranged from 148 to 637 $\mu\text{g}/\text{m}^3$ (Pronk *et al.* 2009). In surface mining operations, concentrations of respirable or submicron elemental carbon ranged from 13 to 23 $\mu\text{g}/\text{m}^3$. In enclosed spaces of mines, diesel exhaust particulate concentrations were up to 1,280 $\mu\text{g}/\text{m}^3$ (EPA 2002).

Exposure of mechanics in bus garages and truck terminals to respirable elemental carbon ranged from 20 to 40 $\mu\text{g}/\text{m}^3$ (Pronk 2009). Levels of diesel exhaust emissions were elevated at a bus garage during peak hours of bus activity (i.e., starting of buses) but rapidly returned to normal in 10 to 15 minutes (Pryor 1983). In another study, mean personal exposure to respirable particulate matter was 267 $\mu\text{g}/\text{m}^3$, and the mean concentration in ambient air was 211 $\mu\text{g}/\text{m}^3$ (Groves and Cain 2000). At a New York City bus stop, respirable particulate matter from diesel exhaust was measured at 46.7 $\mu\text{g}/\text{m}^3$ and was estimated to constitute 53% of the particulate matter in ambient air at that site (EPA 2002).

Exposure of truck drivers to elemental carbon in submicron particulate matter generally ranged from 1 to 10 $\mu\text{g}/\text{m}^3$ (Pronk *et al.* 2009). Temperature was an important factor, with higher exposures occurring at higher temperatures (Zaebst *et al.* 1991). This study found no discernible difference between truckers' exposure levels (3.8 $\mu\text{g}/\text{m}^3$) and highway background concentrations (2.5 $\mu\text{g}/\text{m}^3$), indicating that the highway environment, rather than the truck itself, was the source of the truck drivers' exposure. Exposure of mechanics to elemental carbon in truck terminals ranged from 20 to 40 $\mu\text{g}/\text{m}^3$.

Exposure of firefighters in fire stations to inhalable elemental carbon ranged from 10 to 40 $\mu\text{g}/\text{m}^3$ (Pronk 2009). Diesel fire trucks idling in a fire station can spread exhaust throughout the entire station (NJDHSS 2001). Firefighters in New York, Boston, and Los Angeles were studied to determine exposure to diesel exhaust particulates (Froines *et al.* 1987). Total exposure to airborne particles was measured with personal air samplers, and sampling was performed only when firefighters were in the fire stations. For the three cities, total airborne particulate exposure had a time-weighted average ranging from below 100 $\mu\text{g}/\text{m}^3$ to 480 $\mu\text{g}/\text{m}^3$. For a "worst-case" scenario, the mean concentrations were as high as 748 $\mu\text{g}/\text{m}^3$. The authors noted that these were busy fire stations in large metropolitan areas. Other factors, such as smoking, building design, age and maintenance of vehicles, activities of the firefighters, and timing of runs, also affected the results.

Occupational exposure to diesel exhaust from off-road vehicles was reported for construction and forklift operators in several settings (Pronk *et al.* 2009). Exposure to elemental carbon ranged from 132 to 314 $\mu\text{g}/\text{m}^3$ for tunnel construction, compared with only 4 to 13 $\mu\text{g}/\text{m}^3$ for outdoor highway construction. Exposure to inhalable or respirable elemental carbon was 4 to 122 $\mu\text{g}/\text{m}^3$ for dockworkers, including forklift operators; 6 to 49 $\mu\text{g}/\text{m}^3$ for workers loading and

unloading ships; and 11 µg/m³ for airline personnel in baggage and screening. Three studies reviewed by the International Agency for Research on Cancer found that toll-booth workers had elevated levels of exposure to diesel exhaust particulates. In many of these studies, however, it was difficult to differentiate between gasoline exhaust and diesel exhaust (IARC 1989).

Regulations

Environmental Protection Agency (EPA)

Clean Air Act

Mobile Source Air Toxics: Listed as a mobile source air toxic for which regulations are to be developed.

Mine Safety and Health Administration (MSHA, Dept. of Labor)

Standards have been developed for diesel exhaust monitoring and exposure mitigation in underground coal mines.

Guidelines

National Institute for Occupational Safety and Health (NIOSH, CDC, HHS)

Listed as a potential occupational carcinogen.

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