

Figure 3. Historical differences between the distillation properties of tractor trailer and railroad diesel fuels: (—) = tractor trailer; (---) = railroad. Sources of data: Bureau of Mines Diesel Fuel Survey 1959; U.S. Department of Energy Diesel Fuel Survey 1980. (Reprinted with permission from Cummins Engine Co., Columbus, OH, 1993.)

bimodal, with a nuclei mode (0.0075–0.056 μm) peak at about 0.02 μm and an accumulation mode (0.056–0.75 μm) peak at about 0.2 μm (Baumgard and Johnson 1992). The carcinogenic polycyclic aromatic hydrocarbons (PAHs) and nitro-PAHs (nitroarenes) attached to these respirable parti-

cles have been the focus of health concerns related to diesel exhaust. Recent studies show that these compounds also can be emitted in the gaseous phase (Johnson et al. 1994).

Engine manufacturers and research laboratories have contributed to the literature over the past 30 years with

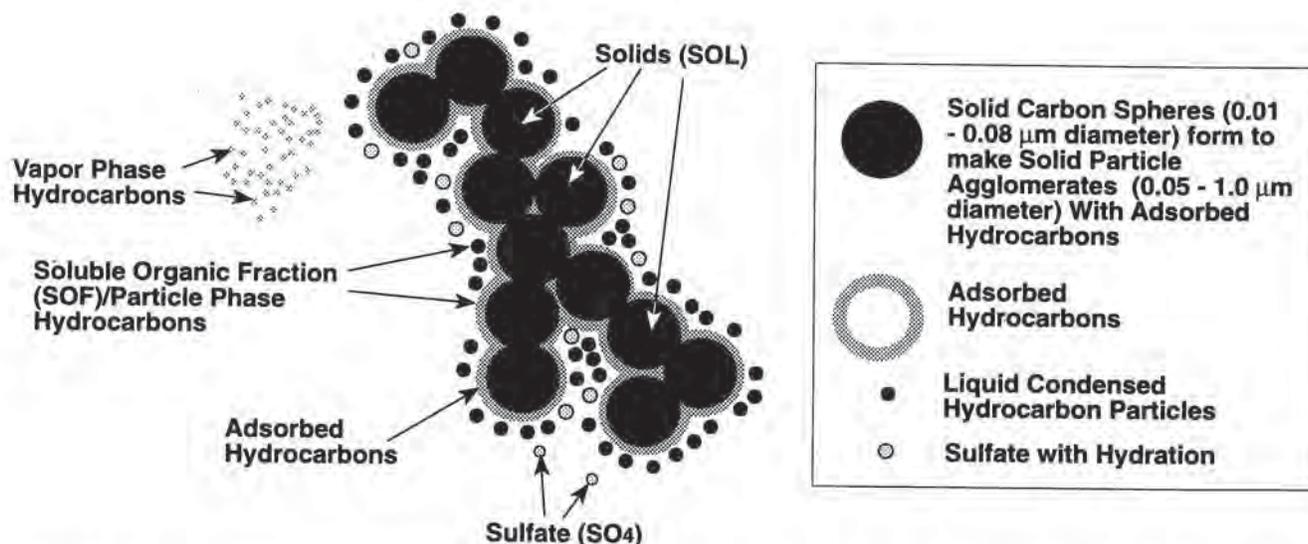


Figure 4. Schematic representation of diesel exhaust particles and vapor-phase compounds. (Adapted with permission from SAE Paper No. 940233, 1994, Society of Automotive Engineers, Inc.)

Table 3. Gaseous Emissions as a Function of Time Period and Engine Type^a

Emissions (g/kW-hr)	1970s ^{b,c}			1980s ^{b,d}			1990s ^b		
	4S-NA	4S-TC	2S-DI	4S-NA	4S-TC	2S-DI	4S-NA	4S-TC	2S-DI
Oxides of nitrogen	6.7-12.7	6.9-16.7	21.1-27.1	5.8-10.1	11.2-12.5	6.0-7.7	3.21-3.28	3.21-3.73	3.58-3.66
Hydrocarbons	2.1-4.5	0.2-2.9	0.4-2.7	1.5-3.3	1.6-1.75	0.6-1.7	0.15-0.22	0.15-0.75	0.08-0.38
Carbon monoxide	3.5-5.5	1.5-2.4	3.0-11.3	2.7-4.8	1.5-2.1	1.3-3.8	3.21-3.28	0.89-1.72	1.12-1.19

^a Abbreviations: 4S-NA = four-stroke, naturally aspirated; 4S-TC = four-stroke, turbocharged; 2S-DI = two-stroke, direct-injected.

^b Data are from U.S. Environmental Protection Agency (1973-1993).

^c Data are from Broering and Holtman (1974).

^d Data are from Opris et al. (1993).

emission measurements. These data were used to show trends in the development of the diesel engine over the years. An historical record of the physical, chemical, and mutagenic character of diesel emissions is summarized in Tables 3 through 8. Different engine labs used different test procedures; these included transient and steady-state engine testing. The data presented in Tables 3 through 8 were drawn from various publications, were grouped into three categories according to engine type (four-stroke, naturally aspirated; four-stroke, turbocharged; and two-stroke, direct-injected), and are given in ranges. Units of measurement are consistent for all emissions presented. Ranges were determined using the data found in the literature; the ranges are approximate given the different test procedures

and technologies used. Data generated after 1974 for gaseous emissions include EPA certification data, whereas data generated after 1988 include EPA particulate matter certification data along with gaseous data on the FTP transient cycle. During the past 20 years, diesel exhaust particle size distributions have remained relatively constant, but mass emissions and number concentrations have decreased. Figure 5 shows the approximate trend in total particulate matter (TPM) versus time.

The character of diesel emissions, especially the particulate matter, has changed in the past 20 years as technology has been introduced to meet smoke, hydrocarbons, NO_x, CO, and, in 1988, particulate matter emission standards. Hence, future exposures will differ in both concentration

Table 4. Particulate Matter and Vapor-Phase Emissions as a Function of Time Period and Engine Type^a

Emissions (g/kW-hr)	1970s ^b			1980s ^c			1990s ^d		
	4S-NA	4S-TC	2S-DI	4S-NA	4S-TC	2S-DI	4S-NA	4S-TC	2S-DI
Total particulate matter	2.1-3.0	0.6-2.5	0.8-1.9	0.25-0.6	0.28-0.58	0.4-0.6	0.18-0.19	0.11-0.39	0.1-0.25
Soluble organic fraction	0.22-0.31	0.08-0.28	0.08-0.2	0.05-0.36	0.07-0.26	0.03-0.06	0.03-0.09	0.03-0.09	0.03-0.09
Solids or carbonaceous fraction	1.8-2.6	0.5-2.2	0.7-1.7	0.2-0.25	0.2-0.31	0.35-0.55	0.02-0.04	0.02-0.04	0.02-0.04
Sulfates ($\mu\text{g}/\text{kW-hr}$)	20-120	40-120	20-50	15-70	27-55	20-50	< 0.5	< 0.5	< 0.5
Vapor-phase organic compounds	NA	NA	NA	0.22-0.25	0.22-0.25	0.22-0.25	0.12-0.39	0.12-0.39	0.12-0.39

^a Abbreviations: 4S-NA = four-stroke naturally aspirated; 4S-TC = four-stroke turbocharged; 2S-DI = two-stroke, direct-injected; NA = data not available.

^b Data are from Hare et al. (1975); Hare and Bradow (1979).

^c Data are from Wall and Hoekman (1984); Gratz et al. (1991); Opris et al. (1993); U.S. Environmental Protection Agency (1973-1993).

^d Data are from Pataky et al. (1994); Bagley et al. (1994).

Table 5. Particle Size Range by Volume as a Function of Time Period and Engine Type^a

	1970s ^b			1980s ^c			1990s ^d		
	4S-NA	4S-TC	2S-DI	4S-NA	4S-TC	2S-DI	4S-NA	4S-TC	2S-DI
Nuclei mode ^e	0.01-0.02	0.01-0.02	0.01-0.02	0.01-0.02	0.01-0.02	0.01-0.02	0.01-0.02	0.01-0.02	0.01-0.02
Accumulation mode ^f	0.2-0.3	0.2-0.3	0.2-0.3	0.15-0.25	0.15-0.25	0.15-0.25	0.15-0.25	0.15-0.25	0.15-0.25

^a Abbreviations: 4S-NA = four-stroke, naturally aspirated; 4S-TC = four-stroke, turbocharged; 2S-DI = two-stroke, direct-injected.

^b Data are from Kittelson et al. (1978); Khatri and Johnson (1978).

^c Data are from Baumgard and Kittelson (1985); Opris et al. (1993).

^d Data are from Baumgard and Johnson (1992); Pataky et al. (1994).

^e 0.0075 to 0.056 μm (particles that have high percentage deposited in lungs).

^f 0.056 to 0.75 μm (agglomerated particles that are partially deposited in lungs depending on size).

and composition from historical and current exposures. This change will be gradual because of the long life of the heavy-duty diesel powered vehicles (last vehicle from a given model year sales-retired 30 years later).

Focusing on particulate matter emissions does not indicate that the other gaseous emissions are unimportant. Hydrocarbons and CO emission levels have generally been well below mass emission standards. Control of NO_x from diesel engines remains difficult and can be made more difficult by particulate matter reduction. The current three-way catalyst technology used to control NO_x from gasoline engines is not applicable to diesel engines. This technology depends on precise stoichiometric control of the fuel:air ratio. Diesel engines necessarily operate over a wide range of mixture ratios, all with excess air.

Diesel engines can be direct injection or indirect injection, two-stroke or four-stroke, and naturally aspirated or turbocharged. In heavy-duty applications most engines in the field are direct injection, four-stroke, and turbocharged aftercooled—a design chosen to optimize fuel economy. The 1970s saw a mix of naturally aspirated engines, turbocharged engines, and turbocharged aftercooled engines in heavy-duty vehicles. Both two-stroke-cycle and four-stroke-cycle engines were in use, along with predominant direct-injection engines.

In the 1980s, a significant shift occurred, largely to turbocharged aftercooled engines, and four-stroke-cycle and direct-injection engines came to predominate. In light-duty applications, indirect-injection designs have dominated, but recently small direct-injection engines have been intro-

Table 6. Polycyclic Aromatic Hydrocarbon Emissions as a Function of Time Period and Engine Type^a

Emissions (ng/m ³) ^b	1970s	1980s ^c	1990s ^d
	4S-NA, 4S-TC, 2S-DI	4S-NA, 4S-TC, 2S-DI	4S-NA, 4S-TC, 2S-DI
Fluoranthene	NA	590-1,300	10-250
Pyrene	NA	2,100-2,300	200-1,700
Benz[<i>a</i>]anthracene	NA	600-1,600	900-5,500
Chrysene	NA	400-1,400	130-3,400
Benzo[<i>b</i>]fluoranthene	NA	180-340	700-6,000
Benzo[<i>k</i>]fluoranthene	NA	20-200	130-1,700
Benzo[<i>a</i>]pyrene	NA	50-250	100-550

^a Abbreviations: 4S-NA = four-stroke, naturally aspirated; 4S-TC = four-stroke, turbocharged; 2S-DI = two-stroke, direct-injected; NA = data not available.

^b Concentration in the soluble organic fraction.

^c Data are from Gratz et al. (1991); Opris et al. (1993).

^d Data are from Bagley et al. (1994); Hansen et al. (1994); Pataky et al. (1994).

Table 7. Nitro-Polycyclic Aromatic Hydrocarbon Emissions as a Function of Time Period and Engine Type^a

Emissions (ng/m ³) ^b	1970s			1980s ^c			1990s ^d		
	4S-NA, 4S-TC, 2S-DI			4S-NA, 4S-TC, 2S-DI			4S-NA, 4S-TC, 2S-DI		
2-Nitrofluorene	NA			5-600			100-3,100		
1,6- and 1,8-Dinitropyrene	NA			400-800			20-400		
1,3-Dinitropyrene	NA			200-600			10-150		
1-Nitropyrene	NA			6-180			10-80		
3-Nitrofluorene	NA			4-1,500			<17		
7-Nitrobenz[a]anthracene	NA			1-30			<17		
6-Nitrochrysene	NA			2-25			<15		

^a Abbreviations: 4S-NA = four-stroke, naturally aspirated; 4S-TC = four-stroke, turbocharged; 2S-DI = two-stroke, direct-injected; NA = data not available.

^b Concentration in the soluble organic fraction.

^c Data are from Gratz et al. (1991); Bagley et al. (1994).

^d Data are from Bagley et al. (1994); Hansen et al. (1994).

duced, primarily because of their better fuel economy. Given sufficient development effort, these engine design parameters are not major determinants of emissions, however. Rather, emissions reductions to date have resulted from modifications to the combustion processes. Exhaust-aftertreatment emission control systems have not yet been applied, with a few minor exceptions, in light-duty vehicles and 1994 medium-duty truck diesel engines.

Modifying fuel composition is a simple and cost-effective approach to reducing emissions. Fuel sulfur results in gaseous sulfur dioxide and particulate sulfates. As of October 1, 1993, sulfur levels in diesel fuel used for on-highway applications were limited to 0.05% or less by weight. Although a number of metal-based fuel additives for smoke reduction have been demonstrated in laboratory and limited field studies, none has been approved for use, primarily because of concerns about additional pollutants the additives would introduce.

Alternative fuels, primarily natural gas and methanol, are suitable for use in diesel engines or in engines derived

from diesel engines and greatly reduce particulate emissions, providing a means of meeting the 1994 standards. These fuels are being used initially in heavy-duty engines in bus fleets.

Recently the EPA promulgated new regulations for the registration of fuel and fuel additives (U.S. Environmental Protection Agency 1994b). These registration requirements cover both gasoline and diesel fuel, as well as fuel additives. Provisions also address the following alternative fuels: methanol, ethanol, compressed natural gas, liquified natural gas, and liquified petroleum gas. The regulations are organized within a three-tier structure. Tier 1 requires fuel and fuel additive manufacturers to perform a literature search on the health and welfare effects of fuel and fuel additive emissions, characterize the emissions, and provide qualitative exposure information. Emission characterization requirements include the measurement of hydrocarbons, CO, NO_x, particulate matter, aldehydes, ketones, alcohols, ethers, PAHs, and atypical products. Tier 2 requires biological testing for the examination of subchronic systemic and

Table 8. Mutagenic Activity as a Function of Time Period and Engine Type^a

Emissions (Revertants/μg)	1970s ^b			1980s ^c			1990s ^d		
	4S-NA	4S-TC	2S-DI	4S-NA	4S-TC	2S-DI	4S-NA	4S-TC	2S-DI
Activity ^e	0.5-8.2	NA	NA	NA	30-70	NA	NA	2-10	NA

^a Abbreviations: 4S-NA = four-stroke, naturally aspirated; 4S-TC = four-stroke, turbocharged; 2S-DI = two-stroke, direct-injected; NA = data not available.

^b Data are from Hunter et al. (1981).

^c Data are from Gratz et al. (1991); Opris et al. (1993).

^d Data are from Pataky et al. (1994); Bagley et al. (1994); Hansen et al. (1994).

^e Concentration in the soluble organic fraction.

organ toxicity as well as the assessment of specific health effects endpoints. When appropriate, Tier 3, which includes follow-up studies or other additional tests, may be required.

Historically up to 50% of diesel emissions particulate matter mass could be traced to the lubricating oil. Thus reducing oil consumption has been a basic goal of engine design. Recent advances demonstrate a reduction of the fraction of particulate matter that results from the lubricant to approximately 20% (Zelenka et al. 1990).

Current engines meet emission control requirements through a variety of engine modifications and refinements. Traditionally, indirect-injection engines have had lower particulate emissions, but improvements in direct-injection engines have eliminated this advantage. Increasing intake air swirl, changing combustion chamber geometry, and reducing crevice volumes all have resulted in reduced particulate matter emissions. The fuel injection system is the critical element in controlling engine emissions. Very-high-pressure injectors (in excess of 1,500 atmospheres) combined with reduced sac volume (the small volume at the tip of the injector), precise timing, control of injection rate, and fuel metering through computer control have reduced all emissions. These changes have reduced the fuel-related soluble organic fraction and the solid fraction of TPM that result from the combustion process. Variable-geometry, intercooled turbochargers pro-

vide some emissions reductions, improve engine performance, and may come into greater use in the future. Engine modifications should allow most engines used in heavy-duty vehicles to meet the 0.1 g/bhp-hr particulate matter standard without exhaust aftertreatment. Oxidation catalytic converters are being used along with engine modifications in medium-duty diesel engines for 1994.

Diesel catalytic converters oxidize hydrocarbons contained in the soluble organic fraction of the particulate matter, which is typically 10% to 30% of the total particulate matter (TPM) for present engines. The soluble organic fraction of emissions for some engines built in the 1970s and early 1980s was 70% to 80%, with lube oil being the main contributor to this higher level. Bagley and coworkers (1991) reported particulate matter and soluble organic fraction reductions of 90% and 99% in a diesel engine using low-sulfur (0.039%) fuel. They also measured a 98% reduction in mutagens associated with particulate matter. These converters also oxidize gaseous hydrocarbons and CO. Exhaust treatment using a catalytic converter, when combined with engine modifications, provides a means of meeting the 0.1 g/bhp-hr standard that is simpler and less costly than using trap oxidizer systems.

CONTROL TECHNOLOGY DEVELOPMENTS

The focus of the engine industry's research and development for meeting standards for 1996 and beyond has been on reducing engine-out emissions. Research has minimized the use of aftertreatment technology because of the additional costs and complexity that would result from this approach as compared with developing advanced technology internal to the engine. Johnson and associates (1994) extensively reviewed various control technologies and the effects they have on regulated and unregulated emissions. Figure 6, from a different study, shows in schematic form the technical strategy needed to reduce TPM by reducing the three primary components: sulfate; the solids or carbonaceous fraction, defined as the soot that is a part of the insoluble fraction (Kawatani et al. 1993); and the soluble organic fraction. The solids or carbonaceous fraction can also be reduced effectively by using a trap (not shown in Figure 6). The trap also would be somewhat effective in reducing the soluble organic fraction, depending on operating conditions. Traps probably will be used only when retrofitting and rebuilding engines or if health studies show serious problems with the present level of solid particles being emitted from diesel engines meeting the 1994 heavy-duty standards.

Figure 7 shows the distribution of the particulate mass among the soluble organic fraction, solids or carbonaceous

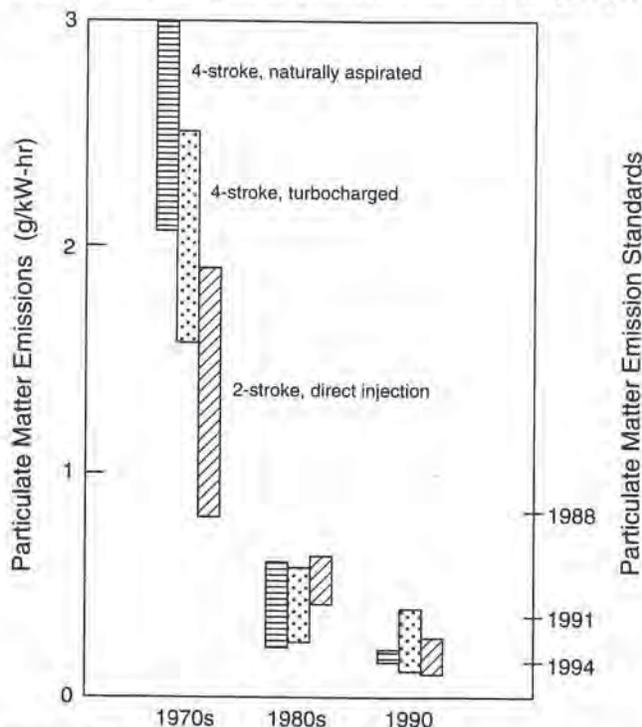


Figure 5. Particulate matter emissions versus time for various diesel engine types, 1970-1990.

fraction, and vapor phase for several combinations of production engines (1988–1991), fuels, and prototype control technologies for two operating conditions. Oxidation catalysts reduce the soluble organic fraction and vapor phase but have little effect on the solids fraction (Pataky et al. 1994). The following sections briefly review the research and development status of traps, catalysts, engine design changes, exhaust gas recirculation, and fuel composition and additive effects on reducing emissions.

TRAPS

The trap system consists of a substrate to collect the particulate matter and some means to periodically burn or oxidize (regenerate) the collected particulate matter from the substrate. The regeneration system design also must ensure that the process is controlled and that it completely regenerates the particulate matter in the trap without melting or cracking the substrate under the high temperature of regeneration. Generally, the regeneration part of the trap can be characterized as either a "passive" or an "active" system. Passive system approaches have generally involved catalyzed coatings on the trap substrate or the use of additives in the fuel such that either the original additive or the additive

reaction products are deposited with the diesel particulate matter on the trap substrate, which then catalyzes the regeneration process. Passive systems using either a copper or cerium fuel additive are being pursued to meet the 1996 new urban bus standards and the 1995 bus standards for rebuilt engines (Pattas et al. 1992; McKinnon et al. 1994). Active systems have sensors that monitor the buildup of particulate matter in the trap; periodically the control system activates specific processes, involving diesel fuel burners or electric heaters, to initiate oxidation of the collected particulate matter. These active systems have generally been complex and costly, and there seems to be less interest in further developing this type of technology.

CATALYSTS

Further research is being carried out to develop oxidation catalysts for reducing the soluble organic fraction of the TPM, the vapor-phase hydrocarbons, and CO emissions from diesel engines. Also, a worldwide research effort directed toward developing catalysts for NO_x reduction is under way. The challenge of developing a NO_x catalyst is to achieve NO_x decomposition in the oxidizing atmosphere of diesel exhaust.

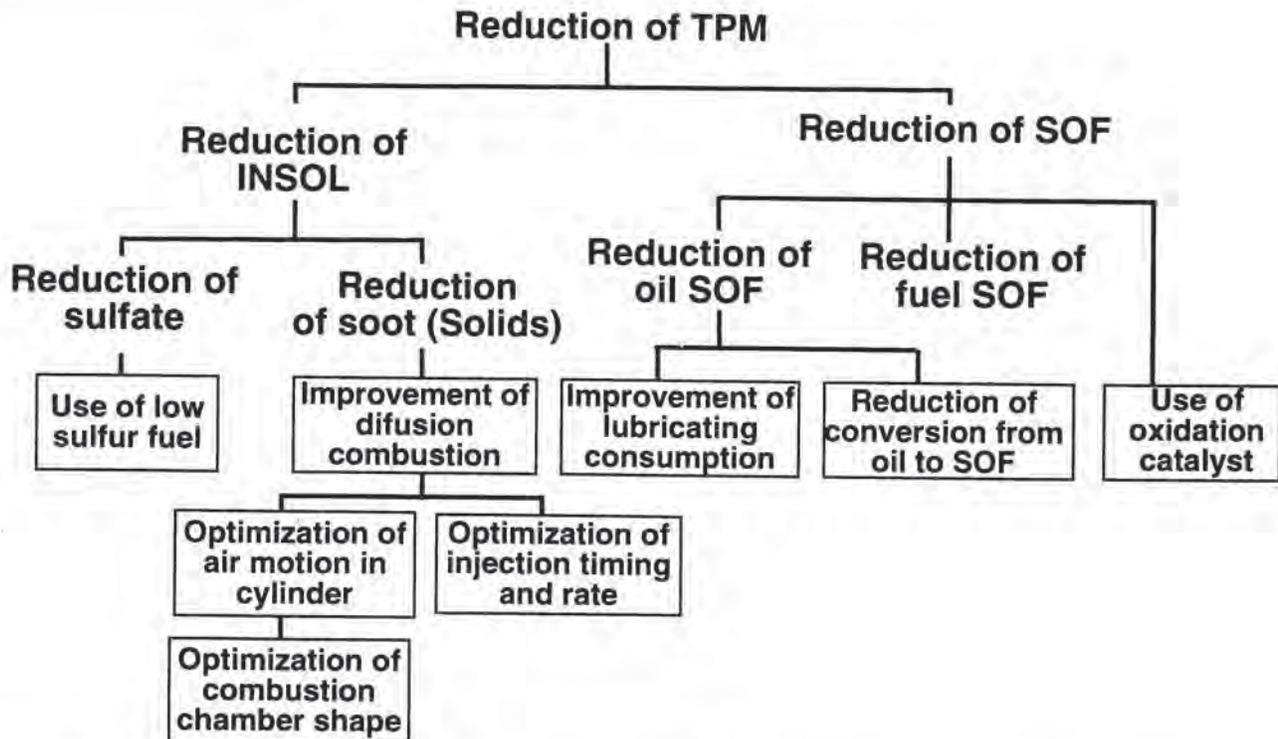


Figure 6. Strategy for reducing total particulate matter; TPM = total particulate matter; INSOL = insoluble fraction; SOF = soluble organic fraction. (Reprinted with permission from SAE Paper No. 940233, 1994, Society of Automotive Engineers, Inc.)

To decompose NO_x in the oxidizing atmosphere of diesel exhaust, two routes are possible (Herzog et al. 1992). Selective catalytic reduction requires the injection of a reducing agent and appears to be too complex for automotive application; more research now appears to be focused on the nonselective catalytic reduction (NCR) system. In one approach to NCR, researchers using specially coated zeolite catalysts have achieved NO_x reductions of 30% (Herzog et al. 1992) as well as soluble organic fraction reductions similar to those achievable with oxidation catalytic converters (i.e., 60% to 80%). Extensive research is needed, however, to develop nonselective catalytic reduction systems that offer greater durability with higher NO_x conversion efficiencies (50% to 60%), soluble organic fraction conversion efficiencies equivalent to those yielded by oxidation catalytic converters, and low sulfate conversion.

ENGINE DESIGN

The soluble organic fraction (fuel and lubricant fractions) and solids or carbonaceous fraction of TPM and NO_x can be controlled to low levels by creative and innovative engine designs. The studies of Zelenka et al. (1990); Herzog et al. (1992), and Kawatani et al. (1993) include useful discussions of engine design changes that result in a low soluble organic fraction, a low solids or carbonaceous fraction, and low NO_x emissions. Key engine design variables that influence these emissions are reviewed below to form a basis for defining an engine design strategy focused on minimizing tailpipe-out emissions with a given fuel. Combustion system design considerations for reducing the fuel-related soluble organic fraction component, the solids or carbonaceous fraction, and the NO_x emissions are discussed first, followed by a discussion of approaches to reducing the oil-related soluble organic fraction component.

The fuel injection system along with the in-cylinder air/combustion system is the most important part of the diesel engine for reducing both TPM and NO_x emissions. Zelenka and coworkers (1990) present data on the importance of peak injection pressure and the trade-off of TPM and NO_x emissions for various injection timing conditions using a unit injector.

Electronic fuel system control is also necessary for minimizing trade-offs among hydrocarbons, NO_x , the solids or carbonaceous fraction, and fuel consumption as a function of speed, load, and ambient conditions. Control of fuel metering and injection timing during cold starting, warmup, transient operation, and for various altitudes is necessary to achieve low TPM, hydrocarbons, and NO_x emissions.

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Zelenka and coworkers (1990) have explored the influence of fuel-air mixing on engine performance by varying fuel system parameters and combustion bowl configurations to achieve both a low solids or carbonaceous fraction and low NO_x emissions. They defined the ideal shape (rate versus time) of the injection for fuel delivery. Current fuel systems cannot fulfill the ideal requirements, and new fuel injection systems need to be developed with techniques for rate-shaping (changes in rate versus time as a function of operating variables) to achieve low NO_x and solids or carbonaceous fraction levels.

Zelenka and coworkers (1990) have shown that tailpipe lube-oil particles in the transient operating cycle test correlate well with lube-oil consumption. The researchers sug-

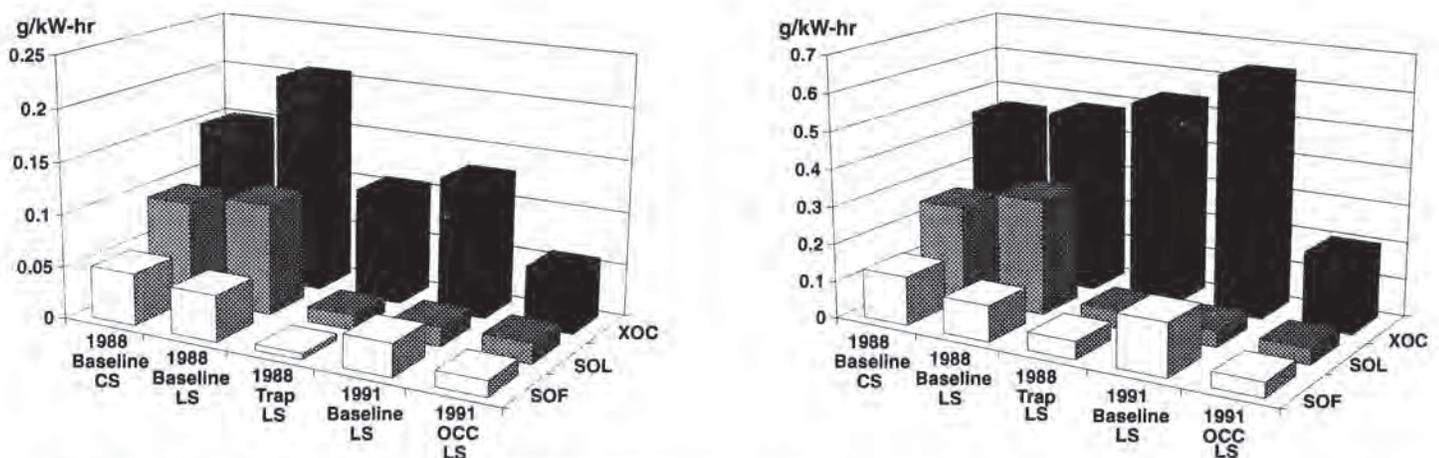


Figure 7. Effect of engine, fuel, and control technology in particulate mass emission distributions: (left) mode 9, 75% load; (right) mode 11, 25% load. CS = conventional sulfur fuel (0.32% by mass); LS = low sulfur fuel (0.01% by mass); OCC = oxidation catalytic converter; SOF = soluble organic fraction; SOL = solids or carbonaceous fraction; XOC = vapor-phase hydrocarbons. (Reprinted with permission from SAE Paper No. 940233, 1994, Society of Automotive Engineers, Inc.)

gest the need to reduce the lube-oil contribution to TPM, which would involve achieving objectives in three major areas related to the oil system:

- Minimization of oil consumption from the cylinder wall.
- Minimization of all possible oil entrances into the intake and exhaust system (e.g., valve stem seals, turbocharger shaft seals, blow-by return).
- Development of lube oils with properties that result in very low lube-oil consumption and with emission characteristics that result in durability for oxidation catalytic converters or other aftertreatment devices.

Zelenka and coworkers (1990) state that the oil consumption from the cylinder wall is the main source of lube-oil particulate matter. They also present data and state that imperfections in piston-ring seals, attributable to bore distortion, are the predominant parameter that affects lube-oil consumption. Kawatani and associates (1993) state that because the solids or carbonaceous fraction and the fuel-related soluble organic fraction have been reduced through combustion system optimization, the lube-oil part of the soluble organic fraction of TPM has greatly increased.

EXHAUST GAS RECIRCULATION

Exhaust gas recirculation is a technology in development for heavy-duty diesels that offers potential for meeting the 4 g/bhp-hr NO_x standards for 1998. Herzog and colleagues (1992) state that most of today's European indirect-injection and direct-injection light-duty diesel vehicles use exhaust gas recirculation as an effective means to reduce NO_x and that it is a proven technology in the light-duty field. The technology has been used in the form of a relatively simple on/off control system, as well as a more sophisticated closed-loop control system, in conjunction with electronic control of fuel injection.

Data from Herzog and colleagues (1992) present the effect of exhaust gas recirculation on NO_x and TPM at different loads and speeds for a heavy-duty diesel engine of the U.S. 1994 technology level without aftertreatment devices. With uncooled exhaust gas recirculation, the intake manifold temperature increases with increases in the recirculation rate. This results in a reduced air:fuel ratio and an increase in TPM, or more specifically an increase in the solids or carbonaceous fraction. Herzog and colleagues (1992) show that the TPM increase can be reduced by cooling the recirculating exhaust gas.

Herzog and colleagues (1992) present data related to the TPM/NO_x trade-off with a simple on/off exhaust gas recirculation system. They also show data generated with feedback control of exhaust gas recirculation and an oxidation

catalytic converter. These data reflect potential systems that could be in production in 1998 to meet the 4 g/bhp-hr NO_x standard for heavy-duty engines. Serious concern remains, however, about reduced engine durability due to increased wear rates with exhaust gas recirculation. Improved oil formulations along with advanced oil systems could result in engines that have acceptable durability and meet the EPA 1998 heavy-duty diesel emission standards for NO_x and TPM.

FUEL AND ADDITIVE EFFECTS

Extensive data are available regarding fuel effects on diesel engine emissions. A Society of Automotive Engineers document (1993) is a particularly up-to-date reference on diesel fuels for the 1990s. It contains a number of papers on the effect of fuel composition and additives on emissions and performance.

Several fuel variables other than sulfur level also affect diesel emissions. Zelenka and coworkers (1990) present data from various studies to support evidence that cetane number affects NO_x emissions. They performed linear averaging to arrive at a mean value of -0.0417 g/bhp-hr NO_x per unit cetane number. On the basis of this mean value, an increase of 10 cetane number units would yield a 0.4 g/bhp-hr NO_x reduction on the transient test without engine modifications.

The diesel engine industry in general would like to have a reformulated diesel fuel before the 1998 standards become effective (Slodowske 1993). The industry would like (1) further sulfur reduction, (2) reduction of aromatics or carbon:hydrogen ratio control, (3) a cetane number increase, (4) distillation curve control, and (5) use of oxygenates. The industry also would like fuel sulfur levels decreased from 0.05% to 0.01% by mass.

The sulfur decrease would reduce the sulfate emissions by 0.01 g/bhp-hr, assuming no change in the conversion efficiency from sulfur to sulfates (Slodowske 1993). This would permit the use of a more active oxidizing catalyst, which would achieve higher control efficiencies on the soluble organic fraction from the fuel and the lubricating oil. It would also improve the possibility that a nonselective catalytic reduction system for NO_x could be developed. A cetane number increase to 55 as a minimum specification would reduce both TPM and NO_x emissions (Slodowske 1993). The addition of oxygenates reduces TPM emissions (particularly the solids or carbonaceous fraction). Liotta and Montalvo (1993) showed a 5% to 20% reduction in TPM with various oxygenates added to a reference diesel fuel used in a 1991 Detroit Diesel Series 60 engine. The oxygenated additives that were blended with

the reference fuel were an aromatic alcohol, an aliphatic alcohol, polyether polyol, three different glycol ethers, methyl soyate, and diglyme. The diesel engine industry believes that cetane number enhancement is the most cost-effective way to change fuel for reduced emissions (Slodowske 1993).

This reformulated fuel would respond to customer complaints with respect to (1) white smoke, (2) cold starting, and (3) engine noise. Further, it would improve fuel economy and enhance performance. The reformulated fuel also would benefit all diesel engines in the field. Also, the development of this reformulated diesel fuel would provide definition for the clean diesel fuel concept as outlined in the 1990 Clean Air Act (Slodowske 1993).

Tree and coworkers (1993) have presented experimental single-cylinder data using a Texaco additive containing isocyanic acid that was incorporated into a thermally stable carrier and blended with the fuel as an additive. This approach is an in-cylinder method for achieving selective catalytic reduction of the NO_x formed in the cylinder. The data from this study indicate that NO_x reductions in a single-cylinder engine were as much as 40% to 50% using 5% by mass of the Texaco additive. The additive at the 5%-by-mass level would be used more as a blending agent than an additive. The authors also indicate that attempts to reproduce the data suggested that the variability and stability of the additive were an issue. The additive approach is designed to overcome many of the disadvantages of aftertreatment selective catalytic reduction systems.

A low-sulfur, low-aromatic, high-cetane-number fuel is an essential part of efforts to meet the 0.1 g/bhp-hr particulate matter and 4 (or lower) g/bhp-hr NO_x emission standards. Sulfur contributes sulfates that are collected as particulate matter in the test procedure. The air pollution implications of whether the sulfur is emitted as sulfur dioxide or sulfate are not significant because the sulfur dioxide is converted to sulfate in the atmosphere. Most studies (e.g., Asaumi et al. 1992) show that limiting aromatic content to 20% to 25% produces desirable reductions in particulate matter and gaseous species without seriously compromising the cold flow properties of the fuel that result from increasing the paraffinic content. Betts and associates (1992), however, conclude from a study of passenger cars that aromatics content has "no significant influence on particulates."

A European auto-oil program is addressing the question of a low-emission, petroleum-derived reformulated diesel fuel in the extensive manner in which reformulated gasoline has been characterized in the United States. It is reasonable to assume that diesel fuel properties can and will be further optimized to produce a cleaner reformulated diesel fuel. Decreasing sulfur and aromatics would further

reduce particulate matter. In addition to lowering sulfur and aromatics, lowering the 90% distillation point temperature would reduce particulate matter (Figure 8) (Cunningham et al. 1990; Sienicki et al. 1990).

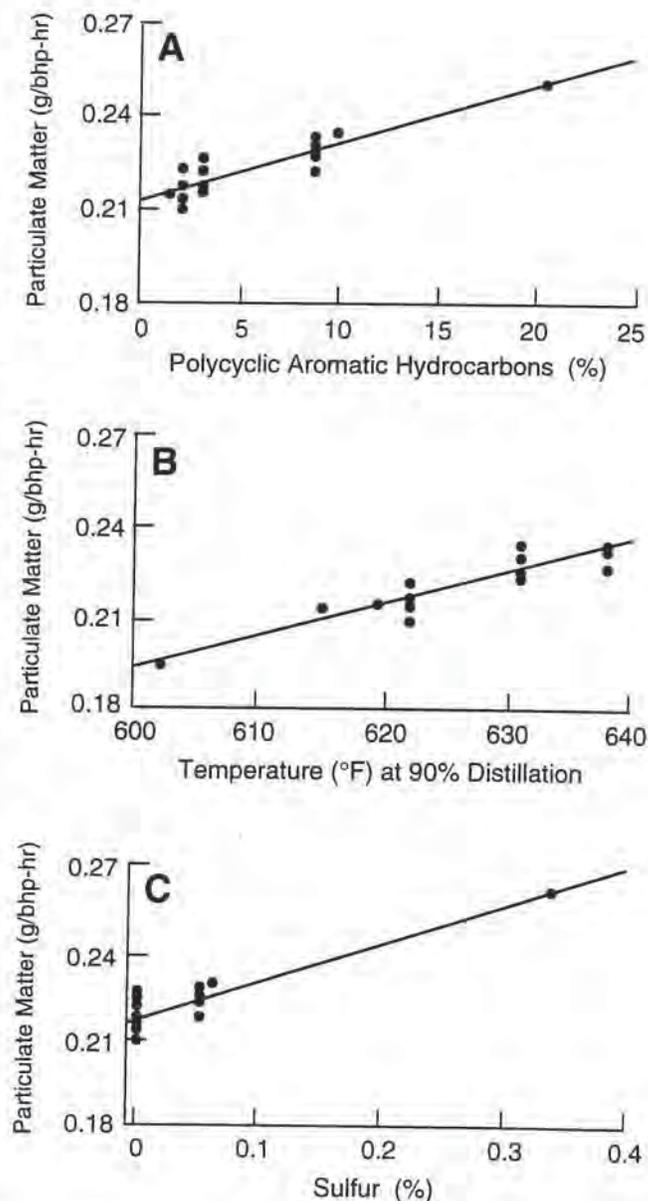


Figure 8. Effect of diesel fuel characteristics on emissions: (A) percentage of PAHs; (B) temperature at 90% distillation; (C) percentage of sulfur. (Adapted with permission from SAE Paper No. 902172, 1990, Society of Automotive Engineers, Inc.)

The use of natural gas and methanol provides an alternative approach to engine technology changes. These fuels have been introduced in bus engines, which were required to meet the 0.1 g/bhp-hr particulate matter standard before heavy-duty trucks. Competition between these fuels and engine technology will be decided on the basis of lifetime costs as experience is obtained with the durability of engines using methanol and natural gas.

FUTURE RESEARCH DIRECTIONS

Further characterization of diesel emissions, particularly the gas and particulate-phase hydrocarbons and nitroarenes, is needed for new control technology and fuels, including engines operated on the FTP transient cycle. Characterization of emissions from diesel engines burning natural gas, methanol, and the anticipated "reformulated diesel" fuels also is required. Engines that meet the 1994 and 1998 heavy-duty vehicle and the 1996 urban bus standards should be included in the characterization studies. Most animal exposure experiments have used light-duty diesel engine emissions, which may not be characteristic of the primary source of human exposure (i.e., heavy-duty diesel engines) or of future light-duty diesel engines. Epidemiological studies generally use occupational exposure from heavy-duty engines. Exposures to locomotive diesel emissions may be different from exposures to heavy-duty motor vehicle engines. The importance of exposure characterization in epidemiological studies is obvious, especially if observations are to be extrapolated to future exposures. Changes in engines, control technologies, and fuel ensure that past and future exposures are not comparable. There is also a need to improve methods for characterizing nitro-PAHs that have lower coefficients of variation and are durable for large and long-term studies (Johnson et al. 1994).

SUMMARY AND CONCLUSIONS

Clearly, diesel engine technology in the field has changed significantly over the past 25 years. The 1970s saw a mix of naturally aspirated, turbocharged, and turbocharged aftercooled engines. The 1980s saw a significant shift largely to turbocharged aftercooled engines. There has been a significant reduction of hydrocarbons, CO, NO_x, and particulate matter emissions, with the greatest reduction in particulate matter emissions occurring in the past three years. Further reductions in particulate matter emissions will occur in urban buses as a result of the 1995 rebuild standards for previously manufactured engines and for new engines produced after 1996. In 1998 NO_x emissions will be reduced again for heavy-duty trucks. The EPA has recently recommended that Califor-

nia adopt heavy-duty NO_x standards of 1.5 g/bhp-hr in 1999 so that the state can achieve the ambient ozone standard. The diesel industry would clearly like to see a reformulated fuel to help it better meet the 1998 heavy-duty truck standards.

The future of diesel engine emissions and control technology will continue to be shaped by a dynamic interaction involving the requirements of health-based regulations, engine technology, and diesel fuel formulation. Future requirements for more stringent control of NO_x, to meet ozone and photochemical nitrate particulate reduction levels, and of directly emitted particles to respond to any new health concerns that might be based on fine particulate matter or specific chemical compounds associated with particles in diesel exhaust, could place difficult demands on engine manufacturers and fuel producers. So far, the strong advantages of diesel engines in the heavy-duty market, including the existing infrastructure, have provided the incentive for developing technology to meet emissions reduction requirements. It is likely that the industry will continue to respond to this incentive, with a greater emphasis on the reformulation of diesel fuels. At a stringent level of required emissions reduction, alternative fuels (e.g., natural gas) or alternative engines (e.g., gas turbines) could displace diesel engines. The future of the diesel engine depends heavily on the potential human health effects of diesel emissions, still largely unresolved.

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ABBREVIATIONS

CARB	California Air Resources Board
CO	carbon monoxide
EPA	U.S. Environmental Protection Agency
FTP	Federal Test Procedure
g/bhp-hr	grams per brake-horsepower times hours
g/kW-hr	grams per kilowatt times hours
NO _x	oxides of nitrogen
PAH	polycyclic aromatic hydrocarbons
TPM	total particulate matter



Atmospheric Transport and Transformation of Diesel Emissions

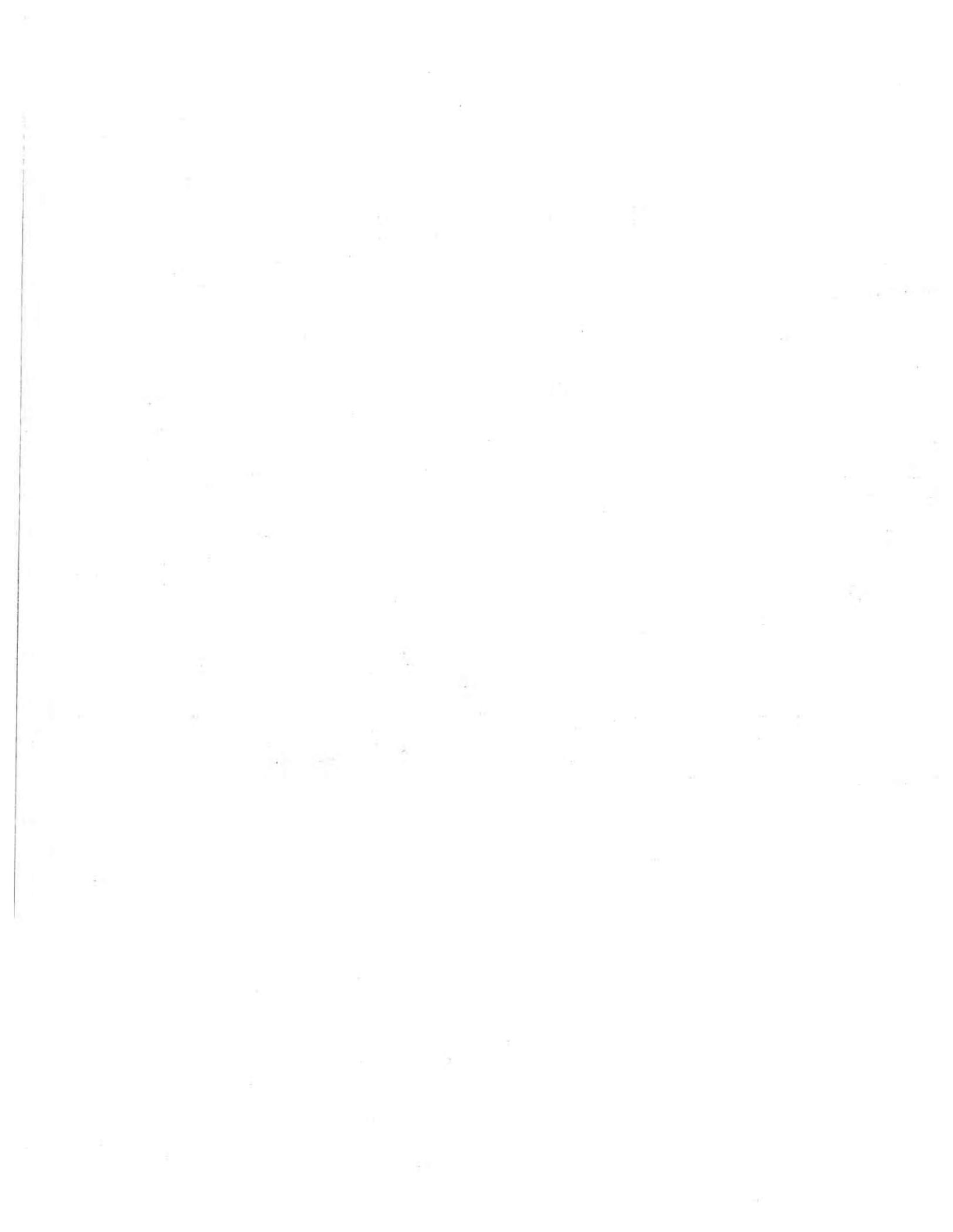
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INTRODUCTION AND BACKGROUND

To elucidate potential health effects of diesel exhaust, it is insufficient to characterize only the primary pollutants directly emitted from diesel vehicles. When chemical compounds present in diesel exhaust (in the gaseous or particulate phase) are released into and then transported through the atmosphere, chemical and physical transformations occur producing secondary compounds that may also affect human receptors.

The rates and mechanisms of these atmospheric transformation processes ultimately determine the atmospheric lifetimes of the initially emitted diesel exhaust pollutants as well as the chemical nature and biological activity of the resulting secondary air pollutants. Thus knowledge of the chemical identity, atmospheric concentrations, distribution between the particulate and gaseous phases, and biological activity of both the primary emissions and secondary transformation products is needed for a comprehensive assessment of the health risks, if any, posed by diesel exhaust.

As documented in the background paper by Sawyer and Johnson (this report), a wide range of organic and inorganic compounds are emitted from diesel engines. For example, vapor-phase exhaust contains inorganic combustion products such as sulfur dioxide (SO₂)*, oxides of nitrogen (NO_x) (principally nitric oxide [NO] and small amounts of nitrogen dioxide [NO₂]), carbon monoxide (CO), carbon dioxide, and ammonia. Also present in the gas phase are a broad spectrum of organic compounds, including alcohols, aldehydes (e.g., formaldehyde, acrolein), organic acids (e.g., formic acid), aromatic compounds (e.g., benzene, toluene), and straight-chain and branched-chain alkanes and alkenes containing up to 18 carbon atoms (see background paper by Sawyer and Johnson, this report; Schuetzle 1983; Johnson 1988; International Agency for Research on Cancer 1989).

A particularly important class of compounds found distributed between both the gaseous and particulate phases are polycyclic aromatic compounds, which include polycyclic aromatic hydrocarbons (PAHs) and their nitrated derivatives (nitro-PAHs) (e.g., phenanthrene, fluoranthene, pyrene, benzo[*a*]pyrene [BaP], and nitropyrene).

The particulate phase in diesel exhaust contains mainly aggregates of spherical carbonaceous particles to which significant amounts of higher molecular weight organic compounds become adsorbed as the hot engine exhaust is cooled to ambient temperature. In general, 15% to 45% of the particle phase consists of organic compounds extractable by solvents. These extracts include PAHs with four or more

rings and hydrocarbons containing more than 18 carbon atoms. Many oxygenated-PAH and nitrated-PAH derivatives are also present. For the most part diesel emissions are qualitatively similar to other combustion emission sources with respect to the classes of chemicals released into the atmosphere.

Evaporative emissions of diesel fuel constituents are less important than for gasoline and are not treated here.

Although available data specifically addressing the atmospheric chemistry and transport of diesel emissions per se are quite limited, a large body of knowledge has accumulated over the past two decades concerning the atmospheric transformations of many of the classes of chemicals as well as individual compounds present in diesel exhaust vapor and particles. A comprehensive treatment of this knowledge, including detailed chemical mechanisms, as it applies to automotive emissions has been provided by Atkinson (1988).

The purpose of this paper is to provide an overview of the importance and implications of the atmospheric transport and transformations of diesel exhaust constituents, and to highlight relevant recent research that bears on the potential biological impacts of resulting transformation products. In particular, we emphasize those classes of primary organic emissions that constitute a disproportionate fraction of diesel emissions relative to emissions from gasoline-fueled vehicles and that may have significant implications for human health effects associated with their atmospheric transformations (e.g., PAHs, nitro-PAHs, and their transformation products). Those classes of inorganic and organic compounds that are common to both gasoline-fueled and diesel-powered vehicles, and whose atmospheric transformations have been extensively treated elsewhere (e.g., NO_x and sulfur) are only reviewed briefly here with references furnished to more extensive discussions in the literature.

Similarly, the scope of this discussion is limited to a brief overview of transport and dispersion processes and physical transformation processes, principally wet and dry deposition. For more detailed and comprehensive treatments of these and related topics, see Sampson (1988) and Atkinson (1988), respectively (and references therein), and appropriate reviews and texts (Stern et al. 1984; Finlayson-Pitts and Pitts 1986, 1993; Seinfeld 1986; Davidson and Wu 1990; Wayne 1991; Barry and Chorley 1992).

It should be noted that diesel emissions contribute only a small fraction of the organic compounds released to the atmosphere from a wide variety of anthropogenic and natural sources (Graedel et al. 1986). As discussed in more detail below, no unique tracer of diesel emissions has been recognized to date. Thus this discussion will focus generi-

* A list of abbreviations appears at the end of this paper.

cally on classes of chemicals or specific compounds identified in diesel emissions, while recognizing that many of these chemicals are well-known representatives of emissions from combustion processes in general.

These combustion emissions undergo atmospheric transport and transformation processes that determine human exposure patterns in at least two ways: (1) by influencing the ambient concentrations of specific emission constituents, and their reaction products, at different locations, and (2) by potentially altering the toxic, mutagenic, or carcinogenic properties of the original emission constituents as well as creating new toxic, mutagenic, or carcinogenic transformation products. To describe these transformation processes, we begin with a brief overview of transport and dispersion as well as the principal physical removal processes. Then we focus on homogeneous and heterogeneous chemical reactions, which, with a few exceptions, are dominantly responsible for the atmospheric transformations of most vapor-phase compounds emitted in vehicle exhaust.

TRANSPORT AND PHYSICAL REMOVAL PROCESSES

METEOROLOGICAL PROCESSES

The major meteorological processes affecting the fate of combustion emissions, as well as other pollutants, include atmospheric transport (movement caused by wind flow over local- to global-scale distances) and dispersion (which results from turbulence). As a result of these mixing and diffusion processes, and depending on their atmospheric lifetimes, both gaseous and particulate pollutants may have only local effects or may be transported over long distances.

For pollutants, such as diesel exhaust, released at or near the surface of the earth, initial mixing leading to horizontal and vertical dispersion is due to small-scale turbulence in the atmosphere (Barry and Chorley 1992). Typically, vertical mixing takes place within the atmospheric boundary layer extending 1 to 2 km in height during the day but only a few hundred meters or less at night. In the absence of fresh emissions, uniform distribution of pollutants in this mixing zone will be achieved generally within a few hours. Interactions between vapor-phase and particle-phase pollutants are facilitated at this time because of the relatively high concentrations.

The complexities of transport and dispersion of emissions arising from vehicles have been the subject of extensive modeling and experimental studies over the past two

decades. The resulting knowledge concerning the theory and application of transport and dispersion processes has been described by Sampson (1988).

GAS-PARTICLE PARTITIONING

Gas-particle partitioning of diesel exhaust constituents, and the resulting distribution of semivolatile organic compounds between the gas and particle phases, can significantly influence the rates and relative importance of the various reaction pathways, including dry and wet deposition, photolysis, and chemical transformation. Treatment of gas-particle partitioning is beyond the scope of this paper but is discussed in detail in the primary literature (e.g., Schuetzle and Frazer 1986; Pankow 1987; Bidleman 1988; Ligocki and Pankow 1989; Pankow and Bidleman 1992; Subramanyam et al. 1994).

PHYSICAL TRANSFORMATION PROCESSES

Physical removal of primary pollutants or of secondary pollutants resulting from chemical transformations in the atmosphere may occur by either wet or dry deposition processes for both gases and particles, or by agglomeration of particles followed by sedimentation (Davidson and Wu 1990).

Dry Deposition

Dry deposition is the direct transfer of pollutants to surfaces by diffusion, impaction, or sedimentation in the absence of the effects of precipitation (Schroeder and Lane 1988). A review of experimental and theoretical knowledge concerning the dry deposition of gases and particles has been provided by Davidson and Wu (1990).

Rates of dry deposition for gases depend on the chemical properties of the gaseous species, the deposition surface, and the atmospheric stability. In highly polluted air-sheds and over long periods, large quantities of pollutants (e.g., NO_x) can be deposited by dry deposition.

Dry deposition velocities for selected gases and particles are shown in Table 1. The dry deposition lifetimes for many gaseous organic compounds fall in the range from weeks to months; however, for certain chemicals that have relatively slow gas-phase reaction rates and high dry deposition velocities, including nitric acid [HNO₃] and SO₂, dry deposition can be the major removal process under typical atmospheric conditions (Atkinson 1988).

For particles, deposition velocity is a function of particle size. The characteristic time for particle removal by dry deposition is a few hours for very small particles (less than 0.01 μm) or very large particles (greater than 100 μm) and

as long as 10 days for particles in the size range of 0.1 to 1 μm . Thus diesel exhaust particles emitted in the respirable size range (0.1 to 1 μm) will have significant residence times, on the order of several days or more, whereas larger diesel exhaust particles (i.e., visible "smoke") will have atmospheric residence times measured in hours (Graedel and Weschler 1981). Balkanski and coworkers (1993) provide direct experimental data on the atmospheric residence times against wet and dry deposition for tropospheric aerosols containing lead (i.e., ^{210}Pb).

Horvath and coworkers (1988) studied the transport and persistence of diesel exhaust particles in Vienna by incorporating an organometallic compound of the heavy earth element dysprosium for four weeks into the sole source of diesel fuel for this geographic area. Upon combustion, this tracer was oxidized to dysprosium oxide that was associated with the particles released by diesel engines in the region. Sampling of ambient air and road surfaces over time

permitted calculation of the proportion of airborne particles contributed by diesel engine emissions. Air concentrations of diesel exhaust particles ranged from 5 to 23 $\mu\text{g}/\text{m}^3$, whereas the fraction of total aerosol particle mass concentration attributed to diesel emissions ranged from 12% to 33% at the 11 sampling stations. Because investigators found higher concentrations of diesel exhaust particles at the more remote sampling sites, they concluded that diesel exhaust particles were readily transported in the atmosphere. No marked diesel exhaust particles were detected one year after the end of the fuel marking period.

Wet Deposition

Wet deposition involves transfer of the pollutant to the surface in rain, snow, or fog. This may occur by (1) Brownian capture, in which the pollutants come into contact with cloud droplets, (2) nucleation, in which a particle can serve as a condensation nucleus for water vapor, (3) dissolution, in which particles or gases dissolve in cloud water or rain drops, or (4) impaction from the collision of rain drops and particles.

Whereas for nonpolar organic compounds wet deposition is of minor importance, for highly water-soluble gases (e.g., HNO_3) wet deposition can be an important atmospheric removal process (Jacob and Hoffman 1983; Chang 1984) because the washout ratio for gases ($W_g = RT/H$, where R is the ideal constant, T is the absolute temperature, and H is Henry's law constant) is directly proportional to the aqueous solubility (C_w) of that gas ($W_g = C_w RT/P$, where P is pressure). Table 2 lists washout ratios for selected organic compounds, most of which are found in vehicle exhaust. As shown in Table 2, washout ratios for particles are typically in the range of 10^5 to 10^6 , one to two orders of magnitude higher than the typically highest washout ratios for gases (Eisenreich et al. 1981; Davidson and Wu 1990).

Wet deposition processes and impacts have been the subject of extensive research over the past two decades as a result of concerns over acidic deposition in aquatic bodies and ecosystems. More detailed treatment of this large body of research is beyond the scope of this discussion.

DIESEL EMISSION TRACERS

The question of what constituents might be used to estimate the contribution of diesel emissions to overall emission inventories has received significant attention but must be considered in the context of potential atmospheric transformations of the tracer candidate compounds. Ideally, candidate atmospheric tracer compounds for diesel emissions should be (1) emitted in relatively high concentrations to facilitate sampling, (2) easily separable from

Table 1. Dry Deposition Velocities for Several Inorganic and Organic Chemicals^a

Phase	Depositing Species	Mean Deposition Velocity (cm/sec)
Gas	Ozone	0.3–0.5 ^b 0.08–0.9 ^c
	Sulfur dioxide	0.1–2 ^d
	Nitric acid	2.5 ^b
	Tetrachloroethene	$\sim 10^{-4}$ ^e
	Nitrobenzene	$\sim 10^{-4}$ ^e
Particle	Particulate sulfur	0.17 ^b
	Calcium sulfate particles	
	1- μm diameter	0.01 ^f
	2- μm diameter	0.03 ^f
	5- μm diameter	0.44 ^f
10- μm diameter	4.6 ^f	
Semivolatile organic	Polychlorinated biphenyls	~ 0.1 –0.5 ^g

^a Adapted from Atkinson (1988).

^b From Dolske and Gatz (1985), with grass as the surface.

^c From Colbeck and Harrison (1985), with grass as the surface.

^d From Davidson and Wu (1990), for various surfaces.

^e From Sehmel et al. (1985).

^f From Jonas and Heinemann (1985), with grass as the surface.

^g From Eisenreich et al. (1981); this range is an average for polychlorinated biphenyls in the gas and particle phases.

other interfering organic compounds, (3) easy to identify and quantify, and (4) chemically stable in the atmosphere (Zielinska 1990). The tracer should also be unique to diesel engine exhaust and present in a known ratio to whole exhaust emissions. Several emission constituents can be considered possible tracers, including alkyl phenanthrenes, 1-nitropyrene (1-NP), hydrocarbons from diesel fuel and lubricating oil, and elemental carbon particles.

Diesel exhaust contains relatively high amounts of alkyl-substituted phenanthrenes (Yu and Hites 1981; Tong and Karasek 1984; Gallagher et al. 1991). The presence of these PAH derivatives in particle- and vapor-phase samples of air from a highway tunnel was attributed primarily to diesel trucks (Benner et al. 1989). Available information, however, does not permit the use of alkylated phenanthrenes as a source indicator for diesel emissions because the contribution of other combustion sources to these compounds is not clear (Zielinska 1990). Also, PAHs as a class are relatively reactive and may not be suitable emissions indicators (Atkinson and Arey 1994).

Another possible tracer for diesel emissions is 1-NP. This compound is a major constituent of the nitro-PAH fraction from extracts of diesel exhaust particles (Paputa-Peck et al. 1983; International Agency for Research on

Cancer 1989) and a significant contributor to the nitro-PAHs present in ambient air particles (Ramdahl et al. 1986). The compound is not produced by the atmospheric nitration reactions responsible for the formation of 2-nitropyrene and 2-nitrofluoranthene; rather 1-NP is thought to originate by direct emissions from combustion sources (Zielinska 1990; Atkinson and Arey 1994).

Alkanes may be more appropriate as emission tracers because of their relative abundance and their relatively long residence time in the atmosphere (Zielinska 1990). Simoneit (1984) examined hydrocarbon profiles of engine fuels and lubricants present in the atmosphere from different urban and rural locations. Diesel engine exhaust was characterized by a relatively low ratio of branched and cyclic hydrocarbons to straight-chain alkanes in comparison with emissions from spark-ignition engines.

The elemental carbon content of atmospheric particles is another possible diesel emission tracer (Zielinska 1990). Because sources other than diesel engines can emit elemental carbon particles, it is important to examine a comprehensive emission inventory for elemental carbon particles in the locale of interest before assuming that elemental carbon can be used as a tracer for diesel exhaust particles. In some locations, elemental carbon may serve well as a tracer for diesel exhaust, whereas in other locations, especially those with heavy wood-burning activity, it may not.

Table 2. Washout Ratios for Selected Organic Chemicals^a

Phase	Chemical	Washout Ratio (W)
Gas	Ethene oxide ^b	4-6
	Phenol ^c	(0.7-25) × 10 ⁴
	Nitrobenzene ^b	(2-4) × 10 ³
	Naphthalene ^d	100-300
	Phenanthrene ^d	(2-4) × 10 ³
	Pyrene ^d	(3-9) × 10 ³
	Benz[<i>a</i>]anthracene ^d	(7-22) × 10 ³
	Hexachlorobenzene ^e	1.5 × 10 ³
Particle	Polychlorinated biphenyls ^e	~(1-10) × 10 ⁴
	Particles ^e	
	0.1- to 1.0- μ m diameter ^e	<10 ⁵
	10- μ m diameter ^e	~10 ⁶
	Tricosane through hexacosane ^f	~2 × 10 ⁴

^a Adapted from Atkinson (1988).

^b From Dana et al. (1985).

^c From Leuenberger et al. (1985).

^d From Ligocki et al. (1985a).

^e From Eisenreich et al. (1981).

^f From Ligocki et al. (1985b).

CHEMICAL TRANSFORMATIONS

The chemical transformation of pollutants in the atmosphere is a particularly important consideration for assessing the human health risk of combustion emissions. There are two major reasons for this. First, Earth's atmosphere is an efficient oxidizing system, and all but the most inert substances can be expected to participate in chemical and photochemical reactions. Second, the resulting secondary pollutants can be expected to differ from their precursors in terms of toxicity, chemical stability, and atmospheric residence time. This further complicates an already complex series of interactions among an extraordinary number and chemical diversity of pollutants.

In general, reactions involving important reactive intermediates in the atmosphere lead to the conversion of primary emitted pollutants into secondary chemicals with a higher oxidation state, resulting in increased polarity and water solubility (Finlayson-Pitts and Pitts 1986, 1993; Schroeder and Lane 1988). Thus, these secondary and often less-volatile pollutants may be removed from the atmosphere by processes, and at rates, different from those controlling the levels of the original pollutants.

Reaction rates are governed by the temporal and spatial distribution, as well as chemical reactivity, of the participating species. Furthermore, these reactions may be homogeneous (occurring in the vapor phase) or heterogeneous (occurring in the particle phase). It is important to note that reactions of chemicals adsorbed to particles in the atmosphere may be different or occur at different rates than those observed in vapor-phase reactions (Atkinson 1988, 1994). As noted above, detailed treatments of atmospheric chemical reactions can be found in several texts (Finlayson-Pitts and Pitts 1986; Seinfeld 1986; Wayne 1991), and comprehensive reviews of the atmospheric chemistry of pollutants emitted by internal combustion engines are also available (Atkinson 1988, 1990, 1994).

For the purposes of this discussion, five major atmospheric reaction pathways are addressed: (1) photolysis reactions during the day, (2) reaction with hydroxyl (OH) radicals during the day, (3) reaction with ozone (O_3) during the day and at night, (4) reaction with nitrate (NO_3) radicals/dinitrogen pentoxide (N_2O_5) at night, and (5) reaction with NO_2 and gaseous HNO_3 during the day and night. Of these, reactions with OH and NO_3 radicals and with O_3 are by far the most important for the majority of organic compounds.

Hydroxyl-radical reactions occur only during the day because this important, highly reactive species is formed in the atmosphere primarily by reactions resulting from the photolysis of O_3 and aldehydes, or directly from photodissociation of nitrous acid (HONO), at wavelengths longer than 290 nm. Ozone, though formed from the photolysis of NO_2 during the day, is sufficiently stable and often present in high enough concentrations that significant amounts can persist into the nighttime hours, especially in the absence of fresh NO emissions from combustion sources. Reactions with NO_3 radicals, formed from the reaction of NO_2 with O_3 , occur in significant concentrations only at night because these radicals dissociate rapidly in sunlight. The detailed reactions leading to the formation of OH and NO_3 radicals and O_3 , as well as their dependence on absorption cross sections, quantum yields, and wavelengths for photolysis reactions, are discussed elsewhere (Finlayson-Pitts and Pitts 1986; Winer 1986; Atkinson 1994). Ranges of concentrations for these reactive species in both clean and polluted atmospheres are approximately 0.05 to 0.5 ppt for OH radicals, 30 to 300 ppb for O_3 , and 0.25 to 400 ppt for NO_3 radicals (Platt et al. 1984; Winer et al. 1984; Winer and Biermann 1994).

Table 3 is a compilation of the major atmospheric chemical reactions that may occur with gas-phase and particle-phase classes of compounds that are important emissions

from diesel engines. As expected, the gas-phase reactions involve chemicals of lower molecular weight with higher vapor pressures.

As shown in Table 3, the most important atmospheric loss process for most of the organic compounds emitted from diesel vehicles in the gas phase is reaction with OH radicals during the day. For certain classes of diesel emissions, however, photolysis, reaction with NO_3 radicals at night, and reaction with O_3 can represent important transformation pathways. It should also be emphasized that reactions that are relatively minor pathways may produce reaction products with potential human health impacts (see below).

In the remainder of this section, we briefly discuss the transformation pathways for important classes of diesel emissions.

INORGANIC DIESEL EMISSIONS

Oxides of Nitrogen

With the exception of nitrous oxide (N_2O) the various primary (NO , NO_2 , N_2O , HONO) and secondary (NO_2 , NO_3 , N_2O_5 , HNO_3 , aerosol nitrates) nitrogen oxide species associated with combustion emissions of NO_x participate in chemical cycles that interconvert these compounds. The major tropospheric transformation process for NO_x is the formation of gas-phase HNO_3 from the daytime reaction of OH radicals with NO_2 . Detailed treatments of the formation and reaction pathways of these inorganic oxides of nitrogen have been given by Atkinson and colleagues (1992c) and Atkinson (1994).

Oxides of Sulfur

The principal chemical transformation of SO_2 in the atmosphere is reaction with the OH radical followed by the formation of sulfuric acid (H_2SO_4) (Stockwell and Calvert 1983). Sulfur dioxide can also be oxidized in the liquid phase in clouds or fog by reaction with hydrogen peroxide (H_2O_2), O_3 , or oxygen (O_2) (in the presence of metal catalysts). Under normal atmospheric conditions, H_2SO_4 is present almost entirely in the particulate phase, and these particles are removed by wet and dry deposition, as is a portion of gaseous SO_2 in competition with the OH-radical reaction. The sulfate particles formed are often wholly or partly neutralized by ammonia uptake. The deposition of SO_2 , H_2SO_4 , and ammonium sulfate into ecosystems has been associated with a wide range of impacts on vegetation, fish, and other aquatic organisms and materials (National Academy of Sciences 1983; U.S. Environmental Protection Agency 1983).

Table 3. Major Atmospheric Reactions of Diesel Emissions

Emission	Reaction	Day or Night	Ultimate Reaction Products	Comments	Reference
Gas-Phase Reactions					
Alkanes	OH radicals or NO ₃ radicals	D	Alkyl nitrates Aldehydes Ketones	Products formed by reactions of various intermediate alkyl radicals with O ₂ and NO (alkyl nitrates), followed by further reactions with O ₂ or by decomposition/isomerization (aldehydes, ketones).	Atkinson 1988, 1994
Alkenes	OH radicals	D	Aldehydes Ketones	Products formed by reaction of various intermediate alkyl radicals with O ₂ and NO, followed by decomposition.	Reaction important only for alkenes more reactive than propene. Fate of intermediate Criegee biradicals uncertain.
	NO ₃ radicals	N	Aldehydes Ketones		
	O ₃	D + N	Aldehydes Ketones Peroxides Organic acids		
Aldehydes					
Formaldehyde	Photolysis or OH radicals	D	CO	Photolysis is a major loss process for formaldehyde.	
Higher aldehydes	Photolysis	D	Hydroperoxyl radicals	Resulting radicals promote smog formation.	
	OH radicals	D	Hydroperoxyl radicals Peroxacyl nitrates Nitrophenols (from benzaldehyde)	Formed by reactions of intermediate radicals with O ₂ and NO ₂ . Formed by reactions of intermediate radicals with NO and NO ₂ .	
Carboxylic acids	OH radicals	D	Hydrogen atoms from formic acid; products unknown from higher carboxylic acids		
Monocyclic aromatic compounds	OH radicals	D	Hydroxylated derivatives and ring-opened carbonyls or Aromatic aldehydes	Major pathway. Minor pathway. Loss of H atom, followed by reactions of intermediate radicals with NO and O ₂ .	
Phenols	NO ₃ radicals	N	Nitrophenols	May occur in addition to or in place of reactions with OH radicals (above).	
PAHs	OH radicals (in presence of NO _x)	D	Hydroxylated derivatives Nitro-PAHs Nitrolactones	Hydroxylated derivatives.	Atkinson et al. 1987; Arey et al. 1989b Atkinson and Arey 1994
	NO ₃ radicals (followed by NO ₂ reaction)	N	Nitro-PAHs	Hydroxyl and NO ₃ radical reaction is predominant loss process for gas-phase PAHs. Exception: PAHs with external cyclopentafused ring. Distinctive set of isomers produced; source of the major ambient nitro-PAHs (2-nitropyrene and 2-nitrofluoranthene).	Atkinson et al. 1987; Zielinska et al. 1988; Arey et al. 1989b; Atkinson and Arey 1994; Atkinson et al. 1990a,b
Nitro-PAHs	Photooxidation	D	Quinones and hydroxyl derivatives from nitropyrenes	Reactions more rapid in gas phase than particle phase (absorbed on quartz).	Holloway et al. 1987
Alkyl-PAHs	OH radicals NO ₃ radicals	N	Methyl nitronaphthalenes from methyl naphthalenes	Isomer pattern consistent with OH radical attack on other PAHs.	Zielinska et al. 1989a
Particulate-Phase Reactions					
Monocyclic aromatic compounds	OH radicals	D	Hydroxylated nitro-derivatives of benzene and toluene		Nishioka et al. 1988
	Photolysis	D	Not characterized	Rate of loss highly dependent on properties of particles.	Behymer and Hites 1985; Kamens et al. 1988
PAHs	Nitration	—	Nitro-PAHs	Different pattern of isomers than from gas-phase reactions of PAHs with N ₂ O ₅ or with hydroxyl and nitrate radicals. (See Table 5.)	Kamens et al. 1993

(Table continues next page.)

Table 3. Major Atmospheric Reactions of Diesel Emissions (*continued*)

Emission	Reaction	Day or Night	Ultimate Reaction Products	Comments	Reference
	Ozonolysis	D + N	Not characterized	Half-lives of most PAHs from 0.5 to 1.0 hour.	Van Vaeck and Van Cauwenberghe 1984
Nitro-PAHs	Photooxidation	D	Quinones, OH derivatives, and oxides from nitropyrenes	Silica-adsorbed compounds are less reactive than gas-phase compounds.	Holloway et al. 1987
Oxy-PAHs	Photolysis	D	Most compounds are stable	Loss of compounds in presence of O ₃ .	Kamens et al. 1989

Reduced Nitrogen and Sulfur Compounds

Reduced sulfur and nitrogen compounds, which usually constitute trace constituents in diesel exhaust, are not treated here. Tyndall and Ravishankara (1991) and Atkinson and associates (1992a) provide a detailed discussion of the atmospheric transformations of these compounds.

ORGANIC DIESEL EMISSIONS

Gas-phase organic compounds from diesel exhaust (and other sources) are important precursors of anthropogenic O₃ formation. The atmospheric transformation pathways for the various classes of organics are as follows.

Alkanes

Diesel fuels contain alkanes ranging in size primarily from about C₈ through about C₂₀ (Carter et al. 1981), and alkanes are the major organic component of diesel exhaust emissions. Alkanes with carbon number higher than C₂₀ are observed in diesel exhaust, possibly due to consumption of lubricant oil. The dominant gas-phase chemical reaction pathway for these compounds is reaction with OH radicals during the day to form aldehydes, alkyl nitrates, and ketones, which react further under atmospheric conditions (Atkinson 1994) and partition into the particulate phase. A second reaction pathway with NO₃ radicals at night is expected to be of minor importance (Carter and Atkinson 1985); however, Penkett and coworkers (1993) have reported recent evidence for removal of alkanes by NO₃-radical reactions over the North Atlantic. The health effects, if any, of the secondary products arising from alkane photooxidation in the atmosphere are not well characterized.

Alkenes

Alkenes present in diesel exhaust primarily contain four or fewer carbons and, as shown by their short atmospheric

lifetimes (see below), most of these compounds react rapidly with all three of the important reactive intermediates in the troposphere: OH and NO₃ radicals and O₃. Reaction of alkenes that have more than two carbons with OH radicals by addition to the carbon-carbon double bonds leads, following multistep reaction sequences, to the formation of aldehydes or ketones or both (Atkinson 1994).

Reactions of alkenes with O₃ proceed by O₃ addition to the double bond to form molozonides, which rapidly decompose into aldehydes and ketones, as well as biradicals, which further decompose or are stabilized. The mechanistic details of these reactions are for the most part still not well understood, however (Carter et al. 1986; Atkinson 1994). Interestingly, recent research has shown that OH radicals are produced, often in high yield, from the O₃ reactions with alkenes (Paulson et al. 1992; Atkinson et al. 1992b; Atkinson and Aschmann 1993).

Under atmospheric conditions, only reaction of NO₃ radicals with alkenes more reactive than the 2-butenes is important (Atkinson 1986), but, following addition to the carbon-carbon double bonds, the reaction mechanisms are not fully characterized. The potential formation of dinitrates of high toxicity from the reaction of β -nitroalkoxy radicals with NO₂ (Bandow et al. 1980; Shepson et al. 1985) requires further research on the yields of such compounds from the range of alkenes present in diesel exhaust.

Monocyclic Aromatic Hydrocarbons

Aromatic hydrocarbons, including benzene, toluene, ethylbenzene, and the xylenes, are important constituents of both diesel fuel and exhaust from diesel vehicles. In the atmosphere, these compounds react at significant rates solely with the OH radical, primarily by addition to the aromatic ring and to a lesser extent by abstraction of a hydrogen atom (Gery et al. 1985; Atkinson 1989), for example, from the carbon-hydrogen bonds of toluene. Addition leads to, for example, OH-toluene adducts, which subsequently react with O₂ and NO₂ (Knispel et al. 1990).

Despite nearly two decades of research, the atmospheric reactions of most aromatic compounds emitted by automotive vehicles are not well understood, and few data on product yield are available. Typically, for those systems for which yields have been studied (see Atkinson 1994), the observed products account for less than 50% of the overall product yields, with the missing products being expected in part in the particulate phases (Stern et al. 1989; Wang et al. 1992). Similarly, the health implications, if any, of most of those reaction products that have been identified are unknown with the exception of a report that methylglyoxal is mutagenic toward *Salmonella typhimurium* strain TA 100 (Shepson et al. 1985) and the observation of nitrophenols (Atkinson et al. 1992a), a potentially significant class of toxic substances. Hydroxylated nitro-derivatives of benzene and toluene are also found in the particulate phase (Nishioka et al. 1988), but it is not clear whether they are formed in the gas or particulate phase.

Given the high atmospheric reactivity of aromatic hydrocarbons and their status as a major emissions category in automotive exhaust, identification of the atmospheric transformation products of aromatic hydrocarbons remains a high priority.

Oxygenated Organic Compounds

Consideration of the atmospheric transformations of the spectrum of O₂-containing organic compounds that either are directly emitted from diesel engines or are formed as the result of transformations of other primary automotive emissions is beyond the scope of this discussion. Many of these compounds are important partially oxidized diesel emissions, however, including aldehydes, ketones, esters, ethers, and α - β -unsaturated carbonyls. Our present understanding of the atmospheric chemistry of these compounds, as well as oxygenated alternative fuels such as methanol and ethanol and their formaldehyde and acetaldehyde coemissions, has been detailed by Atkinson (1988, 1994), who has called for further research (Atkinson 1988) concerning both the atmospheric transformations of these compounds and their potential human health effects.

Polycyclic Aromatic Hydrocarbons

A substantial portion of the research on the atmospheric transformations of combustion emissions over the past decade and a half has concerned the reactions of PAHs and their derivatives and analogues. The impetus for this attention arose from the well-established mutagenic and carcinogenic effects of many members of this important class of compounds and their nitro-derivatives (International Agency for Research on Cancer 1983, 1984, 1989; Tokiwa and Ohnishi 1986), as well as their dominant contribution to the mutagenic and carcinogenic activity of combustion

emissions (von Lersner 1983) and ambient atmospheres (Pitts 1983; Nishioka et al. 1988; Lewtas et al. 1990; Arey et al. 1992; Helmig et al. 1992b; Atkinson and Arey 1994).

The atmospheric transformations of the PAHs and nitro-PAHs are governed by their distribution between the vapor and particulate phase. It is now well established (Arey et al. 1987, 1989a; Pankow 1987; Atkinson et al. 1988; Coutant et al. 1988; Pankow and Bidleman 1992) that in ambient air the two- to four-ring PAHs and two-ring nitro-PAHs are generally present primarily as gas-phase species, whereas the PAHs with five rings or more are found primarily in the particulate phase.

Particulate-Phase Reactions. Over the past 15 years a large number of experiments have been conducted concerning the reactions of adsorbed PAHs. Many of these studies have been carried out for substrates that may not be representative of atmospheric particles (e.g., silica and Teflon-impregnated glass fiber filters) or at unrealistically high concentrations of, for example, O₃. Moreover, because of the strong substrate dependence of these adsorbed-phase reactions (Behymer and Hites 1985), no firm conclusions can be drawn about the importance of these reactions under atmospheric conditions, although it appears that photolysis and reaction with O₃ may be important for certain PAHs and their derivatives (Atkinson and Arey 1994). We briefly review below the findings of a number of representative studies.

Photolysis. A significant body of information exists that indicates that the stability of PAHs and their derivatives in light is highly dependent on the characteristics of the particles to which they are bound. Under laboratory conditions, PAHs adsorbed to certain particles (silica, alumina, some fly ash samples from coal combustion) were decomposed to varying degrees by light (Yokley et al. 1986; Holloway et al. 1987; Behymer and Hites 1985). PAHs adsorbed to flaked graphite or to other coal fly ashes, however, were resistant to photodecomposition (Yokley et al. 1986; Behymer and Hites 1985). The dominant factor responsible for this protective effect was the color of the fly ash sample, which in turn was related to carbon content. It was postulated that PAHs penetrated into the pores of the particle and were thus protected by absorption of the incident light by the black particle (Yokley et al. 1986).

Behymer and Hites (1985) noted further that the half-lives of PAHs on black particles were several days and that the photostability of the 18 PAHs examined was independent of the chemical structure. These authors calculated that PAHs would be stable to light if absorbed onto particles with a carbon content greater than 5%. Because the average elemental carbon content of diesel particles

varies from 40% to 70% (Japar et al. 1984; Williams et al. 1989), photodecomposition of diesel particle-adsorbed PAHs may not be a significant loss process for these chemicals.

It should be noted, however, that PAHs adsorbed to particles under actual combustion conditions may exhibit different behaviors. Kamens and colleagues (1988) demonstrated rapid photodecomposition of PAHs (half-lives of approximately one hour) in diluted soots collected from a residential wood-smoke stove and a gasoline combustion engine when exposed to sunlight. Furthermore, unlike the results from Behymer and Hites (1985), different PAHs exhibited a four-fold range in stability. No information was provided on the carbon content or light absorption capacity of these soot samples, so it is not known whether the lability of the PAHs was related to these factors as previously demonstrated for PAHs adsorbed to fly ash samples from coal combustion (Yokley et al. 1986; Behymer and Hites 1985). Because photolysis of these PAHs produced reaction products of increased polarity, indicating the possible presence of oxygenated PAH derivatives, Kamens and associates (1989) investigated the photostability of several oxy-PAHs on wood-smoke particles. Unlike the PAHs, the concentrations of oxy-PAHs remained constant with the exception of a four- to five-fold increase in 1,8-naphthalic acid anhydride. This increase suggested this compound was a photooxidation product of a PAH.

Ozone. Several studies indicate that PAHs, present either as individual compounds adsorbed to a solid substrate or as components of soot particles, rapidly react with environmentally relevant concentrations of O_3 . Pitts and coworkers (1986) exposed individual PAHs adsorbed on filters to up to 200 ppb O_3 under active flow or passive exposure conditions. Approximately 30% to 50% of the five individual PAHs tested reacted within 10 minutes. Longer reaction times (10% to 80% loss after three-hour exposure) were observed when these same PAHs were monitored in an ambient air particle sample. The potent carcinogen BaP was the most reactive PAH of those studied (Pitts et al. 1986).

The PAHs in diesel exhaust particles were rapidly lost (half-lives of one-half to one hour) following exposure to an airflow containing a high concentration (1.5 ppm) of O_3 (Van Vaeck and Van Cauwenbergh 1984). Again, BaP was highly reactive, with the benzofluoranthene isomers being among the least reactive PAHs. In experiments with wood-smoke particles passively exposed to 0.22 ppm O_3 , Kamens and colleagues (1989) demonstrated that both PAHs and oxy-PAHs were significantly degraded. Half-lives for oxy-PAHs varied from 80 to 200 minutes. These data also corroborated the results of the previous studies showing

that BaP was highly reactive to ozone. In none of these studies were attempts made to characterize the reaction products.

Nitrogen Species. As in the case of photolysis and O_3 , reaction with NO_2 or HNO_3 or both and with N_2O_5 has been shown to lead to the loss of PAHs adsorbed on various substrates (Pitts 1983; Pitts et al. 1985b, 1986; Kamens et al. 1993). The reactions involving nitrogen species, however, appear to be relatively slow under atmospheric conditions (Pitts et al. 1985b; Kamens et al. 1990, 1993).

Gas-Phase Reactions. Our present understanding of the gas-phase atmospheric transformations of PAHs and nitro-PAHs is based largely on a line of investigation begun more than 15 years ago by Pitts and coworkers (Pitts et al. 1978, 1985a,b,c; Pitts 1983, 1987) and extended and brought to fruition in a series of systematic studies by Atkinson and Arey and their colleagues (Atkinson and Arey 1994 and references therein) in both laboratory and ambient air systems. This research has demonstrated that the majority of ambient nitro-PAHs are formed in the atmosphere from the gas-phase reactions of PAHs of four rings or fewer, and that gas-phase transformations affect not only the mutagenic activity of gaseous species in ambient air but also the activity of particle-associated compounds. Thus knowledge of the gas-phase reactions of PAHs and their derivatives is essential to understanding the potential human health effects of this important class of compounds.

Available evidence suggests that dry deposition (Eisenreich et al. 1981) and wet deposition (Ligocki et al. 1985a) are of little importance as atmospheric transformation processes for gas-phase PAHs. Thus we focus on homogeneous gas-phase reactions involving OH and NO_3 radicals and O_3 .

Hydroxyl-Radical Reactions. The kinetic and mechanistic data for gas-phase OH radical reactions with two- to four-ring PAHs and two-ring nitro-PAHs have been summarized by Atkinson and Arey (1994). These reactions proceed by two pathways: addition to the aromatic ring to form energy-rich hydroxycyclohexadienyl-type radicals and OH-radical interaction with the substituent groups, through either hydrogen-atom abstraction from carbon-hydrogen bonds or OH-radical addition to double bonds (Atkinson 1989).

Although the products of these reactions are not well understood, in the case of naphthalene and biphenyl they result (in the presence of NO_x) in the formation of hydroxy- and nitro-PAHs (Atkinson et al. 1984, 1987). Atkinson and Arey (1994) have described the specific nitro-PAH isomers formed and their product yields from the gas-phase OH-radical-initiated reactions of a series of PAHs; these are presented in Table 4. The authors point out that the nitrofluoranthenes and nitropyrenes resulting from the gas-

phase reactions of fluoranthene and pyrene, respectively, condense onto particles in the atmosphere. Thus, for the four-ring PAHs, particle-phase nitro-PAHs are formed from gas-phase PAH precursors. A mechanism has been postulated (Atkinson et al. 1989a; Atkinson and Arey 1994), and is shown in Figure 1, for the OH-radical-initiated reaction of fluoranthene in the presence of NO_x .

It should be noted that the nitro-PAHs formed from OH-radical-initiated reactions of the PAHs listed in Table 4 are often different isomers from those observed in diesel exhaust particles (Atkinson and Arey 1994). For example, as shown in Table 5, the most abundant nitroisomers of pyrene, fluorene, and fluoranthene observed in diesel exhaust are 1-NP, 2-nitrofluorene, and 3-nitrofluoranthene,

Table 4. Nitroarene Products Formed from Gas-Phase Reactions of Polycyclic Aromatic Hydrocarbons with Hydroxyl and Nitrate Radicals (in the Presence of Oxides of Nitrogen), with Their Yields^a

Polycyclic Aromatic Hydrocarbon	Reaction with	
	Hydroxyl	Nitrate
Naphthalene	1-Nitronaphthalene (0.3%) 2-Nitronaphthalene (0.3%)	1-Nitronaphthalene (17%) 2-Nitronaphthalene (7%)
1-Methylnaphthalene	All 1-methylnitronaphthalene isomers except 1-methyl-2-nitronaphthalene (~0.4%)	All 1-methylnitronaphthalene isomers (~30%)
2-Methylnaphthalene	All 2-methylnitronaphthalene isomers except 2-methyl-1- and 2-methyl-3-nitronaphthalene (~0.2%)	All 2-methylnitronaphthalene isomers (~30%)
Acenaphthene	5-Nitroacenaphthene } (~0.2%) 3-Nitroacenaphthene } 4-Nitroacenaphthene }	4-Nitroacenaphthene (40%) ^b 3-Nitroacenaphthene (~2%) ^b 5-Nitroacenaphthene (~1.5%) ^b
Acenaphthylene	4-Nitroacenaphthylene (2%)	No nitroisomers formed
Fluorene	3-Nitrofluorene (~1.4%) 1-Nitrofluorene (~0.6%) 4-Nitrofluorene (~0.3%) 2-Nitrofluorene (~0.1%)	
Phenanthrene	Two nitroisomers (not 9-nitrophenanthrene) in trace yields	Four nitroisomers (including 9-nitrophenanthrene) in trace yields
Anthracene ^c	1-Nitroanthracene 2-Nitroanthracene	1-Nitroanthracene 2-Nitroanthracene
Pyrene	2-Nitropyrene (~0.5%) 4-Nitropyrene (~0.06%)	4-Nitropyrene (~0.06%)
Fluoranthene	2-Nitrofluoranthene (~3%) 7-Nitrofluoranthene (~1%) 8-Nitrofluoranthene (~0.3%)	2-Nitrofluoranthene (~24%)
Acephenanthrylene	Two nitroarene isomers (~0.1%)	None observed
Biphenyl	3-Nitrobiphenyl (5%)	No reaction observed

^a Adapted from Atkinson and Arey (1994).

^b Yield is for the nitrate-radical addition pathway to the fused aromatic rings (Arey et al. 1989b). Reaction is expected to proceed by hydrogen-atom abstraction from the carbon-hydrogen bonds of the cyclopenta-fused ring under atmospheric conditions.

^c 9-Nitroanthracene was also observed in both the hydroxyl- and nitrate-radical reactions, but may not be a product of these reactions because it is also formed from exposure to nitrogen dioxide and nitric acid.

respectively (Paputa-Peck et al. 1983; Williams et al. 1986; MacCrehan et al. 1988; May et al. 1992), whereas the isomers formed from the OH-radical reactions of these PAHs are 2-nitropyrene (Arey et al. 1986; Atkinson et al. 1990a), 3-nitrofluorene (Helmig et al. 1992a), and 2-nitrofluoranthene (Arey et al. 1986; Atkinson et al. 1990a), respectively.

Reactions with Ozone. To date, gas-phase reaction with O_3 has been reported only for the cyclopenta-fused compound acenaphthylene (Atkinson and Aschmann 1988) and for phenanthrene (Kwok et al. 1994). Ozone reaction is also expected to occur for acephenanthrylene (Zielinska et al. 1988).

Nitrate-Radical/ N_2O_5 Reactions. Considerable attention has been given to the reactions of naphthalene and higher PAHs with NO_3 radicals generated in laboratory systems by the thermal decomposition of N_2O_5 (i.e., $NO_3/N_2O_5/NO_2$ /air mixtures). Based on kinetic data, PAH transformation processes appear to be kinetically equivalent to reaction with N_2O_5 (Pitts et al. 1985a; Atkinson et al. 1987, 1990a,b; Atkinson and Aschmann 1987, 1988) and proceed, in the case of naphthalene (Figure 2) and other unsubstituted PAHs, by initial addition of the NO_3 radical to the aromatic rings (Atkinson et al. 1990b; Atkinson 1991), leading to the formation of nitroarenes (Pitts et al. 1985a; Sweetman et al. 1986; Atkinson et al. 1987, 1990a; Arey et al. 1989b; Zielin-

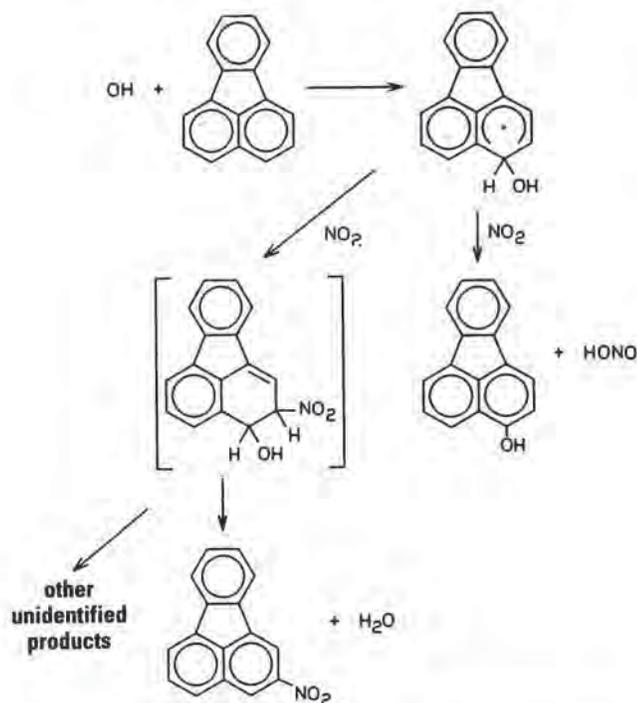


Figure 1. Mechanism proposed for reaction of OH radical with fluoranthene in the presence of NO_x . (Reprinted from Atkinson and Arey 1994.)

Table 5. Dominant Nitro-Polycyclic Aromatic Hydrocarbon Isomers Observed in Diesel Exhaust Versus Those Formed from Gas-Phase Reactions of Polycyclic Aromatic Hydrocarbons

Polycyclic Aromatic Hydrocarbon	Most Abundant Isomers	
	Observed in Diesel Exhaust	Formed from Hydroxyl-Radical-Initiated Reactions
Pyrene	1-Nitropyrene ^a	2-Nitropyrene ^b
Fluorene	2-Nitrofluorene ^a	3-Nitrofluorene ^c
Fluoranthene	3-Nitrofluoranthene ^a	2-Nitrofluoranthene ^b

^a Data are from Paputa-Peck et al. (1983); Robbat et al. (1986); May et al. (1992).

^b Data are from Arey et al. (1986); Atkinson et al. (1990a).

^c Data are from Helmig et al. (1992a).

ska et al. 1989a). The nitroarene yields from these reactions are given in Table 4. Reactions involving substituent groups on, for example, fused-ring PAHs do not appear to lead to the formation of nitroarenes (Arey et al. 1989b). Recent kinetic data (Atkinson et al. 1994; Kwok et al. 1994) suggest that NO_2 reaction with NO_3 -naphthalene adducts (and by inference with OH-naphthalene adducts) may dominate in urban and rural air masses over reaction of these adducts with O_2 , thereby favoring formation of nitro-PAH from these adducts.

Photolysis. Although the photolysis of various nitro-PAH isomers has been observed in both outdoor and environmental chamber irradiations (Atkinson et al. 1989b; Arey et al. 1990), no evidence supports the photolysis of gas-phase two- to four-ring PAHs under actinic irradiation (Biermann et al. 1985; Atkinson and Aschmann 1986, 1988).

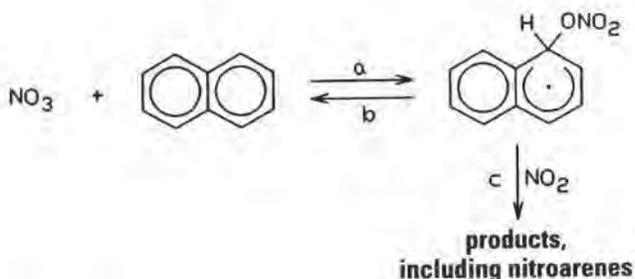


Figure 2. Mechanism proposed for reaction of NO_3 radical with naphthalene in the presence of NO_x . (Reprinted from Atkinson and Arey 1994.)

ATMOSPHERIC LIFETIMES

By combining kinetic data with knowledge of the ambient air concentrations of key reactive intermediates, the atmospheric lifetimes of inorganic and organic emissions as well as oxygenates and PAH and nitro-PAH constituents in diesel exhaust can be calculated (Atkinson 1988; Atkinson and Arey 1994); lifetimes for such constituents are listed in Tables 6 and 7. As shown in Table 6, the major atmospheric transformation process for most organic compounds emitted in diesel exhaust, particularly the alkanes and monocyclic aromatic hydrocarbons, is daytime reaction with the OH radical. For alkenes, reaction with O₃ can also be important; for some diesel emissions (e.g., for phenol), NO₃-radical reactions or photolysis (e.g., for aldehydes) can be significant transformation pathways.

As shown in Table 7, the dominant atmospheric transformation process for the PAHs not containing cyclopenta-fused rings is reaction with OH radicals during the day and NO₃ radicals at night, with lifetimes of about one day or less. For acenaphthene, acenaphthylene, and other cyclopenta-fused PAHs, reaction with NO₃, as well as with OH radicals, can also occur at a significant rate. This is also the case for the reaction of O₃ with PAHs with unsaturated cyclopenta-fused rings. The data in Table 7 also show that the nitroarenes exhibit a marked decrease in reactivity toward OH radicals and that photolysis will be the dominant tropospheric loss process for nitronaphthalenes (Atkinson et al. 1989b; Arey et al. 1990).

When considering both the transformation product yield data (Table 4) and atmospheric lifetimes (Tables 6 and 7), it is important to recognize that reactions that appear to be relatively minor removal processes may not be unimportant if they produce reaction products with potential human health effects. In this section of the paper, we provide examples of reaction pathways that lead to secondary transformation products in ambient atmospheres that exhibit substantial biological activity. Finally, a knowledge of the atmospheric lifetimes of diesel exhaust components allows assessment of whether the effects of such emittants will be local/regional (<200 km), continental (1,000–5,000 km), or global (10,000 km) in scale. Clearly, short lifetimes (i.e., measured in hours to one day) will correspond to local or regional exposure, whereas lifetimes of a few days will relate to continental-scale exposure; atmospheric lifetimes longer than about a week will allow a pollutant to be distributed globally, albeit in much diluted concentrations.

AMBIENT AIR OBSERVATIONS AND THE MUTAGENICITY OF THE ATMOSPHERIC TRANSFORMATION PRODUCTS OF GAS-PHASE POLYCYCLIC AROMATIC HYDROCARBONS

Results from the laboratory and environmental chamber studies cited above for the OH-radical-initiated reactions of gas-phase PAHs are now supported by ambient air measurements. Specifically, Arey and coworkers (1989a) have shown that the night:day concentration ratios observed for PAHs at Glendora, California, exhibited a linear correlation with their OH-radical rate constants. Thus the more reactive PAHs showed systematically higher night:day concentrations than did the less reactive PAHs.

Moreover, the specific PAH and nitro-PAH isomers observed in ambient air are consistent with their formation in the atmosphere as a result of the gas-phase reactions of the two- to four-ring PAHs (Atkinson and Arey 1994 and references therein). In particular, ambient air contains nitro-PAH isomers that are different from the electrophilic nitration products reported to be in diesel exhaust but are consistent with the nitro-PAH isomers found in environmental chamber simulations of the atmospheric reactions of the PAHs. For example, Arey and Atkinson and coworkers (Arey et al. 1986, 1987; Atkinson et al. 1988; Zielinska et al. 1989b) have consistently observed higher concentrations in ambient air samples of the secondary product 2-nitrofluoranthene than in those of the directly emitted 1-NP. These observations emphasize the importance of atmospheric transformations of the four-ring PAHs in leading to the formation of the major particle-associated nitro-PAHs observed in ambient air (i.e., those of molecular weight 247). Additional important evidence for the formation of nitroarenes as the result of gas-phase atmospheric transformations is provided by Atkinson and Arey (1994).

Finally, although it is well recognized that mutagenic activity does not necessarily imply other forms of biological activity, it is useful to consider measurements of the direct-acting mutagenicity of extracts of ambient air samples (Harger et al. 1992), which provide additional evidence for the need to consider atmospheric transformation products in assessing the potential biological activity of diesel exhaust components.

In these studies investigators observed that the total direct-acting mutagenicity (using a microsuspension modification of the Ames *Salmonella* assay [TA98-S9]) of gas-phase samples collected on polyurethane foam plugs was higher than that observed in extracts of particle-phase samples collected on Teflon-coated glass-fiber filters. In addi-

Table 6. Calculated Atmospheric Lifetimes^a for Gas-Phase Reactions of Selected Automotive Emissions with Atmospherically Important Intermediate Species^b

Emission	Atmospheric Lifetimes Due to Reaction with ^b			
	Hydroxyl	Ozone	Nitrate	Solar Radiation ^c
Nitrogen dioxide	1.3 days	12 hours	24 minutes	2 minutes
Nitric oxide	2.5 days	1 minute	1.2 minutes	
Nitrous acid	2.5 days	>33 days		~10 minutes
Nitric acid ^d	110 days			
Sulfur dioxide	16 days	>200 years	>1.8 × 10 ⁴ years	
Ammonia ^e	90 days			
Methylamine ^e	8 hours	2 years		
Hydrogen sulfide	3.1 days	>2 years	>1.6 days	
Methyl mercaptan	5 hours		24 minutes	
Propane	12 days	>7,000 years		
<i>n</i> -Butane	5.6 days	>4,500 years	3.6 years	
<i>n</i> -Octane	1.9 days		1.2 years	
Ethene	1.9 days	9 days	1.2 years	
Propene	7 hours	1.5 days	6 days	
1-Butene	5.6 hours	1.5 days	5 days	
<i>trans</i> -2-Butene	2.5 hours	2 hours	1.6 hours	
Acetylene	19 days	6 years	>5.6 years	
Propyne	2.5 days	3 years	1.4 years	
Butadiene	0.6 days	~270 days		
Formaldehyde	1.9 days	>2 × 10 ⁴ years	84 days	4 hours
Acetaldehyde	0.6 days	>7 years	20 days	60 hours
Benzaldehyde	1.2 days		24 days	
Acrolein	0.6 days	60 days		
Crotonaldehyde	5 hours	18 days		
Methylvinylketone	0.6 days	3 days		
Acetone	62 days			15 days
2-Butanone	14 days			
Dimethyl ether	4.4 days	>40 days		
Methanol	16 days	>190 days		
Ethanol	5 days	>130 days		
Formic acid	31 days			
Methyl nitrite	~75 days	3 years		8 minutes
Benzene	11 days	600 years	>6.4 years	
Toluene	2.5 days	300 years	3.6 years	
<i>m</i> -Xylene	7 hours	75 years	0.8 years	
1,2,4-Trimethylbenzene	4.4 hours	35 years	50 days	
Phenol	6 hours		8 minutes	

^a A compound's lifetime is defined as the time needed to decay to 37% of its original concentration.

^b For concentrations of hydroxyl radical, 12-hour average of 1.6×10^6 molecules/cm³ (Prinn et al, 1992); ozone, 24-hour average of 7×10^{11} molecules/cm³ (Logan 1985); nitrate radical, 12-hour average of 5×10^8 molecules/cm³ (Atkinson 1991).

^c For solar zenith angle of 0°.

^d Also reacts with ammonia to form ammonium nitrate.

^e Also reacts with gaseous nitric acid to form nitrate salts.

tion, Harger and colleagues (1992) made the important observation that, whereas the gas-phase sample contained nearly 50% of the overall mutagenicity in the nitro-PAH-containing fraction, the majority (90%) of the mutagenicity in the particle-phase sample was due to compounds more polar than the nitro-PAHs. This, and other evidence, has led to the suggestion that the majority of ambient air direct-acting mutagenicity may be associated with OH-radical-initiated reaction products other than nitro-PAHs (Atkinson and Arey 1994).

For example, 2- and 4-nitrodibenzopyranones, products of the OH-radical-initiated reaction of gas-phase phenanthrene, have been observed in ambient air samples collected in Southern California (Helmig et al. 1992b,c), Boise, Idaho, and Philadelphia, Pennsylvania (Lewtas and Nishioka 1990; Nishioka and Lewtas 1992), as well as in the urban dust collected in Washington, DC (National Institute of Standards and Technology Standard Reference Material

1649) (Helmig et al. 1992c). The 2-nitrodibenzopyranone isomer accounted for about 20% of the total direct-acting mutagenicity in the microsuspension assay of the crude extracts of a Riverside, California, ambient air particulate matter sample (Helmig et al. 1992b). Clearly, this newly identified class of PAH transformation products constitutes an important group of ambient air mutagens.

In summary, atmospheric transformations of primary diesel emissions produce additional chemical species (e.g., nitro-PAHs), some of which are mutagenic. The human health effects, if any, of most of these compounds are unknown at present. In addition to producing nitro-PAHs, three- and four-ring gaseous PAHs emitted in diesel exhaust have been shown to undergo reactions with OH and NO₃ radicals in the gas phase to produce nitropolycyclic lactones. These transformation products condense onto particles in the atmosphere and, as noted above, have been identified in ambient air particulate matter samples col-

Table 7. Calculated Atmospheric Lifetimes of Polycyclic Aromatic Hydrocarbons and Polycyclic Aromatic Hydrocarbon Derivatives Due to Photolysis and Gas-Phase Reactions with Hydroxyl and Nitrate Radicals and with Ozone^a

Polycyclic Aromatic Hydrocarbon	Atmospheric Lifetimes Due to Reaction with			
	Hydroxyl ^b	Ozone ^c	Nitrate ^d	Solar Radiation ^e
Naphthalene	8.0 hours	>80 days	1.5 years	
1-Methylnaphthalene	3.3 hours	>125 days	250 days	
2-Methylnaphthalene	3.3 hours	>40 days	180 days	
2,3-Dimethylnaphthalene	2.3 hours	>40 days	125 days	
Biphenyl	2.0 days	>80 days	>105 years	
Acenaphthene	1.7 hours	>30 days	1.2 hours	
Acenaphthylene	1.6 hours	~43 minutes	6 minutes	
Fluorene	1.1 days			
Phenanthrene	13.0 hours	42 days	4.6 hours	
Anthracene	13.0 hours			
Fluoranthene	~3.5 hours ^f		~85 days	
Pyrene	~3.5 hours ^f		~30 days	
1-Nitronaphthalene	2.7 days	>28 days	18 years	1.7 hours
2-Nitronaphthalene	2.6 days	>28 days	20 years	2.2 hours
2-Methyl-1-nitronaphthalene	>1.7 days	>55 days	4.2 days	2.1 hours

^a Adapted from Atkinson and Arey (1994).

^b For a 12-hour daytime average hydroxyl-radical concentration of 1.6×10^6 molecules/cm³ (Prinn et al. 1992).

^c For a 24-hour average ozone concentration of 7×10^{11} molecules/cm³ (Logan 1985).

^d For a 12-hour average nighttime nitrate-radical concentration of 5×10^8 molecules/cm³ (Atkinson 1991) and nitrogen dioxide concentration of 2.4×10^{11} molecules/cm³.

^e For an average 12-hour daytime nitrogen dioxide photolysis rate per second of $J_{\text{NO}_2} = 5.2 \times 10^{-3}$.

^f Using an estimated hydroxyl-radical reaction rate constant per second of 5×10^{-11} cm³ • molecules based on a rate constant correlation with ionization potential (Biermann et al. 1985).

lected from diverse locations. Based on current evidence, as much as 30% of the ambient particulate matter mutagenicity in the *Salmonella* test (TA98-S9, microsuspension modification) can be accounted for by PAH gas-phase atmospheric transformation products measured in extracts of such particulate matter (Atkinson and Arey 1994).

CONCLUSION

Atmospheric transport, chemical transformations, and dry and wet deposition are a complex set of processes that affect diesel emissions. These interactions, particularly the chemical transformations, are important to human health because they may increase or decrease the toxic, mutagenic, and carcinogenic activity of individual diesel emission components, as well as alter the atmospheric residence times of those components.

For the most part, diesel emissions contain chemicals that are representative of those produced by other combustion sources and, therefore, cannot be treated as a separate source category in terms of atmospheric reactions (although diesel exhaust may contain a higher proportion of PAHs and nitro-PAHs). At present, no unique tracers of diesel emissions have been identified, although several possible candidates have been noted for further study.

The most important chemical reactions of constituents of diesel exhaust are with O_3 , light, and OH and NO_3 radicals. Because of the known mutagenic and carcinogenic properties of PAHs and nitro-PAHs, significant attention has been directed toward these compounds and their atmospheric transformation products. A critical lack of information remains, however, on the identity, residence times, and biological activity of many of the reaction products of PAHs and their derivatives in the atmosphere.

The OH-radical-initiated nitration reactions of PAHs are of particular concern to human health because the nitro-PAH products are often more mutagenic and carcinogenic than the original PAHs. Thus the major pathway for PAH transformation in the atmosphere is by reaction with OH radicals or NO_3 or both. Such reactions result in lifetimes that are calculated as less than one day for most PAHs and that lead to the formation of secondary mutagenic nitro-PAHs and oxygenated nitro-PAHs, which are ubiquitous in atmospheric air samples, both gas-phase and particulate.

In summary, many of the secondary nitro-PAHs are unique products of atmospheric chemical reactions and are not detected in direct emissions from combustion sources. Mutagenic oxygenated nitro-PAHs formed from OH-radical-initiated gas-phase reactions have been detected in ambient air particulate matter samples from a wide range of locations. As much

as 30% of the ambient particulate matter mutagenicity in the *Salmonella* microsuspension test appears to be accounted for by PAH atmospheric transformation products measured in extracts of such particulate matter. Clearly, it is essential that health risk assessments for diesel emissions also account for the biological activity of atmospheric transformation products.

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ABBREVIATIONS

BaP	benzo[a]pyrene
CO	carbon monoxide
HNO ₃	nitric acid
H ₂ O ₂	hydrogen peroxide
HONO	nitrous acid
H ₂ SO ₄	sulfuric acid
NO	nitric oxide
NO ₂	nitrogen dioxide
NO ₃	nitrate
NO _x	oxides of nitrogen
N ₂ O	nitrous oxide
N ₂ O ₅	dinitrogen pentoxide
1-NP	1-nitropyrene
O ₂	oxygen
O ₃	ozone
OH	hydroxyl
PAH	polycyclic aromatic hydrocarbon
ppb	parts per billion
ppm	parts per million
ppt	parts per trillion
SO ₂	sulfur dioxide



Assessment of Occupational Exposure to Diesel Emissions

Winthrop F. Watts, Jr.

U.S. Bureau of Mines

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INTRODUCTION

Measurement of human exposure to toxic agents is the first step in determining the exposure-dose-response relationship. It is a fundamental step in risk assessment. Measuring exposure to diesel exhaust pollutants is particularly challenging due to the complexity and variability of exhaust components. This background paper emphasizes measurements made in the workplace, reviewing occupational exposure surveys completed after the publication of the International Agency for Research on Cancer report of 1989. These surveys assessed diesel exhaust exposure using diesel particulate matter or measurements of specific polycyclic aromatic hydrocarbons (PAHs)* or both as indicators of exposure. Diesel particulate matter is emphasized because it is a major component of diesel exhaust, is suspected to contribute to the health hazard, and is measurable. PAHs are closely associated with diesel particulate matter and are suspected to have a role in cancer initiation.

Diesel pollutants form during the combustion process. As these compounds pass through an exhaust pipe, chemical and physical changes occur that alter their composition and concentration. Atmospheric reactions further alter the chemical and physical composition. Because diesel exhaust is chemically complex and constantly in a state of flux, it is not feasible to monitor all exhaust pollutants. The most common approach to monitoring is to select a surrogate measure or measures of exposure that are representative of diesel exhaust as a whole and have some relationship to adverse health effects. In some instances, the surrogate measure is used to predict the levels of other pollutants in diesel exhaust. Unfortunately, many of the compounds found in diesel exhaust are also emitted from other combustion sources and are thus not unique to diesel exhaust.

Occupational exposure studies have advantages over environmental studies conducted in the outdoor ambient atmosphere. Diesel pollutant concentrations measured in the workplace are generally higher and are therefore more easily measured. The exposed workplace population is better defined, and the duration of exposure is more predictable and quantifiable. In addition, the sources of combustion pollutants in the workplace are usually identifiable. Environmental studies, on the other hand, are more difficult to interpret. Diesel pollutant concentrations are generally much lower and are therefore more difficult to measure. The exposed population is more mobile, and the duration of exposure is generally not well defined. Also, the contribution of diesel exhaust to environmental pollutant concentrations is more difficult to determine because of the multiple sources of

combustion products and, at least in the United States, the relatively small contribution of diesel exhaust to ambient pollutant levels.

This background paper is divided into three major sections: occupational health standards, diesel exhaust aerosol measurement, and diesel pollutant exposure in the workplace. Each section concludes with a brief summary.

OCCUPATIONAL HEALTH STANDARDS

Occupational exposure surveys of diesel exhaust frequently measure regulated pollutants, or pollutants that are suspect carcinogens even if no permissible exposure limits have been established. In the United States, the American Conference of Governmental Industrial Hygienists recommends threshold limit values (TLVs), and the National Institute for Occupational Safety and Health establishes recommended exposure limits. Neither the American Conference of Governmental Industrial Hygienists nor the National Institute for Occupational Safety and Health has regulatory authority. The Occupational Safety and Health Administration and the Mine Safety and Health Administration, which are regulatory agencies in the U.S. Department of Labor, establish and enforce permissible exposure limits based on the best available information and a formal rule-making process. As shown in Table 1, these organizations recommend a range of allowable values for diesel exhaust gaseous constituents, including carbon monoxide

Table 1. Range of Allowable Gaseous Exposure Limits for Eight-Hour Time-Weighted-Average Occupational Exposures^a

Pollutant	Range ^b (ppm)
HCHO ^c	0.016 to 2.0
CO	25 to 50
CO ₂	5,000 to 10,000
NO	25
NO ₂ ^d	1.0 to 5.0
SO ₂	2.0 to 5.0

^a The National Institute for Occupational Safety and Health has a 10-hour time-weighted-average value.

^b Ranges are from the American Conference of Governmental Industrial Hygienists, Mine Safety and Health Administration, National Institute for Occupational Safety and Health, and Occupational Safety and Health Administration standards.

^c Suspected carcinogen; the Mine Safety and Health Administration has only a 15-minute short-term value.

^d The National Institute for Occupational Safety and Health and the Occupational Safety and Health Administration have only 15-minute short-term values.

* A list of abbreviations appears at the end of the paper.

(CO), carbon dioxide (CO₂), sulfur dioxide (SO₂), nitrogen dioxide (NO₂), nitric oxide (NO), and formaldehyde (HCHO). Table 1 shows 8-hour or 10-hour time-weighted-average values where available; where these are not available, 15-minute short-term exposure values are included. The Mine Safety and Health Administration, U.S. Department of Labor (1989) has proposed revised air quality regulations, but these are not shown.

There is no specific U.S. permissible exposure limit for diesel particulate matter at this time. Diesel aerosol is of respirable size and thus is limited under a variety of permissible exposure limits for respirable dust, including the Mine Safety and Health Administration's respirable coal mine dust standard of 2.0 mg/m³. The Mine Safety and Health Administration has announced that it will consider regulating diesel particulate matter (Mine Safety and Health Administration, U.S. Department of Labor 1992). Recently the American Conference of Governmental Industrial Hygienists (1995) added diesel exhaust to the Notice of Intended Changes for 1995–1996 with a recommended TLV of 0.15 mg/m³ and a designation of suspected human carcinogen.

Respirable combustible dust is used to estimate diesel particulate matter concentrations in Canadian noncoal mines. Gangal and Dainty (1993) and Gangal and associates (1990) determined the amount of respirable combustible dust in a respirable dust sample by subtracting the mass that is removed from the sample by combustion at 500°C from the total sample mass. An estimate of the diesel particulate matter concentration is made by multiplying the respirable combustible dust measurement by an empirical correction factor of 0.67. This adjusts for the contribution of unburnt fuel, evaporated lube oil, and other carbonaceous material to the diesel particulate matter estimate. For aerosol samples collected in a coal mine or in other environments where nondiesel carbonaceous aerosol is present, respirable combustible dust analysis is not appropriate to estimate diesel particulate matter levels.

British Columbia has established a respirable combustible dust standard of 1.5 mg/m³ for underground noncoal mines (Victoria British Columbia, Ministry of Energy, Mines and Petroleum Resources, Resource Management Branch 1992). The Canada Centre for Mineral and Energy Technology recommends that this standard eventually be reduced to 0.75 mg/m³ as recommended by I.W. French and Associates, Ltd. (1990).

In the Federal Republic of Germany, diesel particulate matter is defined by the coulometric determination of total carbon content in fine dust particles (Bauer et al. 1991). Based on this analytical procedure, the following technical exposure limits were established: 0.6 mg/m³ for diesel particulate matter in underground noncoal mines and underground construction sites and 0.2 mg/m³ for other occu-

pational environments. Coal mines were not regulated. The technical exposure limit of a hazardous material is the minimum concentration possible with current technology and serves as a guidance mechanism for implementing necessary protective measures and monitoring policies in the workplace (Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area 1993). This method of measurement is not appropriate for coal mines or other areas where substantial amounts of carbonaceous material are present from nondiesel sources.

Of the PAHs, only chrysene (0.2 mg/m³) and coal tar pitch volatiles (0.2 mg/m³ as benzene soluble material) have Occupational Safety and Health Administration permissible exposure limits (American Conference of Governmental Industrial Hygienists 1992). The Occupational Safety and Health Administration permissible exposure limit for coal tar pitch volatiles specifically includes anthracene, benzo[*a*]pyrene, phenanthrene, acridine, chrysene, and pyrene, which are also found in diesel exhaust. No permissible exposure limits have been established for other gas-phase or particle-bound PAHs. The American Conference of Governmental Industrial Hygienists designates diesel exhaust components benz[*a*]anthracene, benzo[*a*]pyrene, benzo[*b*]fluoranthene, and chrysene as "suspected human carcinogens" but recommends no TLVs. The benzene extractable portion of coal tar pitch volatiles is designated as a "confirmed human carcinogen" with a TLV of 0.2 mg/m³ by the American Conference of Governmental Industrial Hygienists (1994).

In summary, occupational health standards are enforced for a number of the gaseous constituents of diesel exhaust, including CO, CO₂, SO₂, NO₂, NO, and HCHO. Of the PAHs, only chrysene and coal tar pitch volatiles have established Occupational Safety and Health Administration permissible exposure limits, although several PAHs are designated as suspected or confirmed human carcinogens. The Mine Safety and Health Administration may regulate diesel particulate matter in the future, and the American Conference of Governmental Industrial Hygienists added diesel exhaust to the Notice of Intended Changes for 1995–1996 with a recommended TLV of 0.15 mg/m³. British Columbia has established an exposure limit for respirable combustible dust of 1.5 mg/m³ in noncoal mines, and Germany has established technical exposure limits for total carbon content in fine dust particles of 0.6 mg/m³ in underground noncoal mines and underground construction sites and 0.2 mg/m³ in general industry.

DIESEL EXHAUST AEROSOL MEASUREMENT

Diesel particulate matter is small in size and is composed of organic and elemental carbon, adsorbed and condensed

hydrocarbons, and sulfate. The proportion of organic to inorganic carbon varies depending on a number of factors, which include fuel, engine type, duty cycle, engine maintenance, operator habits, use of emission control devices, and lube oil consumption. In general, nonextractable elemental carbon accounts for a greater fraction of diesel particulate matter mass than extractable organic material (Perez and Williams 1989).

Figure 1 depicts the trimodal particle size distribution that arises from different mechanisms of aerosol generation (Cantrell and Rubow 1992). Primary combustion aerosols (including diesel exhaust aerosol) are formed as very small particles in the 0.001 to 0.08 μm range, but physical mechanisms such as condensation and coagulation quickly transfer the aerosol mass from the nuclei mode to the accumulation mode. These processes result in a mass median diameter of approximately 0.2 μm for diesel aerosol. Mechanically generated aerosols, on the other hand, typically contain particles greater than 1 μm in diameter, with only a small portion of the mass under 1 μm .

The difference in the aerodynamic diameter particle size between combustion and mechanically generated aerosols is used to separate diesel aerosol from noncombustion aerosols in the collecting process. Respirable aerosol sampling has a 50% cutpoint at 3.5 μm and collects a fraction of particles up to 10 μm in size. Diesel aerosol has a mass median aerodynamic diameter of 0.2 μm , and 90% of the particles are less than 1.0 μm in size. Thus, respirable aerosol sampling collects all diesel and nondiesel aerosol particles falling in the respirable size range. These two fractions are separated using inertial impaction on substrates, which removes large nondiesel particles and a small

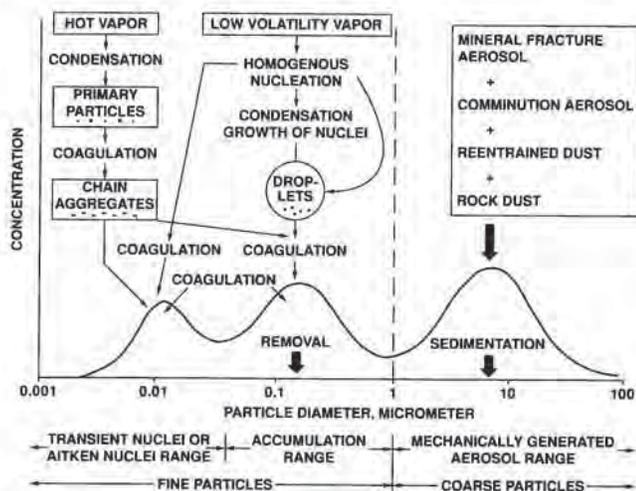


Figure 1. Trimodal particle size distribution arising from different mechanisms of aerosol generation.

percentage of large diesel particles. Given the presence of a mixture of diesel exhaust particles and mineral dust, the submicrometer aerosol is predominantly diesel in origin. This submicrometer diesel aerosol is collected on a filter downstream of the impaction substrate. Gravimetric analyses determine the mass fraction in each size range. Also, the filter containing the submicrometer material can be analyzed by other methods to increase the sensitivity and specificity for diesel particulate matter. This is an advantage over other aerosol measurement techniques, which either do not collect a sample or destroy the sample during analysis. Another advantage this method has over traditional respirable dust sampling is that it separates large particles, which are predominately nondiesel in origin, but still allows the respirable fraction to be calculated. Finally, large quantities of submicrometer material can be collected for chemical analyses using high-volume samplers with size-selective inlets.

The aerosol sampling techniques described above and used in the occupational exposure surveys described below collect all particulate matter meeting specific aerosol sampling penetration criteria. As discussed by McCawley (1990), penetration criteria are not predictive of deposited dose. Dose is a function of the fraction of particulate matter that is deposited in the lung or another area and not necessarily a function of the particulate matter that penetrates the airways. Reliance on measurements of total diesel particulate matter as indicators of exposure may overestimate the actual deposited dose of diesel particulate matter in lung tissue because the mass median diameter of diesel aerosol is 0.2 μm , which is near the point of minimum deposition for the alveolar portion of the lung. Health effects assessments based solely on measurements of total diesel particulate matter exposure may lead to inaccurate conclusions. If detailed size distribution data are available, then a correction can be applied to total diesel particulate matter measurements to estimate the deposited dose. Unfortunately, industrial hygiene surveys rarely collect these data because most often the objective is to determine compliance with an existing permissible exposure limit or to determine the efficiency of a control strategy. Raabe (1984) provides further details on size-selective sampling criteria for thoracic and respirable mass fractions.

SIZE-SELECTIVE SAMPLING

Gravimetric Analysis

Size-selective sampling is used extensively in mining to evaluate the performance of emission control devices and to determine the concentrations of respirable dust and diesel particulate matter in the mine atmosphere. These

samples can be further analyzed for other components of diesel particulate matter, such as elemental carbon. As noted previously, this type of measurement does not mimic lung deposition and is therefore not necessarily representative of dose. The method is described in more detail below.

McCawley and Cocalis (1986) designed and constructed a size-selective sampler to separate submicrometer aerosol from the respirable fraction in underground coal mines. This sampler was a modification of a previous sampler that Jones and associates (1983) designed. Marple and associates (1986) showed in the laboratory and Cantrell and coworkers (1987), Cantrell and Rubow (1990a,b), and Rubow and coworkers (1990a) demonstrated in underground coal mines that size-selective sampling using inertial impaction coupled with gravimetric analysis can be used to provide estimates of diesel particulate matter concentrations that are accurate within 10%. Rubow and coworkers (1990b) developed a personal diesel exhaust aerosol sampler based on these principles. The sampler operates at a flow rate of 2 L/min, which is compatible with commercial personal sampler pumps.

Primary limitations on personal diesel exhaust aerosol sampler performance are aerosol loss within the sampler, contamination of the portion of the sample less than 0.8 μm by mineral dust aerosol, and accuracy of the gravimetric analysis performed on the sample. The final sample of material less than 0.8 μm contains most of the diesel particulate matter present in the mine air plus a small amount of mineral dust contamination (usually less than 10%). According to Cantrell and Rubow (1990a), if a sample flow rate of 2 L/min is used and gravimetric analysis is to within 0.1 mg, the aerosol concentration for the fraction of aerosol less than 0.8 μm should have a theoretical limit of detection of $0.3 \text{ mg/m}^3 \pm 50\%$, with a confidence level of 95%. This lower limit of detection is a worst-case estimate based on the Mine Safety and Health Administration's current gravimetric analysis practice, mine aerosol interferences, and tolerances in sampler manufacture. With gravimetric analysis to within 0.005 mg, the lower limit of detection would be 0.2 mg/m^3 . Measurements have shown that the personal diesel exhaust aerosol sampler is capable of a precision of 0.015 mg/m^3 .

Size-selective sampling coupled with gravimetric analysis has limitations. In environments where submicrometer aerosol sources are well defined and have relatively high concentration, this method is effective. When other forms of submicrometer aerosol are present or concentrations are low, other analysis methods with greater specificity and sensitivity are required to quantify the diesel aerosol fraction.

Elemental Carbon Analysis

Size-selective sampling can collect a sample of submicrometer particulate matter that can be analyzed gravimetrically and by other analytical methods. These methods are frequently more specific and sensitive than the gravimetric method. Recent research has focused on analyzing the submicrometer or respirable fraction for elemental carbon. Elemental carbon accounts for a significant fraction of diesel particulate matter emissions, acts as a carrier of suspected mutagens and carcinogens, and is readily detectable by thermal-optical analysis. The association between particle exposure and health effects, discussed elsewhere, further strengthens the use of elemental carbon as a surrogate for diesel particulate matter exposure. According to Cadle and Groblicki (1982), elemental carbon has an analytical definition that is operationally defined by the method of analysis.

Fowler (1985) concluded that elemental carbon is the most reliable overall measure of exposure to diesel exhaust because selecting an extractable organic compound or class of compounds as a reliable surrogate of exposure is difficult. The soluble organic fraction associated with diesel exhaust aerosol is highly variable in composition and chemically complex, and uncertainty exists about the compounds responsible for mutagenic and carcinogenic activity. Also, low concentrations and the presence of interfering chemical compounds make analysis difficult.

The National Institute for Occupational Safety and Health (Birch 1992) is investigating the use of a temperature-based thermal-optical method for speciation of organic (volatile and nonvolatile) and inorganic (carbonate) compounds and elemental carbon. Aerosol samples are collected by inertial impaction to classify particles by size. As noted previously, particles less than 1.0 μm in size are predominately from combustion sources. Thermal-optical analysis is used to detect and quantify different types of carbon. Volatilized carbon is oxidized to CO_2 and subsequently reduced to methane, which is quantified by flame ionization detection. The second stage of analysis begins by reducing the combustion chamber temperature, introducing oxygen, and reheating to 750°C. During this stage, elemental carbon and char content are determined. The estimated limit of detection in the laboratory is 2 μg of either elemental or organic carbon per filter, which translates to a concentration of about $1 \mu\text{g/m}^3$, assuming 2 m^3 of sample air volume. Johnson and associates (1981) describe this analytical method in more detail.

Zaebst and coworkers (1991) conducted an experiment to investigate possible environmental tobacco smoke interference with elemental carbon measurements. Tobacco aerosol was generated in a controlled environment by three men smoking a total of eight cigarettes per hour. Respirable

particulate matter was on the order of $1,100 \mu\text{g}/\text{m}^3$. Elemental carbon constitutes an average of 1.8% of the total carbon from tobacco smoke; organic carbon constitutes 98.2% of the total carbon.

As part of the same study, Zaebs and coworkers (1991) conducted an experiment to investigate the precision and reproducibility of the thermal-optical method to determine elemental carbon in diesel exhaust. Diesel aerosol was generated under four load-and-speed conditions and diluted in a dilution tube at Ford Motor Company's Research and Engineering Facility in Dearborn, Michigan. Exhaust was injected into the dilution tube from a light-duty diesel engine, operated on a dynamometer at 48 km per hour. Elemental carbon constituted an average of 62% of the total particulate mass on the filters and 64% of the total carbon loading. Total carbon, both elemental and organic, constituted 91% of the total mass on the filters. The mean coefficient of variation of the elemental carbon method was 7.3%.

Zaebs and coworkers (1991) argue for the use of elemental carbon as a surrogate measure of diesel exhaust exposure and for the thermal-optical method of analysis. Their arguments are as follows: (1) most diesel exhaust aerosol mutagenicity appears associated with the particulate phase, and lung tumor induction in laboratory rats is primarily associated with the particulate phase; (2) clearance in animals is adversely affected by particle deposition, and "inert" substances deposited in the lung alone may induce lung cancer; (3) submicrometer elemental carbon detection by thermal-optical analysis has sensitivity 100-fold greater than the gravimetric method, and the diesel particulate fraction is mostly carbon; and (4) nearly all elemental carbon from vehicular traffic is attributable to diesel exhaust.

As noted earlier, the percentage of elemental carbon in total diesel particulate matter fluctuates. Major factors contributing to this fluctuation include engine type, duty cycle, fuel, lube oil consumption, state of engine maintenance, and the presence or absence of an emission control device. Fluctuations in the ratio of elemental to organic carbon can cause an inaccurate estimate of the total diesel particulate matter present. The estimate is more accurate if both organic and elemental carbon are measured and an adjustment is made for the presence of nondiesel carbon sources.

More detailed information on the analyses of carbonaceous compounds resulted from the Carbonaceous Species Methods Comparison Study, which was conducted at Citrus College in Glendora, California, between August 11 and 21, 1986. Papers from that study were summarized by Hering and associates (1990).

In summary, measuring diesel particulate matter using size-selective sampling coupled with gravimetric and/or thermal-optical analysis takes advantage of the submicrometer size and the elemental carbon content of the diesel particles. With gravimetric analysis to within 0.005 mg, the lower limit of detection would be $0.2 \text{ mg}/\text{m}^3$. The thermal-optical method has a limit of detection of $2 \mu\text{g}$ of either elemental or organic carbon per filter, which translates to a concentration of about $1 \mu\text{g}/\text{m}^3$, assuming 2 m^3 of sample air volume. However, the reliance on elemental carbon as a surrogate measure of total diesel particulate matter can, in some instances, result in an inaccurate estimate of the amount of total diesel particulate matter present.

DIESEL POLLUTANT EXPOSURE IN THE WORKPLACE

The International Agency for Research on Cancer (1989) reviewed occupational and environmental exposures to pollutants in diesel exhaust. Occupational studies of railroad workers, miners, bus garage workers, truck drivers, forklift truck operators, and firefighters exposed to diesel exhaust were summarized, as were studies of workers exposed to both gasoline and diesel exhaust, including toll-booth attendants, mechanics, and others. Concentrations of a variety of substances were reported, including CO, NO, NO₂, oxides of nitrogen (NO_x), SO₂, respirable and total dust, HCHO, and a few specific PAHs. These data were obtained from a mixture of time-weighted-average personal exposure samples, short-term area samples, and diesel exhaust samples. In general, the personal exposure pollutant concentrations that the International Agency for Research on Cancer report summarized were well below current occupational health standards.

Since the publication of the International Agency for Research on Cancer report, several studies have been published on diesel exhaust exposures among coal and noncoal miners, railroad workers, forklift truck operators, firemen, and truck drivers. These studies are of interest because they report pollutant levels, attempt to account for background contaminants, and use new sampling and analytical techniques that are more specific for assessing exposure to diesel pollutants, especially diesel particulate matter. None of the studies provides information on the dose of diesel particulate matter deposited in the lung. All of the studies attempt to quantify either total diesel particulate matter or total elemental carbon and other pollutants.

The respirable combustible dust, size-selective aerosol, and elemental carbon measurements discussed below cannot be directly related to past respirable or total dust meas-

measurements with any degree of certainty. There is no way of determining what fraction of the respirable or total aerosol from past measurements was elemental carbon or what fraction was diesel in origin. However, in the case of measurements made in underground mines, the reported concentrations are certainly lower now than they were 15 or 20 years ago. Enhanced hazard recognition, better ventilation, altered work practices, improved engine maintenance, engine design modifications, improved fuel quality, and the use of exhaust control technology have all contributed to reducing exposure of miners to diesel exhaust.

MINERS

Gangal and Dainty (1993) reported the levels of respirable combustible dust in 21 Canadian noncoal mines. A total of 223 personal and area samples were collected at these mines. Mean respirable combustible dust concentrations ranged from 0.17 to 1.30 mg/m³, with maximum concentrations ranging from 1.02 to 3.10 mg/m³. Estimates of diesel particulate matter concentration were obtained by multiplying these values by 0.67, the correction factor used in Canada. The range of mean diesel particulate matter exposure was 0.1 to 0.9 mg/m³, and the range of maximum concentrations was 0.7 to 2.1 mg/m³. These measurements suggest that, on average, exposure to diesel particulate matter in Canadian noncoal mines is less than the 1.5 mg/m³ recommended level.

Watts and associates (1989, 1992) and Cantrell and colleagues (1992, 1993) reported coal mine air quality data collected in five underground coal mines with diesel-powered haulage equipment (shuttle cars). Diesel coal haulage vehicles typically use Caterpillar or Motorenwerke Mannheim indirect injection engines in the 56- to 112-kW range (6- to 11-L displacements). These vehicles are equipped with water scrubbers to remove flames and sparks and to cool the exhaust.

Daily area samples were collected in the clean air section intake, in the haulageway where diesel activity was taking place, on shuttle cars, and in the return airway where contaminated air exits the section. Both full-shift and partial-shift samples were collected using a variety of aerosol instruments, including the personal diesel exhaust aerosol sampler and the micro-orifice uniform-deposit impactor. Two of the mines were also monitored for the major gaseous pollutants found in diesel exhaust—CO, CO₂, NO, NO₂, and SO₂—either by collecting bag samples for subsequent gas analysis or by using Palmes dosimeters.

The mean average diesel particulate matter concentrations determined by personal diesel exhaust aerosol samplers for all five mines are summarized in Table 2. Section intake air concentrations were below 0.2 mg/m³. The mean

concentration at the haulage site was 0.89 mg/m³, with a standard deviation of 0.44 mg/m³. Diesel particulate matter contributed 52% of the respirable aerosol at this location. These results were very close to the mean diesel particulate matter concentrations calculated from size distribution measurements obtained using the micro-orifice uniform-deposit impactor: 0.95 mg/m³ with a standard deviation of 0.5 mg/m³. The relatively high standard deviations reflect the differences in aerosol concentrations between mines and to a lesser extent the day-to-day differences within the same mine. Concentrations of CO, CO₂, NO, NO₂, and SO₂ were all well below regulated levels.

Other investigators have used size-selective sampling methods to quantify submicrometer aerosol concentrations in diesel-equipped coal mines. McCawley and Cocalis (1986) reported concentrations of aerosol less than 1 μm in size from two underground coal mines using diesel shuttle cars; measurements were made using the Anderson Model 298 cascade impactor. Mean submicrometer aerosol concentrations for the two mines ranged from 0.1 mg/m³ at the section intake to 0.8 mg/m³ at the continuous mining machine operator's position. Mean NO and NO₂ concentrations were also reported for the two mines, and the concentrations were well below regulated levels.

Haney (1990) conducted tests of a single-jet impactor at five underground coal mines using diesel equipment. Miner exposure to diesel particulate matter ranged from 0.18 to 1.00 mg/m³, and area samples collected in haulageways agreed within 0.12 mg/m³ of section worker exposure. At three mines, the single-jet impactor and personal diesel exhaust aerosol sampler were used together at a sampling location. More than 60 paired data points were obtained; respirable aerosol measurements agreed within 25%, and diesel particulate matter measurements agreed within 0.06 mg/m³.

Diesel particulate matter measurements using the personal diesel exhaust aerosol samplers are quite similar to the

Table 2. Mean Concentrations of Diesel Particulate Matter in Five Coal Mines as Measured by the Personal Diesel Exhaust Aerosol Sampler^a

Location	n ^b	Concentration (mg/m ³)		
		Mean	SD	Median
Haulage	42	0.89	0.44	0.75
Shuttle car	51	0.67	0.23	0.65
Return	100	1.43	0.97	1.06

^a Data are from Watts and associates (1992).

^b n = number of samples.

measurements that McCawley and Cocalis (1986) and Haney (1990) reported. All measurements made to date suggest that diesel particulate matter contributes a substantial percentage (40% to 60%) of the respirable dust in areas of underground coal mines where diesel haulage equipment is used.

During the in-mine studies reported by Watts and colleagues (1989, 1992) and Cantrell and associates (1992, 1993), samples were collected and analyzed for PAHs and mutagenic activity. Bagley and coworkers (1991, 1992) reported these data. High-volume samplers equipped with inertial impactors to collect size-differentiated particles were operated at a flow rate of 1.13 m³/min, with mean sample times ranging from 19 to 42 minutes. The diesel fraction was less than 1 µm in size. Samples were collected only during periods of mining activity and are not necessarily representative of personal exposure. The high-volume samplers were collocated with personal diesel exhaust aerosol samplers and the micro-orifice uniform-deposit impactor discussed previously. Filter samples were kept cold until Soxhlet extraction with dichloromethane. The soluble organic fraction was tested for Ames activity, and concentrations of fluoranthene, pyrene, and benzo[a]pyrene were determined using high-performance liquid chromatography.

The high-volume samplers were operated for short periods in haulageways when diesel activity was significant. Mean daily diesel particulate matter concentrations for the four mines ranged from 0.85 to 3.26 mg/m³. Detailed chemical and mutagenic results for diesel-aerosol associated parameters are summarized in Table 3. These values are not necessarily representative of personal exposure.

Bagley and associates (1994) provide additional detailed data on PAH and mutagenicity levels in coal and noncoal mines. This National Institute for Occupational Safety and Health contract final report summarizes their findings from evaluations of emission control systems used in underground mines, such as disposable diesel exhaust filters, catalyzed ceramic filters, and diesel oxidation catalysts. The report also describes the methods that were used to obtain and analyze these data.

Westaway (1988) and Westaway and Faulds (1983) reported PAH levels in Canadian salt and nickel mines and compared them with PAH levels found in the city of Sudbury, Canada. Area samples were collected using high-volume samplers operated from 10 minutes to 24 hours. The samplers were not equipped with inertial impactors to separate and collect the submicrometer fraction. Filters were extracted with benzene and methanol using a combination of sonication and Soxhlet extraction. The extract was purified and separated into individual PAHs using thin-layer chromatography, and PAHs were quantified using spectrofluorometric analysis. Table 4 presents the results, which show that the total underground concentration of PAHs is higher than the comparable concentration in the city of Sudbury by a factor of 5. These results are not necessarily representative of exposure, nor are they specific for diesel exhaust.

Ambs and coworkers (1991) reported on the installation of a disposable diesel exhaust filter in the exhaust systems of four haulage vehicles used in an underground coal mine. A week-long field study was conducted to evaluate the performance of the filter system using the size-selective

Table 3. Mean In-Mine Extractable Organic Matter, Mutagenicity, and Polycyclic Aromatic Hydrocarbon Levels Associated with Diesel Particulate Matter Samples from Four Coal Mines^a

Parameter	Unit	Mine ^b			
		I	K	L	O
Soluble organic fraction	mg/m ³	0.40 (33)	0.17 (12)	0.08 (24)	0.18 (20)
Soluble organic fraction	pct	24 (31)	19 (5.2)	5.7 (13)	13 (22)
Activity ^c	Rev/m ³ d	970 (60)	440 (24)	NT ^e	690 (44)
Fluoranthene	ng/m ³	390 (38)	140 (16)	48 (30)	160 (16)
Pyrene	ng/m ³	270 (34)	70 (14)	32 (55)	180 (20)
Benzo[a]pyrene	ng/m ³	61 (39)	16 (6.7)	<0.046 ^f	18 (22)

^a Data are from Bagley and associates (1991, 1992).

^b Values are given as mean concentrations with the coefficient of variation (in %) given in parentheses.

^c Ames activity reported without S9 activation using strain TA98.

^d Rev = revertants.

^e NT = not tested due to insufficient extractable mass.

^f All values are less than minimum detectable levels.

methods discussed above. During this period, diesel equipment was operated with and without filters in place. Measurements were made using the micro-orifice uniform-deposit impactor and the personal diesel exhaust aerosol sampler. The samplers were collocated in the clean air intake to the mining section, the haulageway area where diesel activity was ongoing, and the return airway where polluted air leaves the mine. Additional personal diesel exhaust aerosol samples were collected on personnel. Results, summarized in Tables 5 and 6, show that using disposable diesel exhaust filters reduces average diesel particulate matter concentration in the haulageway by 94%, with a standard deviation of 6%. Note that concentrations and standard deviations shown in Tables 5 and 6 are average values uncorrected for production and ventilation changes. The reduction percentage is corrected for intake concentration, ventilation, and production changes, and the correction factors are shown. Detailed size distribution and indium fuel tracer data further confirm that submicrometer mine aerosol is composed mainly of diesel particulate matter, which was effectively removed when the disposable diesel exhaust filter was installed. Figure 2 shows average size distributions measured with and without the disposable diesel exhaust filter in place. They were made using data collected by the micro-orifice uniform-deposit impactor.

Table 4. Polynuclear Aromatic Hydrocarbon Concentrations Found in Canadian Dieselized Underground Mines and in the City of Sudbury, Ontario, Canada^a

Polynuclear Hydrocarbon	Aromatic		City Mean ^b (ng/m ³)
	Nickel	Salt	
Pyrene	80.2	256.0	14.6
Fluoranthene	5.6	19.7	1.1
Benz[<i>a</i>]anthracene	8.9	18.5	1.6
Benzo[<i>e</i>]pyrene	18.2	62.2	5.3
Perylene	0.5	0.3	0.1
Benzo[<i>k</i>]fluoranthene	2.6	5.4	0.6
Benzo[<i>a</i>]pyrene	1.9	1.2	0.3
Benzo[<i>ghi</i>]perylene	6.9	9.3	0.9
Dibenzo[<i>def,mno</i>]chrysene	0.5	0.6	0.1
Dibenzo[<i>ah</i>]anthracene	1.9	3.5	0.3
Naphtho[1,2,3,4- <i>def</i>]-chrysene	4.6	8.4	1.1
Benzo[<i>rst</i>]pentaphene	0.9	1.9	0.1
Total PAHs	132.7	387.0	26.1

^a Data are from Westaway (1988).

^b Concentrations are rounded to 0.1 ng/m³.

Diesel aerosol removed by the filter is shown as the cross-hatched bars less than 2 μm . Remaining submicrometer aerosols are from vehicles not equipped with the filter and from atmospheric aerosol. Figure 2 clearly shows the contribution of submicrometer diesel aerosol to the respirable aerosol mass and the effectiveness of the disposable diesel exhaust filter, confirming the usefulness of the size-selective sampling approach.

Ambs and associates (1994) repeated the evaluation of the filter at two additional coal mines and confirmed the previous results. Mean diesel particulate matter concentrations in the haulageway of those mines ranged from 0.83 to 1.74 mg/m³ with no disposable diesel exhaust filter and from 0.16 to 0.28 mg/m³ with the disposable diesel exhaust filter installed. The evaluation of the disposable diesel exhaust system provides additional data to support the contention that diesel engines produce nearly all of the submicrometer aerosol found in dieselized coal mines. The use of an exhaust filter effectively removes this aerosol from the mine atmosphere.

FORKLIFT TRUCK AND FIRE ENGINE OPERATORS

The National Institute for Occupational Safety and Health (1990) evaluated the effectiveness of several techniques for controlling exposure of dockworkers to forklift truck diesel emissions. During the course of the investigation, the National Institute for Occupational Safety and Health collected personal and area samples for diesel pollutants, including submicrometer elemental carbon. Elemental carbon is present at very low levels in source emissions containing cigarette smoke, sand, dirt, and fibers, but represents a large proportion of diesel particulate matter. The National Institute for Occupational Safety and Health used thermal-optical analysis to determine the elemental and organic carbon fractions of samples collected using inertial impaction, as previously discussed.

Two surveys were conducted to evaluate the effectiveness of high-temperature exhaust filtration units, propane-fueled engines, and ceiling exhaust fans to reduce diesel pollutant concentrations. Only data from full-shift personal samples, collected on diesel forklift truck operators, are reported here. Data from Dock 1 represent forklifts equipped with and without filters, and data from Dock 2 represent forklifts without filters.

During each survey, the National Institute for Occupational Safety and Health collected personal and area samples for submicrometer organic and elemental carbon, NO₂, CO, benzene-extractable material, 17 specific PAHs, Ames activity, and other pollutants. Of the pollutants measured

Table 5. Diesel Particulate Matter Reductions in Mine Air Achieved Through the Use of a Disposable Diesel Exhaust Filter: Diesel Particulate Matter Measurements Made Using a Micro-orifice Uniform-Deposit Impactor^a

Sample Site	Concentration With Filter ^b (mg/m ³)	Correction Factor	Concentration Without Filter ^b (mg/m ³)	Correction Factor	Reduction Percent ^c
Intake	0.065 (0.005)	1.0	0.075 (0.001)	1.16	NA ^d
Haulage	0.10 (0.01)	0.9	0.56 (0.05)	1.63	96 (2)
Return	0.08 (0.02)	0.89	0.84 (0.07)	1.63	98 (3)

^a Data are from Ambs and associates (1991).^b Mean (SD).^c Corrected for ventilation and production changes.^d NA = not applicable.

during the surveys, only elemental carbon provided a clear basis for differentiation between the propane-fueled and diesel engines. The filters reduced elemental carbon by 92% at Dock 1 but had little effect on organic carbon, as shown in Table 7. Use of the filters resulted in geometric mean concentrations not significantly different from background elemental carbon concentrations (1.6 µg/m³) measured 1 mile from the dock. The National Institute for Occupational Safety and Health concluded that the presence of environmental tobacco smoke substantially influenced the organic carbon concentration. Measurements for other pollutants were frequently below the level of detection and did not provide any evidence that could be used to differentiate between the propane-fueled or diesel engines, or to conclude that any one motor type was more or less hazardous in terms of health effects.

The National Institute for Occupational Safety and Health (1992) conducted a health hazard evaluation of diesel exhaust exposure inside three fire stations. Diesel exhaust pollution occurred when equipment was operated inside the fire stations and exhaust emissions contaminated fire station crew living quarters. Personal and area samples were collected only while the firemen were within the fire stations to determine elemental carbon concentrations, and general area samples were collected for other diesel pollutants, including CO and benzene solubles.

The arithmetic mean elemental carbon concentration for 18 personal exposure samples collected inside the three fire stations was 30 µg/m³. This mean was corrected for the average ambient elemental carbon concentration of 10 µg/m³ measured outside the fire stations; the corrected range of concentration was 6 to 70 µg/m³. In general, area samples

Table 6. Diesel Particulate Matter Reductions in Mine Air Achieved Through the Use of a Disposable Diesel Exhaust Filter: Diesel Particulate Matter Measurements Made Using a Personal Diesel Exhaust Aerosol Sampler^a

Sample Site	Concentration With Filter ^b (mg/m ³)	Correction Factor	Concentration Without Filter ^b (mg/m ³)	Correction Factor	Reduction Percent ^c
Intake	0.06 (0.02)	1.00	0.06 (0.02)	1.16	NA ^d
Haulage	0.12 (0.02)	0.90	0.50 (0.02)	1.63	94 (6)
Return	0.09 (0.03)	0.89	0.80 (0.03)	1.63	98 (4)
Shuttle car	0.17 (0.05)	0.84	0.81 (0.03)	1.63	93 (7)
Foreman	0.13 (0.02)	1.01	0.48 (0.02)	1.63	90 (8)
Personnel	0.09 (0.02)	0.67	0.46 (0.02)	1.63	100 (5)

^a Data are from Ambs and associates (1991).^b Mean (SD).^c Corrected for intake concentration, ventilation, and production changes.^d NA = not applicable.

analyzed for elemental carbon had higher concentrations. Concentrations ranged from less than background levels to more than $680 \mu\text{g}/\text{m}^3$ in the apparatus bays. Area samples revealed CO concentrations less than applicable standards, and the data for benzene-extractable material are difficult to interpret due to the possible presence of nondiesel sources of organic carbonaceous aerosols such as cigarette smoke.

TRUCK DRIVERS

The National Institute for Occupational Safety and Health (1989) conducted an industrial hygiene survey of the trucking industry. It was found that gas-phase surrogates of diesel exhaust exposure such as CO, CO₂, SO₂, NO₂, sulfuric acid (H₂SO₄), NO_x, HCHO, and volatile hydrocarbons were all below established occupational exposure criteria. Levels of elemental carbon were found to constitute approximately 60% of the carbonaceous particulate fraction, with concentrations ranging between 33 and $94 \mu\text{g}/\text{m}^3$.

As part of a case-control mortality study of trucking industry workers, exposures to diesel particulate matter were measured among four exposed job groups: highway drivers, local drivers, mechanics, and dockworkers using forklift trucks (Zaebst et al. 1991). The main purpose of the study was to estimate occupational exposures using submicrometer elemental carbon as a surrogate measure of diesel particulate matter. During the course of the field study, background aerosol samples were also collected in a residential area and near the highway and analyzed for submi-

crometer elemental carbon. Background levels ranged from 1 to $3 \mu\text{g}/\text{m}^3$ and included elemental carbon emitted from all sources.

Results of the field study are summarized in Table 8. The dockworkers and drivers were operating diesel vehicles, and the mechanics were exposed to diesel exhaust in the maintenance area. It is interesting to note that drivers of diesel trucks are exposed to levels of elemental carbon that are similar to background levels, suggesting that drivers' exposure comes from the highway environment rather than their vehicles' exhaust. This finding has interesting implications, should the epidemiological study show higher relative risks for exposed teamsters compared with nonexposed teamsters. The authors also provided additional data on exposure broken down by cold and hot weather.

RAILROAD WORKERS

As part of a series of epidemiological studies, Woskie and coworkers (1988) and Schenker and associates (1990) conducted a study to characterize railroad workers' exposure to diesel exhaust. Respirable particulate matter, adjusted to remove the contribution of cigarette smoke, was used as a surrogate measure of diesel particulate matter. Respirable dust samples were collected at four small railroads in the northern United States. Filters were preextracted with dichloromethane and preweighed. After sampling, filters were reweighed, pooled, and extracted to determine the contribution of cigarette smoke as determined by nicotine content. Based on these findings, an adjusted respirable particle exposure was determined and used as a measure of diesel particulate matter. Table 9 summarizes the personal

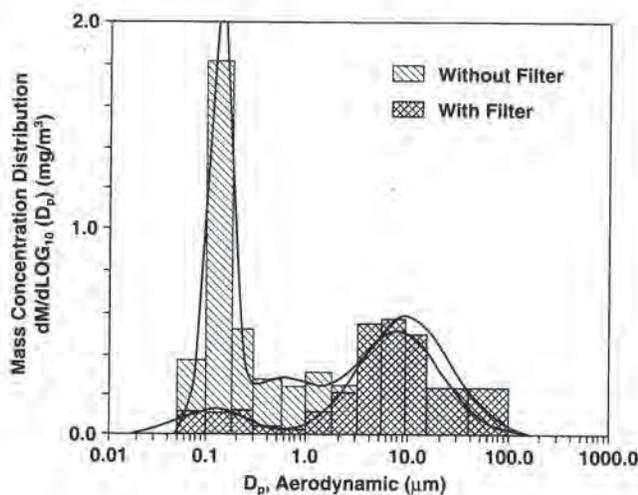


Figure 2. Mine aerosol size distributions measured with and without the disposable diesel exhaust filter in place using the micro-orifice uniform-deposit impactor; $dM/d\text{LOG}_{10}(D_p)$ = change in mass/change in \log_{10} particle diameter; D_p = particle aerodynamic diameter. (Reprinted from Ambs et al. 1991.)

Table 7. Personal Elemental and Organic Carbon Concentrations from a National Institute for Occupational Safety and Health Survey of Dockworkers Using Diesel Forklift Trucks^a

Dock	Form of Carbon	Geometric Mean	95% Confidence Interval
Unfiltered Exhaust ($\mu\text{g}/\text{m}^3$)			
1	Elemental	23.2	18.6 to 29.1
1	Organic	49.4	37.9 to 64.3
2	Elemental	54.6	46.1 to 64.7
2	Organic	138	95.6 to 200
Filtered Exhaust ($\mu\text{g}/\text{m}^3$)			
1	Elemental	1.9 ^b	1.5 to 2.3
1	Organic	47.9	36.8 to 62.3

^a Data are from National Institute for Occupational Safety and Health (1990).

^b 92% reduction.

exposure results. Although the respirable particulate matter concentrations in Table 9 are adjusted for the presence of tobacco smoke, they do not take into account the possible presence of other respirable dusts such as sand, dirt, and fibers.

Another part of this study, reported by Hammond and associates (1993), used high-volume samplers at fixed locations within four locomotive repair shops to determine the concentrations of total dust, respirable dust, soluble organic components, and vapor-phase components. The geometric mean respirable dust concentration was $96 \mu\text{g}/\text{m}^3$, with a geometric standard deviation of $2.14 \mu\text{g}/\text{m}^3$ for 23 samples. The geometric mean total dust concentration was $164 \mu\text{g}/\text{m}^3$, with a geometric standard deviation of $1.86 \mu\text{g}/\text{m}^3$ for 26 samples. The geometric mean for vapor-phase components was $432 \mu\text{g}/\text{m}^3$ for nine samples. Approximately 30% to 40% of the particle mass was extractable in dichloromethane, and the extracts were mutagenic, mostly in the polar fraction. The mutagenic activity was about one order of magnitude greater than the mutagenic activity in urban air. None of the vapor-phase material contained mutagenic activity. This study further characterized the air quality in railroad shops but provides no direct information on diesel particulate matter exposure. Other sources of pollution may have contributed to the measured values. Like the studies of Woskie and associates (1988) and Schenker and associates (1990), this study did not determine the concentration of elemental carbon, the submicrometer portion of the respirable particulate matter, or the respirable combustible dust fraction, which are more direct measures of diesel particulate matter exposure.

In summary, occupational exposure studies of miners, forklift truck operators, truck drivers, and railroad workers have measured diesel particulate matter concentrations

Table 8. Elemental Carbon Concentrations from a Survey of Trucking Industry Workers^a

Job Group	Elemental Carbon ($\mu\text{g}/\text{m}^3$)	
	Geometric Mean	95% Confidence Interval
Dockworkers	27.2	23.8, 31.0
Mechanics	12.1	10.0, 14.7
Local drivers	4.0	3.2, 5.0
Road drivers	3.8	3.1, 4.7
Highway—background	2.5	1.7, 3.6
Residential—background	1.1	0.7, 1.5

^a Data are from Zaebs and associates (1991).

using different sampling and analytical methods. These studies reported mean diesel particulate matter concentrations ranging from 0.004 to $1.74 \mu\text{g}/\text{m}^3$. When measured, the concentrations of other pollutants were below regulated levels.

SUMMARY

Diesel exhaust is chemically complex, containing literally hundreds of different substances. This complexity makes it impossible to monitor all exhaust pollutants to determine exposure. Exposure assessments generally monitor regulated pollutants or select a surrogate measure, or measures, of exposure. The surrogate measure should be representative of diesel exhaust as a whole, have some relationship to adverse health effects, and, if possible, be unique to diesel exhaust. Unfortunately, many of the compounds found in diesel exhaust are also emitted from other combustion sources.

A limited number of exhaust constituents have permissible exposure limits. These include the gases CO, CO₂, NO, NO₂, SO₂, HCHO, and some PAHs. Canada has recommended a limit for respirable combustible dust of $1.5 \text{ mg}/\text{m}^3$ in noncoal

Table 9. Personal Exposures of Railroad Employees to Respirable Particulate Matter Other Than Cigarette Smoke^a

Job Group	Respirable Particles ($\mu\text{g}/\text{m}^3$)		Exposure Group ^b
	Geometric Mean	Geometric SD	
Clerks	17	7.2	U
Signal maintainers	49	1.9	L
Engineer/firer			
Freight	73	2.3	M
Yard	49	2.4	M
Passenger	39	2.2	M
Braker/conductor			
Freight conductor	52	2.2	M
Freight braker	88	1.8	M
Passenger	85	2.1	M
Yard	92	2.0	M
Hostler	191	1.9	M
Electrician	134	2.2	H
Machinist	114	2.3	H
Supervisor, other	130	1.9	H

^a Data are from Woskie and associates (1988).

^b A priori exposure category: U = unexposed, L = low exposure, M = medium exposure, H = high exposure.

mines. Germany has established technical exposure limits of 0.6 mg/m^3 for the total carbon content in fine dust particulate matter in underground noncoal mines and underground construction sites and technical exposure limits of 0.2 mg/m^3 for other occupational environments. The United States has no permissible exposure limit for diesel particulate matter at this time.

Diesel particulate matter is formed during combustion; as a result, the aerosol is small in size, with a mass median aerodynamic diameter of $0.2 \text{ }\mu\text{m}$. Diesel particulate matter is composed of organic and elemental carbon, adsorbed and condensed hydrocarbons, and sulfate. The proportion of organic carbon to inorganic carbon varies depending on such factors as fuel, engine type, duty cycle, engine maintenance, operator habits, use of emission control devices, and lube oil consumption. In general, nonextractable elemental carbon accounts for a greater fraction of diesel particulate matter mass than extractable organic compounds.

The difference in aerodynamic diameter particle sizes between combustion and mechanically generated aerosols is used to separate diesel aerosol from noncombustion aerosols by inertial impaction. Submicrometer diesel particulate matter is collected on a filter downstream from the impaction substrate. Gravimetric analysis determines the mass fraction in each size range. Also, other methods can be used to analyze the filter containing the submicrometer material to increase the sensitivity and specificity for diesel particulate matter. This is an advantage over other aerosol measurement techniques, which either do not collect a sample or destroy the sample during analysis. However, size-selective sampling collects all diesel particulate matter meeting specific aerosol sampling criteria and may not be representative of the amount of diesel particulate matter deposited in the airways. Reliance on measurements of total diesel particulate matter as indicators of exposure may overestimate the actual deposited dose of diesel particulate matter in lung tissue and lead to inaccurate health effects assessments.

Recent occupational exposure studies have measured diesel particulate matter concentrations in the workplace. The most frequently used methods for assessing diesel particulate matter exposure include respirable dust sampling followed by gravimetric analysis of the combustible and noncombustible fractions, size-selective sampling for particulate matter less than $0.8 \text{ }\mu\text{m}$ in size followed by gravimetric analysis, and size-selective sampling followed by elemental carbon analysis. These studies have found mean diesel particulate matter levels to range between 0.004 and 1.74 mg/m^3 . Occupational exposures are highest

in confined spaces, such as mines, where heavy diesel equipment is used and fresh air is supplied by forced ventilation. In general, workplace exposure to diesel particulate matter is several orders of magnitude higher than the outdoor ambient exposures reported in the background paper by Cass and Gray.

At present, the best surrogate measure of diesel particulate matter in the occupational environment appears to be elemental carbon. Elemental carbon generally accounts for about 40% to 60% of diesel particulate matter mass and is detectable at relatively low levels using size-selective sampling and thermal-optical analysis. Elemental carbon is detectable apart from the organic carbon found in cigarette smoke and diesel exhaust. Additionally, data summarized in the background paper by Busby and Newberne suggest that carbon particles can cause cancer in laboratory rats. As noted earlier, the percentage of elemental carbon in total diesel particulate matter fluctuates. The fluctuation in the ratio of elemental carbon to organic carbon can cause an inaccurate estimate of the total diesel particulate matter present. The estimate increases in accuracy if both organic and elemental carbon are measured and an adjustment is made for the presence of nondiesel carbon sources. Consideration should also be given to the measurement of a few specific PAHs that are known carcinogens. Unfortunately, these compounds are typically found at very low levels and are not unique to diesel exhaust.

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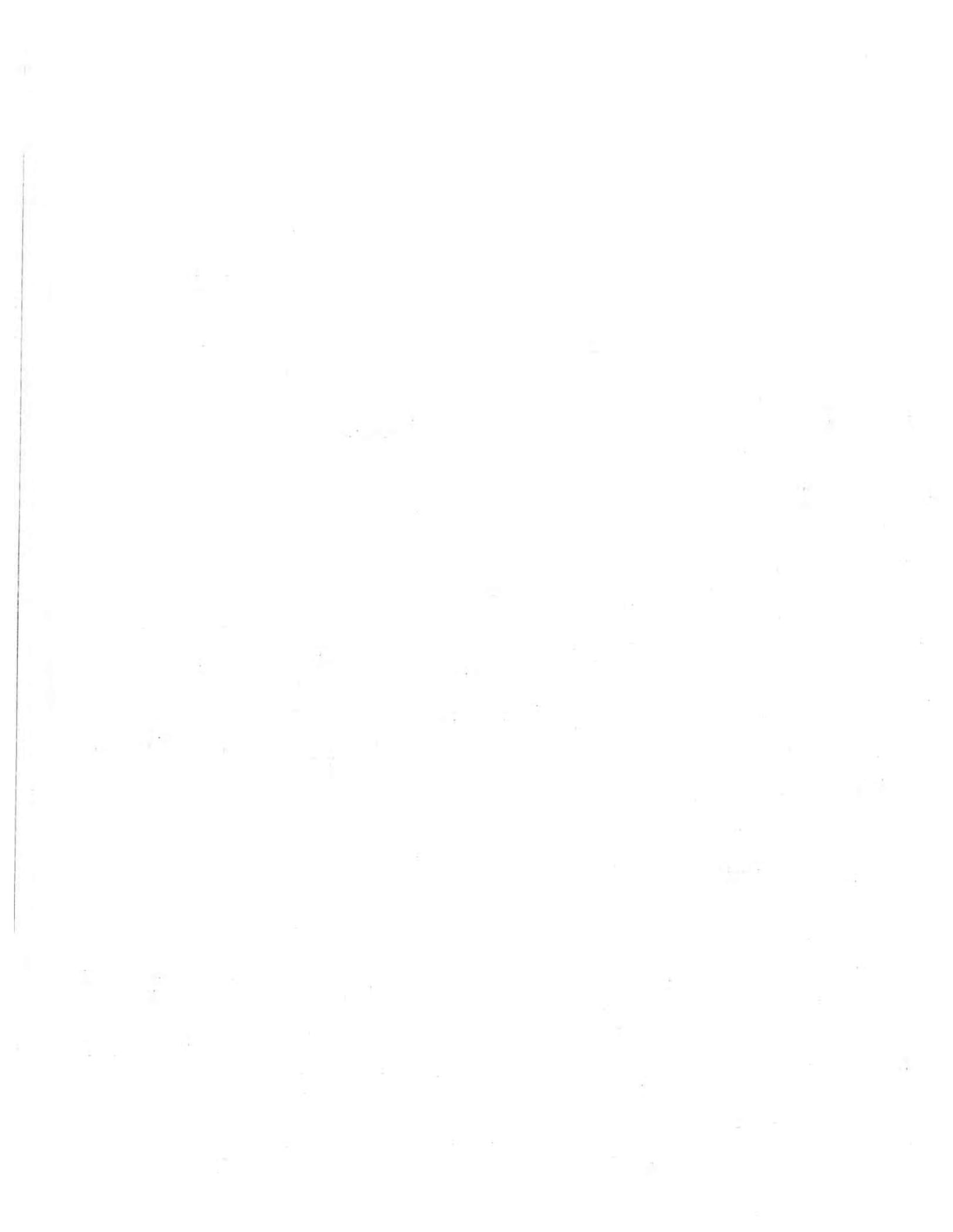
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ABBREVIATIONS

CO	carbon monoxide
CO ₂	carbon dioxide
HCHO	formaldehyde
H ₂ SO ₄	sulfuric acid
NO	nitric oxide
NO ₂	nitrogen dioxide
NO _x	oxides of nitrogen
PAH	polycyclic aromatic hydrocarbon
SD	standard deviation
SO ₂	sulfur dioxide
TLV	threshold limit value



Regional Emissions and Atmospheric Concentrations of Diesel Engine Particulate Matter: Los Angeles as a Case Study

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INTRODUCTION

Since the early 1980s, a study of source contributions to atmospheric carbon particle concentrations has been under way in the Los Angeles area. Data on the particulate emissions from each of the major source types that emit carbon particles have been matched to atmospheric transport models in order to define the partial contribution of each of the major sources to ambient particle concentrations at community air monitoring sites. From this work, a case study of the effect of diesel engine exhaust on ambient air quality can be extracted. The estimates of ambient diesel exhaust particulate matter concentrations derived from the air quality model, when combined with other health data, may be useful in estimating the effects of exposure to diesel exhaust in a large metropolitan area.

This background paper begins with an overview of carbon particle emissions to the Los Angeles air basin from all sources acting together. It indicates that diesel engine exhaust is the dominant source of elemental carbon particle emissions in the Los Angeles area. More than just diesel trucks are involved, however; diesel engines are used in many other applications in a large city. The realization that elemental carbon particles can be a useful surrogate for diesel exhaust in some cases then is used to motivate a review of elemental and organic carbon particle concentrations in the atmosphere. Next, air quality models that can compute the effect of emission sources on atmospheric carbon particle concentrations are described. The case study then applies air quality models to the Los Angeles emissions and air quality database to quantitatively estimate the spatial distribution of diesel exhaust particle concentrations in Los Angeles in the mid-1980s.

REGIONAL PARTICULATE MATTER EMISSIONS FROM DIESEL ENGINES IN SOUTHERN CALIFORNIA

Airborne particles containing various proportions of organic carbon and elemental carbon are emitted from more than 70 different types of air pollution sources, including diesel engines, gasoline-powered motor vehicles, stationary source oil- and gas-fired boilers, wood-burning fireplaces, and food-cooking operations. The diesel engine category alone includes the operation of diesel-powered heavy-duty trucks, as well as many less-obvious diesel engine applications, such as light-duty diesel autos and trucks, diesel-powered construction equipment, diesel railroad locomotives, diesel-powered ships, and stationary diesel engines used in industry.

To assess the relative magnitude of the various sources, comprehensive procedures for performing an inventory of carbon particle emissions to the atmosphere were developed by Cass and coworkers (1982) and later were updated by Gray (1986). In both studies, examples were given using the emissions situation in the Los Angeles area. First, the universe of possible contributing sources was identified. Then, fuel consumption or the level of activity (e.g., production rate) of each source type was documented. Fuel use or activity levels were used to compute total particulate matter emissions from each source type over two geographic areas: (1) the South Coast Air Basin shown in Figure 1, and (2) the smaller 80 × 80 km area shown in the center of Figure 1 that contains the core of the metropolitan Los Angeles urban area (83% of the air basin population). Next, the total particulate matter emissions were divided to separately account for the emissions of respirable fine particles (i.e., particles with a diameter smaller than 2 μm). Finally, the fine particle emissions were subdivided chemically to create separate inventories for fine particle total carbon emissions and fine particle elemental (black) carbon emissions (total carbon equals organic carbon plus elemental carbon). The results of this emissions survey that are relevant to diesel engine exhaust are summarized in Table 1 and in Figure 2.

A brief discussion of the origin of certain key pieces of the emissions inventory presented in Table 1 is instructive. Heavy-duty diesel trucks were the largest source of emissions from diesel engines in 1982 in Los Angeles. The particulate matter emissions (± standard deviation) from heavy-duty diesel trucks in that year were estimated to be 865 ± 161 mg/km based on measurements made in a highway tunnel by Pierson and Brachaczek (Table 2, 1983). Baines and coworkers (1979) reported a Los Angeles diesel particulate matter emission factor substantially identical to this value. Ninety-three percent of these particulate matter emissions were estimated to occur in fine particle sizes smaller than 2 μm in diameter. The emissions of fine particles from diesel engines in 1982 were estimated to consist of 83.7% carbon by mass; much of the remaining mass consists of hydrogen, some oxygen and nitrogen associated with organic compounds, and sulfate derived from sulfur in the fuel. That percentage of total carbon emitted is consistent with the average of nine source tests performed on light-duty diesels by Japar and coworkers (Table I, 1984; federal test procedure runs only, with carbon determination by the thermal-optical method of Johnson and associates 1981). It is also in excellent agreement with the results of Pierson and Brachaczek (1983) for the 1977 Tuscarora Tunnel experiment, which yielded 83.8% carbon in the particu-

late emissions from heavy-duty diesel trucks on the highway. The organic carbon:elemental carbon ratio (23.4:76.6) used here to represent diesel exhaust in 1982 matches that of Japar and coworkers (1984) for light-duty vehicles and is at the same time in excellent agreement with the results of Pierson and Brachaczek (1983) for heavy-duty diesel trucks on the highway (29:71) and also is close to the results reported by Johnson and associates (1981) (27:73).

In more recent years, emissions control procedures applied to new diesel trucks have succeeded in reducing particle emissions substantially below those appropriate to the 1982 period studied here. For example, dynamometer tests of two new 1986 model diesel trucks reported by Hildemann and associates (1991) show fine particle emission rates (\pm standard deviation) of only 408 ± 68 mg/km containing 73.1% carbon by mass, with an organic carbon:elemental carbon ratio of 45:55. Obviously, as newer diesel trucks are phased into the vehicle fleet the aerosol carbon emissions from diesel trucks will decline substantially.

Table 1 shows that diesel engines contributed only approximately 3% of the total particle mass emitted to the Los Angeles area atmosphere in 1982. At that time, most of the particulate matter in the atmosphere was emitted by fugitive sources, including emissions of paved-road dust. By focusing, however, on the emissions of easily respirable

particles smaller than $2 \mu\text{m}$ in diameter, diesel exhaust aerosol is identified as having greater importance, accounting for 7% of the mass of fine aerosol emissions.

Further subdivision of the fine particle emissions to identify carbonaceous particle emissions is relevant because sources of organic aerosol emissions may be linked to possible health effects via their polycyclic aromatic hydrocarbon content. Additionally, black elemental carbon particles absorb light and can contribute disproportionately to visibility reduction. Table 1 shows that more than 20% of the fine aerosol carbon particles in the Los Angeles area are emitted from diesel engines. Although diesel engines account for only about 6% of fuel use in the Los Angeles area, they contribute two-thirds of the elemental carbon particle emissions. These data are shown for the air basin as a whole in Table 1 and in Figure 2 for the 80×80 km heavily urbanized area shown in the center of Figure 1.

As a convenient generalization, the great majority of elemental carbon particles in the Los Angeles atmosphere is attributable to diesel engine exhaust. Therefore measurements and air quality modeling studies directed at understanding elemental carbon particle emissions and air quality relationships in this urban area can confirm that the effects of diesel exhaust on ambient air quality are understood properly.

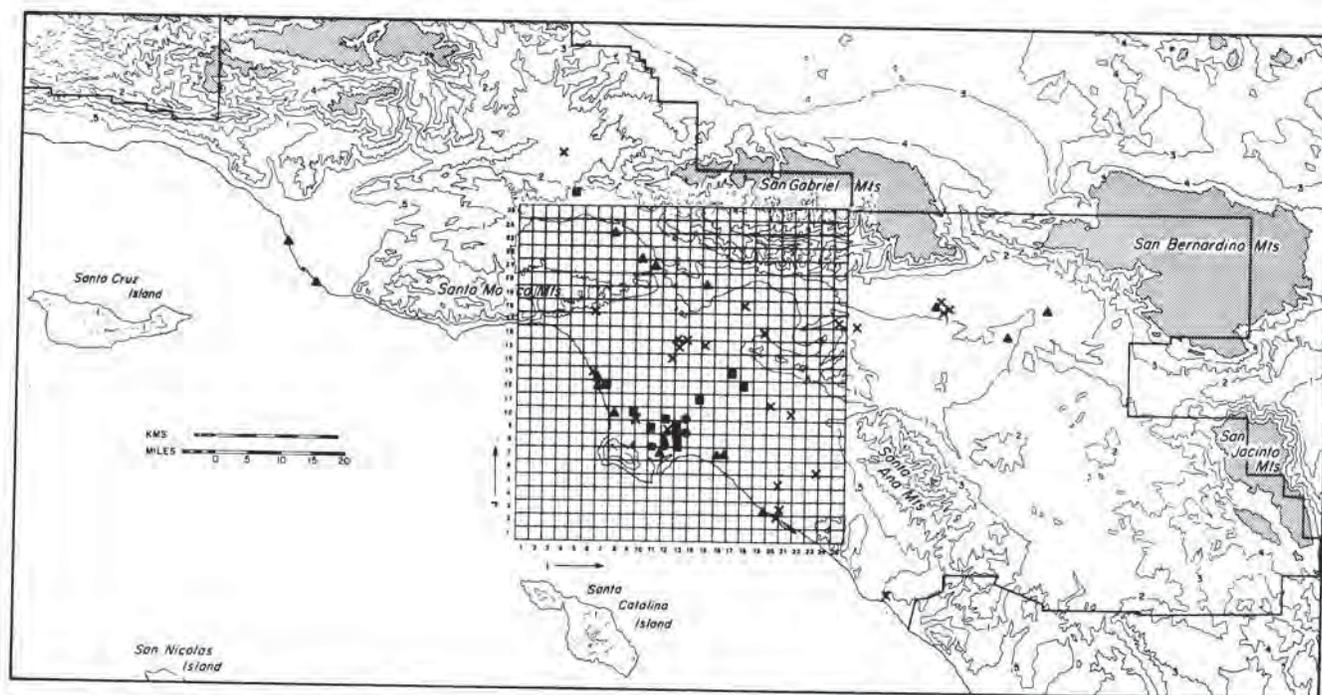


Figure 1. Map of the South Coast Air Basin of California, showing an 80×80 -km area that encompasses the most heavily urbanized portion of the area.

Table 1. Fuel Use and Particulate Matter Emissions Within the Entire South Coast Air Basin of California for 1982^a

Source Type	Estimated 1982 Fuel Use (10 ⁹ BTU/day)	Total Particulate Emissions (kg/day)	Fine Particulate Emissions (kg/day)	Fine Total Carbon (kg/day)	Fine Elemental Carbon (kg/day)
Diesel highway vehicles					
Diesel autos	16.3	1,399	1,301	1,089	834
Diesel light trucks	3.0	191	178	149	114
Heavy diesel vehicles	172.2	9,511	8,846	7,404	5,672
Off-highway diesels					
Diesel ships	6.3	310	288	241	185
Railroad diesels	22.4	1,836	1,707	1,429	1,095
Other off-highway vehicles	39.0	3,065	2,850	2,385	1,827
Diesel industrial engines	7.0	769	715	29	29
Diesel subtotal	266	17,081	15,885	12,726	9,756
Other fuel combustion					
Gasoline engines	1,343	22,191	9,207	6,283	1,523
Jet fuel	49	434	434	417	320
Distillate oil	49	1,110	1,070	161	93
Residual oil	167	3,075	2,570	396	104
Natural gas	1,956	11,070	10,185	1,031	251
Refinery gas	334	3,030	2,788	195	0
Liquified petroleum gas	28	161	146	16	5
Digester gas	7	123	122	25	6
Coke oven gas	38	284	261	18	0
Coal	0.5	193	120	115	25
Other fuels subtotal	3,972	41,671	26,903	8,657	2,327
Industrial processes	— ^b	36,969	25,435	8,488	600
Fugitive sources^c	—	507,778^d	164,086	29,600	2,314
Total	4,238	603,499	232,309	59,471	14,997

^a Data are summarized from Appendix C of the study by Gray (1986).

^b Dash indicates that data were not available.

^c Fugitive sources include construction dust, road dust, tire dust, brake wear dust, forest fires, structural fires, and cigarettes, as well as food cooking and other diverse activities in the community.

^d In the case of fugitive sources, the emissions stated are for particle sizes less than 10 μm ; although all other values in this column are for total suspended particulate matter, emissions from the combustion sources cited typically occur in particle sizes less than 10 μm .

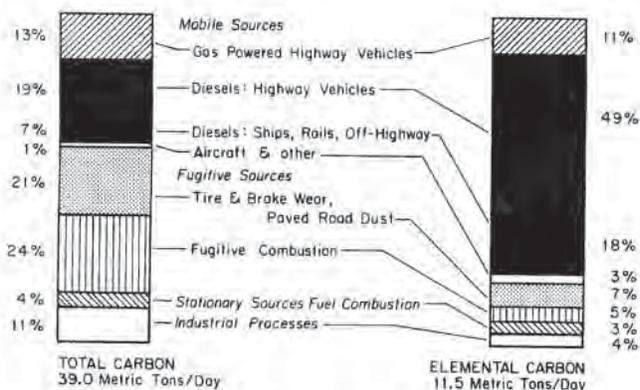
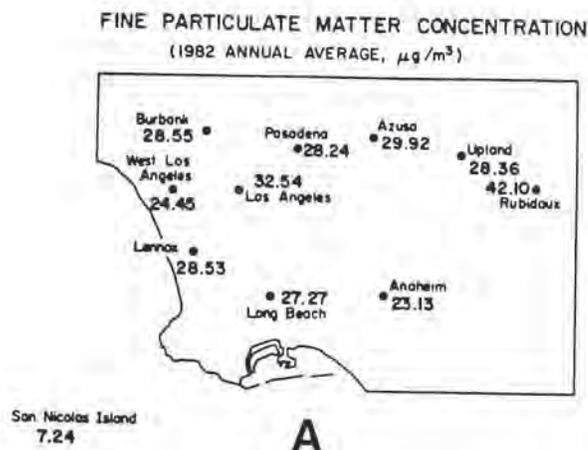


Figure 2. Sources of fine aerosol carbon emissions in the 80- x 80-km heavily urbanized portion of the South Coast Air Basin of California in 1982.

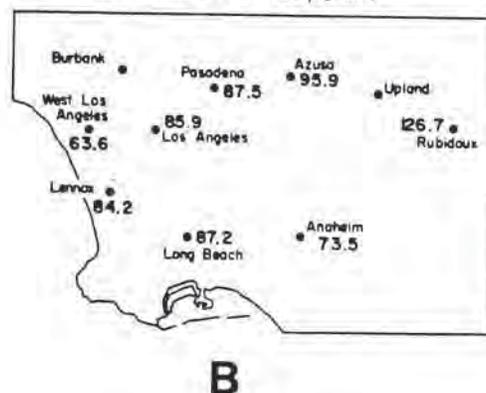
CARBON PARTICLE CONCENTRATIONS IN THE LOS ANGELES ATMOSPHERE

Two air monitoring experiments have been conducted to establish baseline carbon particle concentration data in southern California. In the first study, Gray and coworkers (1986) established a network of 10 sites for monitoring ambient fine particles throughout the Greater Los Angeles area at locations shown in Figure 3. The sites chosen were the same as the local air pollution control district air monitoring stations to allow comparison of fine particle data with total suspended particulate matter concentrations. A background air monitoring site was placed on San Nicolas Island to measure the particle concentrations present in air entering the city from upwind over the ocean. During 1982, 24-hour average fine particle (diameter less than 2.1 μm) samples were collected using low-volume filters located downstream of cyclone separators at six-day intervals, and a complete material balance on the chemical composition of the fine aerosol at each air monitoring site was constructed.

As shown in Figure 3B, the annual average total suspended particulate matter concentrations in the Los Angeles area in 1982 ranged from a high of 127 $\mu\text{g}/\text{m}^3$ at Rubidoux, near Riverside, California, to a low of 63.6 $\mu\text{g}/\text{m}^3$ at West Los Angeles, near the coastline. Fine particle concentrations averaged approximately one-third of the total suspended particulate matter mass concentration at all sites. The highest fine particle concentrations (Figure 3A) were observed at downtown Los Angeles (32.5 $\mu\text{g}/\text{m}^3$ annual mean) and at Rubidoux (42.1 $\mu\text{g}/\text{m}^3$). By comparison, the fine particle mass concentration upwind of the city at San Nicolas Island was much lower at only 7.2 $\mu\text{g}/\text{m}^3$ (Figure 3A), confirming that most of the local fine particle loading in the Los Angeles atmosphere was due to local pollutant emissions.



TOTAL SUSPENDED PARTICULATE CONCENTRATION (1982 ANNUAL AVERAGE, $\mu\text{g}/\text{m}^3$)



FINE AEROSOL MASS/TOTAL SUSPENDED PARTICULATE (1982 MEAN)

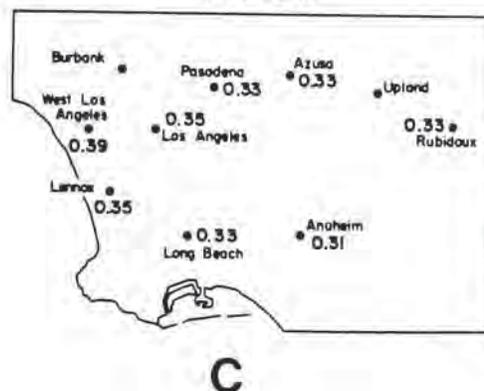


Figure 3. Comparison of annual average fine particulate matter concentrations and total suspended particulate matter concentrations at air monitoring sites in the Greater Los Angeles area in 1982. (Reprinted with permission from Gray et al. 1986.)

A material balance on the chemical composition of the fine particle concentrations is shown in Figure 4. At most of the on-land air monitoring sites in the western portion of the air basin, about 40% of the fine particulate matter mass concentration in 1982 consisted of carbonaceous particles. Approximately one-third of that aerosol carbon was in the form of elemental carbon particles, with the remaining two-thirds consisting of organic compounds. The absolute magnitude of the annual average fine particle total carbon, organic carbon, and elemental carbon concentrations is shown in Figure 5. Elemental carbon particle concentrations averaged about $5 \mu\text{g}/\text{m}^3$ at downtown Los Angeles and at Burbank in 1982, near the center of the urban area, falling to about $3 \mu\text{g}/\text{m}^3$ as one moved away from the areas of heaviest population and traffic density. In contrast, at San Nicolas Island, elemental carbon particle concentrations averaged less than $0.3 \mu\text{g}/\text{m}^3$, showing that soot concentrations in Los Angeles were almost entirely due to local emissions sources.

The seasonal variation in carbon particle concentrations and air quality also can be examined using this data set. In Figure 6, the monthly average total carbon concentration in fine particles is shown at Lennox and Upland, California. At most of the monitoring sites in the western portion of the air basin, such as Lennox, a pronounced seasonal variation in total carbon particle and in elemental carbon particle concentrations was recorded, with high values in the winter months and lower values in the summer. The seasonal variations reported are due to meteorological conditions, rather than to changes in emission rates. In the winter months, because overnight and early morning mixing depths in the atmosphere are very low, pollutants that are directly emitted from ground level sources (e.g., motor vehicle exhaust) are concentrated. Also, resultant wind velocities in the

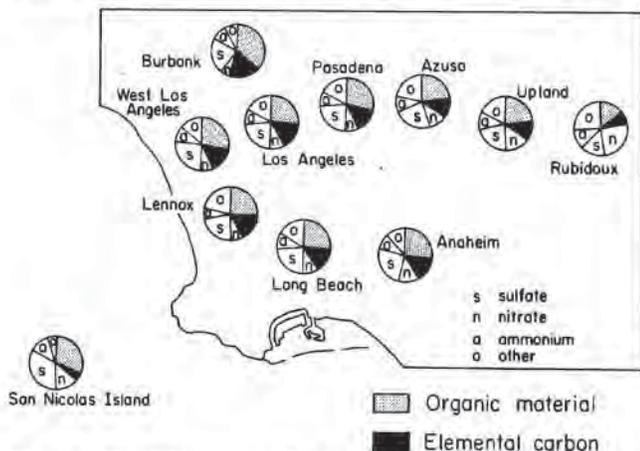


Figure 4. Material balance on the chemical composition of annual mean fine particle concentrations in the Greater Los Angeles area in 1982. (Reprinted with permission from Gray et al. 1986.)

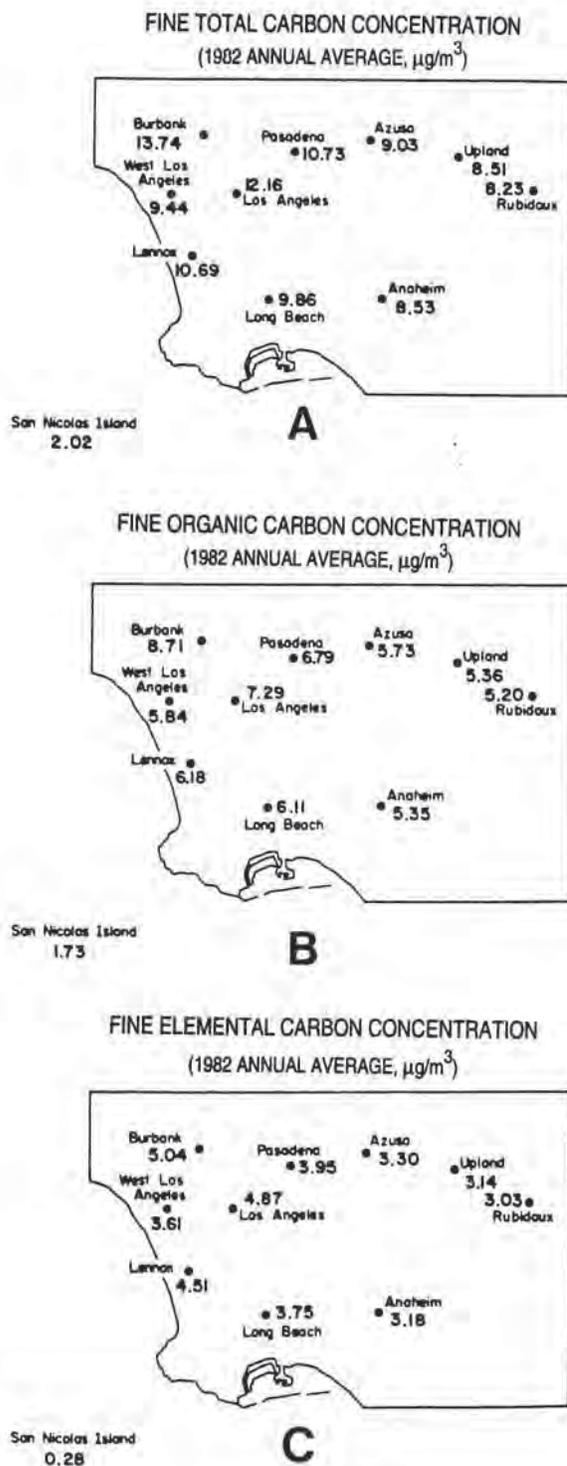


Figure 5. Annual average fine carbonaceous particulate matter concentrations ($\mu\text{g}/\text{m}^3$) in the Greater Los Angeles area. (Reprinted with permission from Gray et al. 1986.)

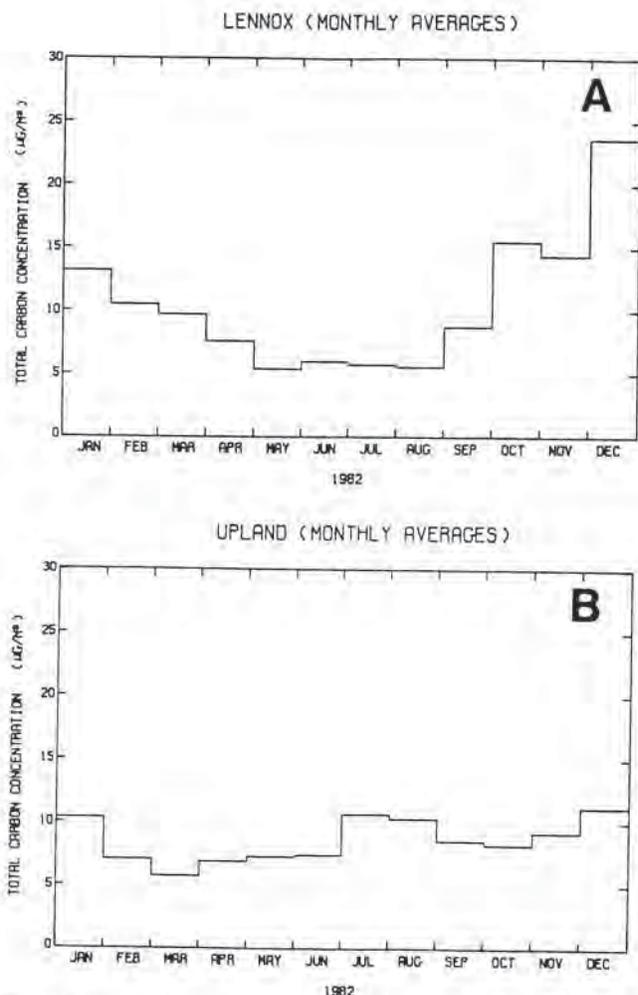


Figure 6. Monthly average fine particle total carbon concentrations. (top) at Lennox and (bottom) at Upland, California.

winter are lower than in the summer, and in some months the net transport direction is toward the ocean from the land. Thus locations such as Lennox, California, are downwind of central Los Angeles in some winter months and experience a resultant increase in the concentration of those particles that are emitted directly from local sources. In summer, the wind direction reverses and relatively cleaner ocean air prevails at sites such as Lennox for a greater part of the day; also, wind speeds and mixing depths increase, resulting in a summertime minimum in carbon particle concentrations at coastal sites.

In contrast, carbon particle concentrations at sites in the eastern portion of the Los Angeles basin, such as Upland, are more nearly constant over the course of the year. This is the case because during periods of adverse mixing in winter, Upland is located upwind of the high-traffic areas in central Los Angeles and thus avoids the transport of

highly concentrated elemental carbon particles. In summer, the increase in wind speeds and mixing depths would be expected to reduce primary pollutant concentrations at Upland (as experienced at Lennox); however, the prevailing wind direction shifts, placing Upland downwind of the major source area in central Los Angeles. As a result, elemental carbon particle concentrations do not fall in the summer at Upland, as they do at Lennox. Thus seasonal changes in dilution and transport direction act to smooth out seasonal concentration changes at Upland, whereas they reinforce wintertime peak concentrations at Lennox.

After establishing a baseline fine particle concentration and elemental carbon particle concentration for 1982, a method was sought for estimating atmospheric elemental carbon particle concentrations historically. Such estimates would permit assessment of the outdoor concentrations of black soot encountered by many Los Angeles area residents over a lifetime, which (as indicated in Figure 2) are closely linked, at least during the 1980s, to diesel engine exhaust in this air basin.

From 1958 to 1981, the Los Angeles Air Pollution Control District operated custom-designed tape samplers that measured the blackness of particulate matter deposits on white filter paper at hourly intervals at monitoring sites throughout the Los Angeles area, as shown in Figure 7. By sampling in parallel with these tape samplers before the network was terminated in the early 1980s, it was shown that the blackness of the particle deposits could be translated into quantitative measurements of black elemental carbon particle concentrations dating back to the late 1950s (Cass et al. 1984). The long-term average elemental carbon particle concentrations noted in Figure 7 are in the range of 4.5 to

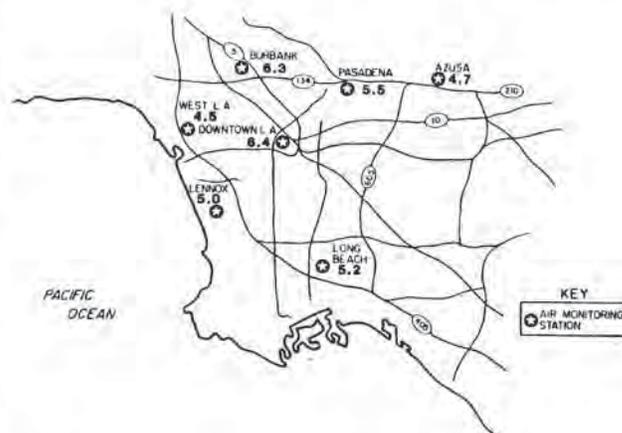


Figure 7. Average elemental carbon concentrations ($\mu\text{g}/\text{m}^3$) estimated from historical tape sampler data in the Los Angeles basin from 1958 to 1981.

6.4 $\mu\text{g}/\text{m}^3$, about 1 $\mu\text{g}/\text{m}^3$ higher than averages measured directly during 1982. Because hourly tape sampler data are available for much of this monitoring period, seasonal and longer term temporal variations in historical exposures can be examined. In Figure 8, those data have been passed through a digital filter to smooth out the fluctuations in the 24-hour average elemental carbon particle concentrations determined from the tape sampler data, thereby revealing seasonal trends. Figure 8 shows that elemental carbon particle concentrations peak routinely during the winter in the western portion of the air basin, as was found during the 1982 field experiments. Concentration fluctuations at Azusa, the easternmost site, were less pronounced, as was observed at Upland. The data also indicate that a slow but steady reduction in elemental carbon particle concentra-

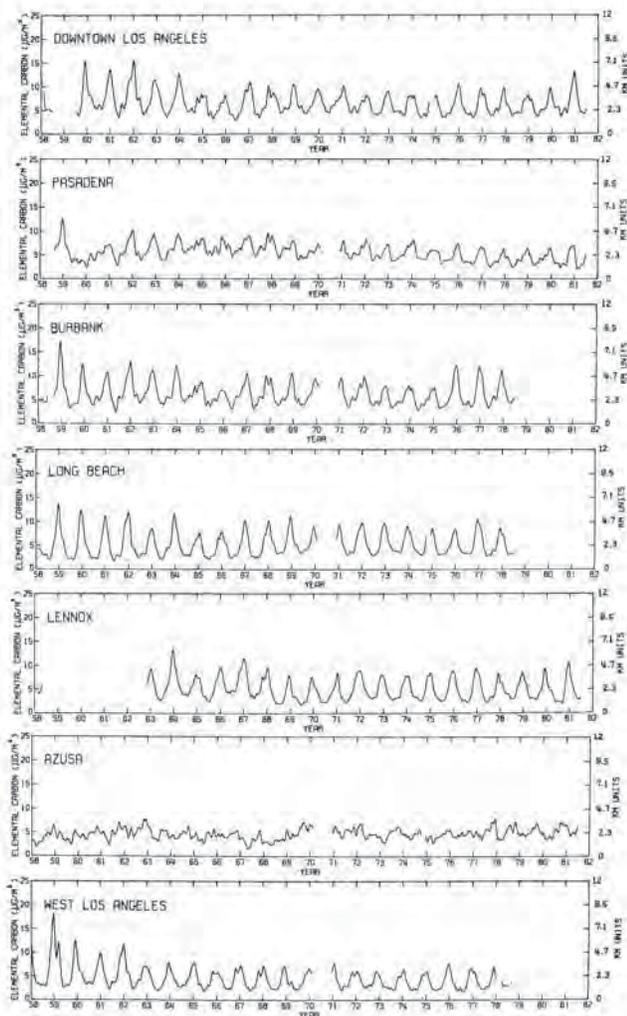


Figure 8. Trends in the elemental carbon particle concentrations in Figure 7. (Reprinted with permission from Cass et al. 1984.)

tions has occurred in such locations as downtown Los Angeles, west Los Angeles, Burbank, and Pasadena. In contrast, the Azusa site, which is located in a portion of the air basin that became increasingly urbanized during this period, experienced an upward trend.

DIESEL EXHAUST CONTRIBUTIONS TO ATMOSPHERIC PARTICULATE MATTER CONCENTRATIONS

An air quality modeling study was conducted by Gray (1986) to determine source contributions to atmospheric carbon particle concentrations in the Los Angeles area. From that study, diesel engine exhaust particles can be identified separately, allowing human exposures to diesel exhaust particles to be gauged.

In order for this assessment to be conducted, a Lagrangian particle-in-cell air quality model was developed in which the emissions from each source in the air basin were represented by a series of hypothetical mass points released from the source into a simulation of atmospheric fluid flow. Each mass point was labeled with the source type from which it originated, the mass of particulate matter released, and the chemical composition of the particulate matter from that source. These particles form a cloud of mass points downwind of each source that varies depending on meteorological conditions. By overlaying a grid system on the air basin map (e.g., see Figure 1) and counting the mass points contributed by a source that fall within the ground level atmospheric layer of each cell of the grid, the spatial distribution of the pollutant concentration due to the source of interest was calculated. Repeating this calculation for each source in the air basin yielded a multiple-source urban air quality model.

This air quality model was used to calculate source contributions to primary carbon particle concentrations in Los Angeles. The grid system shown in the center of Figure 1 was overlaid on a map of the stationary source locations and traffic densities in the Los Angeles area. Then emission rates from more than 70 different types of primary particle sources, including each of the diesel engine uses shown in Table 1, were determined within each cell of the grid. The effective height of emissions insertion into the atmosphere from each source was determined along with the diurnal variation and seasonal variation of the emissions from each source type.

These emissions data were applied to the air quality model along with a yearlong time series of the observed wind speed, wind direction, and mixing depths in the atmosphere. The air basin's average elemental carbon par-

ticle concentrations and primary fine particle total carbon concentrations were computed for each month of 1982. The model also tracked the fate of emissions from each source type separately. Air quality model predictions were later verified by comparing them with the measurements of elemental carbon particle concentrations made during the 1982 field experiments described earlier.

These air quality model predictions for fine particle elemental carbon concentrations are compared with observed values for Los Angeles and Long Beach, respectively, in Figures 9A and 10A. The horizontal line that forms a continuous step function displays the concentrations predicted by the air quality model directly from the emissions data; the small circles show the measured monthly mean elemental carbon particle concentration with its associated uncertainty ($\pm 2\sigma$). As shown, the air quality model results generally match the data from ambient concentration observations. The analytical precision of a single ambient measure-

ment of elemental carbon particle concentration and total carbon particle concentration is only ± 0.31 and ± 0.64 $\mu\text{g}/\text{m}^3$, respectively. The principal contributor to the error bounds on the measured monthly means shown in Figures 9 and 10 arises not from experimental error but rather from the fact that concentration measurements were made at six-day intervals. During months with great day-to-day variability in pollutant concentrations, the fact that not all days were sampled adds to the uncertainty in pollutant concentrations.

Given that the air quality model worked well, it was interrogated to determine the ambient elemental carbon particle concentrations attributable to diesel engine sources. Figures 9B and 10B show that, not surprisingly, diesel engine emissions dominate elemental carbon particle concentrations in downtown Los Angeles and Long Beach. Highway diesel vehicles are the largest contributors, with diesel engines in railroad locomotives and off-highway

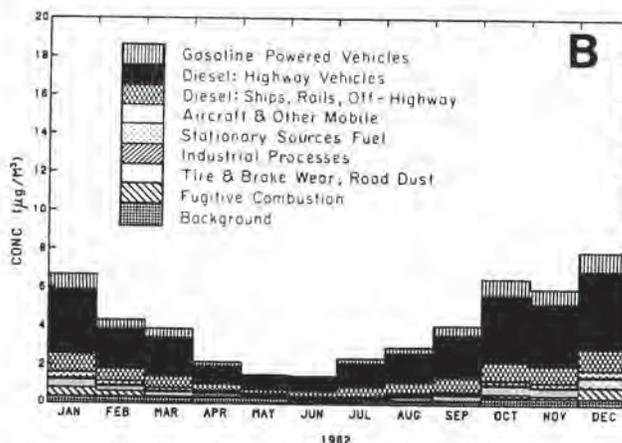
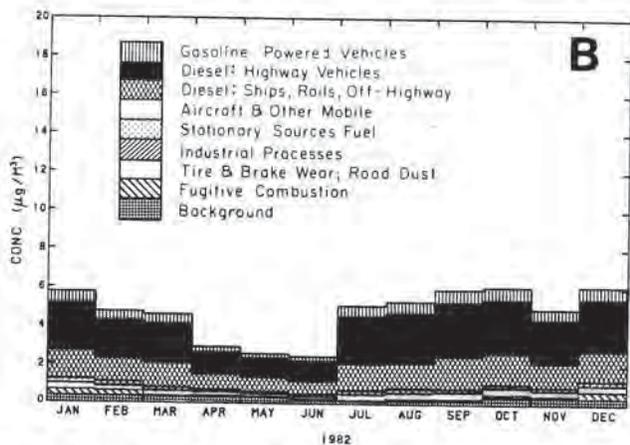
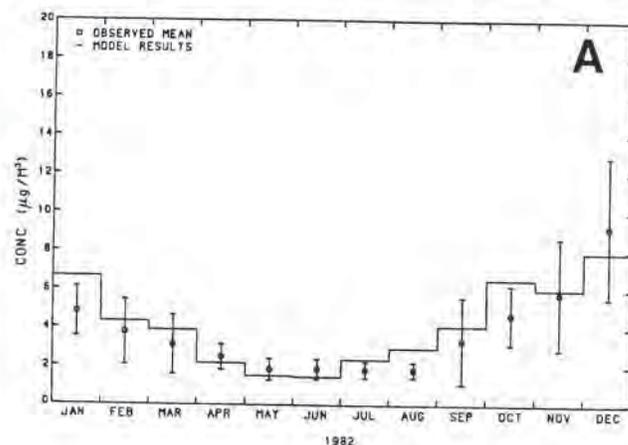
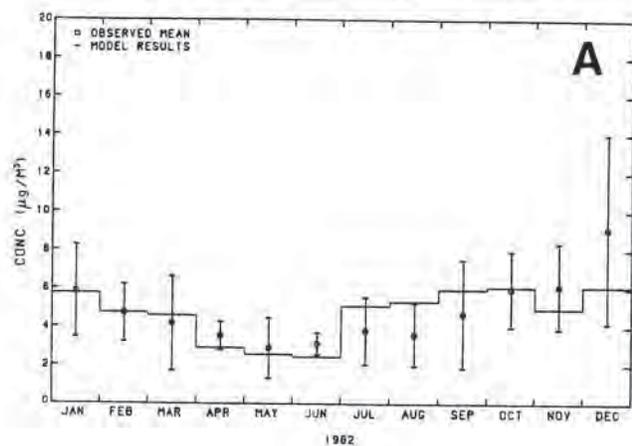


Figure 9. Air quality data for Los Angeles. A: Monthly mean elemental carbon concentrations—air quality model results versus observed values. B: Source class contributions to elemental carbon particle concentrations.

Figure 10. Air quality data for Long Beach. A: Monthly mean elemental carbon concentrations—air quality model results versus observed values. B: Source class contributions to elemental carbon concentrations.

vehicles (e.g., construction equipment) also making a significant contribution. As the figures show, total elemental carbon particle concentrations attributable to diesel engine exhaust in peak winter months averaged about $4 \mu\text{g}/\text{m}^3$ in downtown Los Angeles and about $5 \mu\text{g}/\text{m}^3$ in Long Beach. Summertime minimum elemental carbon particle concentrations attributable to diesel engines averaged about $2 \mu\text{g}/\text{m}^3$ in Los Angeles and about $1 \mu\text{g}/\text{m}^3$ in Long Beach.

The predictions of fine particle elemental carbon concentrations attributable to diesel engines shown in Figures 9 and 10 can be used to back-calculate the total diesel engine exhaust aerosol mass concentrations. Within the emission inventory of Table 1, diesel exhaust particles were represented as being 93% by mass below $2.1 \mu\text{m}$ in diameter in order to compute fine particle emissions from total emissions; 83.7% of fine particle mass was taken to be carbonaceous, and 76.6% of that fine aerosol carbon was taken to be black elemental carbon. Working backward, fine particle elemental carbon concentrations attributable to diesel engines predicted by the model should be multiplied by 1.68 to estimate the total mass concentrations of diesel exhaust particles in the atmosphere. On the basis of this calculation, a model prediction that the fine particle elemental carbon concentration attributable to diesel engines was $4 \mu\text{g}/\text{m}^3$ indicated that the total particulate matter concentration from diesel engines was $6.7 \mu\text{g}/\text{m}^3$.

The air quality model also can be used to examine the spatial distribution of diesel engine exhaust concentrations. In Figures 11 and 12, the fine particle total carbon concentrations attributable to on-highway heavy-duty diesel trucks predicted by the model are mapped spatially over the area overlaid with a grid in Figure 1. Figure 11 shows that during the low-concentration summer months, fine particle carbon concentrations attributable to heavy-duty diesel trucks peaked over the high-traffic areas of central Los Angeles, with the incremental total carbon concentration attributable to such trucks equal to about $1 \mu\text{g}/\text{m}^3$. (The total aerosol mass concentration attributable to on-highway diesel trucks can be computed by multiplying the fine particle total carbon concentration data by 1.28.) During winter, as shown in Figure 12, peak concentrations attributable to diesel trucks occur closer to the coastline, near Lennox, California, with peak fine particle total carbon concentrations from on-highway trucks alone in 1982 calculated to be about $5 \mu\text{g}/\text{m}^3$ (again, multiply diesel fine particle total carbon concentrations by 1.28 to compute the total particle mass concentration attributable to diesel trucks). A summary of diesel engine exhaust particulate matter concentrations predicted by the model at air monitoring sites in the Los Angeles area is given in Table 2.

The methods of measuring and modeling air quality developed in the course of the present case study are

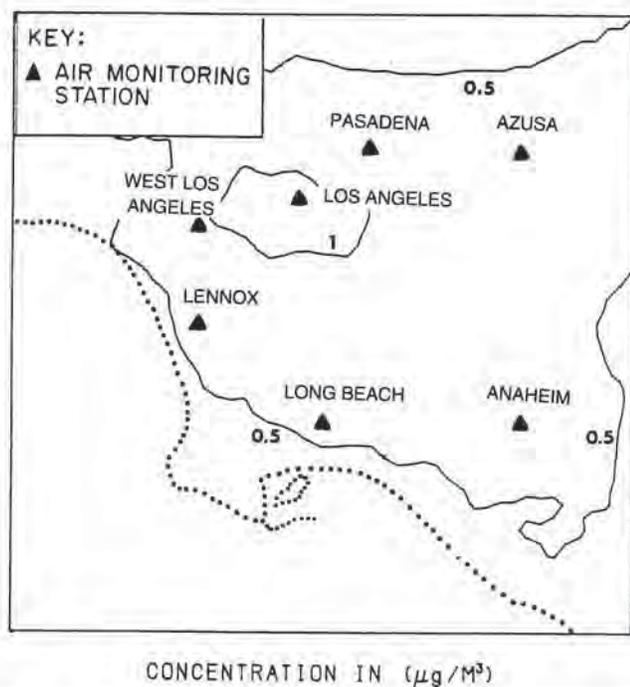


Figure 11. Primary fine particle total carbon air quality increment (in $\mu\text{g}/\text{m}^3$) attributable to heavy-duty diesel trucks, June 1982.

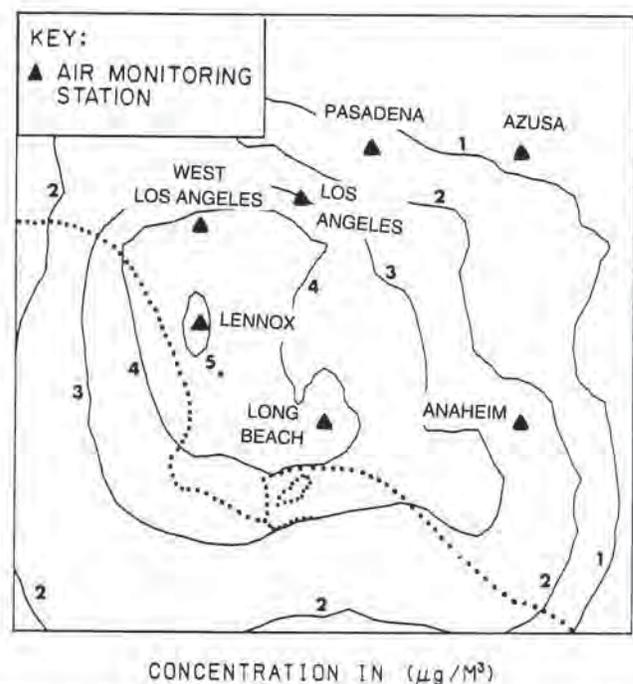


Figure 12. Primary fine particle total carbon air quality increment (in $\mu\text{g}/\text{m}^3$) attributable to heavy-duty diesel trucks, December 1982.

Table 2. Annual Mean Total Particulate Matter Concentrations Attributable to Diesel Engine Exhaust ($\mu\text{g}/\text{m}^3$), Calculated at South Coast Air Basin Air Quality Monitoring Sites in 1982^a

Monitoring Site	Diesel Autos	Light-Duty Trucks	Heavy-Duty Trucks	Diesel Ships	Diesel Railroads	Off-Road Diesels	Industrial Diesels	Total
Azusa	0.19	0.03	1.19	0.01	0.24	0.21	0.004	1.87
Long Beach	0.46	0.06	2.97	0.06	0.80	0.21	0.01	4.57
Lennox	0.49	0.07	3.24	0.01	0.59	0.26	0.01	4.67
Pasadena	0.27	0.04	1.66	0.01	0.30	0.25	0.01	2.54
West Los Angeles	0.49	0.07	3.26	0.01	0.19	0.27	0.01	4.30
Downtown Los Angeles	0.47	0.06	3.00	0.01	1.72	0.31	0.01	5.58
Anaheim	0.36	0.05	2.33	0.03	0.40	0.32	0.01	3.50

^a Computed from the results of the air quality modeling study by Gray (1986).

general in nature and can be applied to other cities. Direct application of these methods to other cities, however, is slowed by the fact that historically most governmental air monitoring networks have not routinely measured elemental carbon concentrations. The contribution of diesel engine emissions to airborne particle levels in cities other than Los Angeles might be roughly estimated by careful scaling based on ambient carbon monoxide (CO) levels. Both CO and diesel exhaust particulate matter undergo slow atmospheric removal processes and are derived from internal combustion engines. Cities with temperature and elevation conditions (which affect CO emissions) comparable to those of Los Angeles and with a relative mix of vehicles similar to that of Los Angeles also should exhibit a ratio of diesel exhaust aerosol to CO concentration that is similar to that in Los Angeles. The CO levels in such cities could be used to roughly estimate diesel exhaust particle concentrations based on the ratio of diesel particulate matter to CO concentration found in Los Angeles. Toward that end, the California Air Resources Board (1983) reported the 1982 annual average CO levels in the following cities in the Los Angeles area: Azusa (1.18 ppm), Long Beach (1.93 ppm), Lennox (3.42 ppm), Pasadena (2.25 ppm), West Los Angeles (2.80 ppm), downtown Los Angeles (2.49 ppm), and Anaheim (1.27 ppm). The corresponding estimates of diesel particulate matter concentrations for these cities are given in Table 2. Any estimates produced for years other than 1982 would have to be corrected to account for the decline in emission rates of both CO and particulate matter over time as better controlled vehicles enter the vehicle fleet.

CONCLUSIONS

The relationship between diesel engine particulate matter emissions and ambient particulate matter concentra-

tions has been examined based on a case study in the Los Angeles area. Emissions data for the Los Angeles air basin show that although diesel exhaust accounts for only 3% of particle mass emissions, its relative importance to easily respirable fine particle emissions is higher, accounting for 7% of fine particle mass emissions. Chemical analysis of diesel engine exhaust shows that it is greatly enriched in black elemental carbon particles (i.e., soot). Although diesel engines accounted for only 6% of fuel use in Los Angeles, they contributed nearly two-thirds of the elemental carbon particle emissions to the Los Angeles atmosphere during 1982. By focusing on elemental carbon particles in the Los Angeles atmosphere, a parameter closely related to diesel exhaust can be examined.

An air quality model for computing source contributions to elemental carbon particle concentrations in the Los Angeles atmosphere was developed and tested against ambient measurements of elemental carbon particle concentrations made during 1982. Modeling results showed that fine particle elemental carbon concentrations attributable to all diesel engine sources acting together averaged about $6 \mu\text{g}/\text{m}^3$ during peak winter months at Lennox, California, the most affected monitoring site, falling to lower fine particle elemental carbon concentrations in the range of 1 to $2 \mu\text{g}/\text{m}^3$ in mid-summer months. This translates into total diesel engine exhaust aerosol mass concentrations that range from about $10 \mu\text{g}/\text{m}^3$ during peak winter months at Lennox, California, again the most affected air monitoring site, to lower values in the range of 1.7 to $3.3 \mu\text{g}/\text{m}^3$ in mid-summer months. Among the Los Angeles area ambient air monitoring sites studied, the annual average total ambient particle concentrations attributable to diesel engine exhaust range from a high of $5.6 \mu\text{g}/\text{m}^3$ in downtown Los Angeles to a low of $1.9 \mu\text{g}/\text{m}^3$ at Azusa.

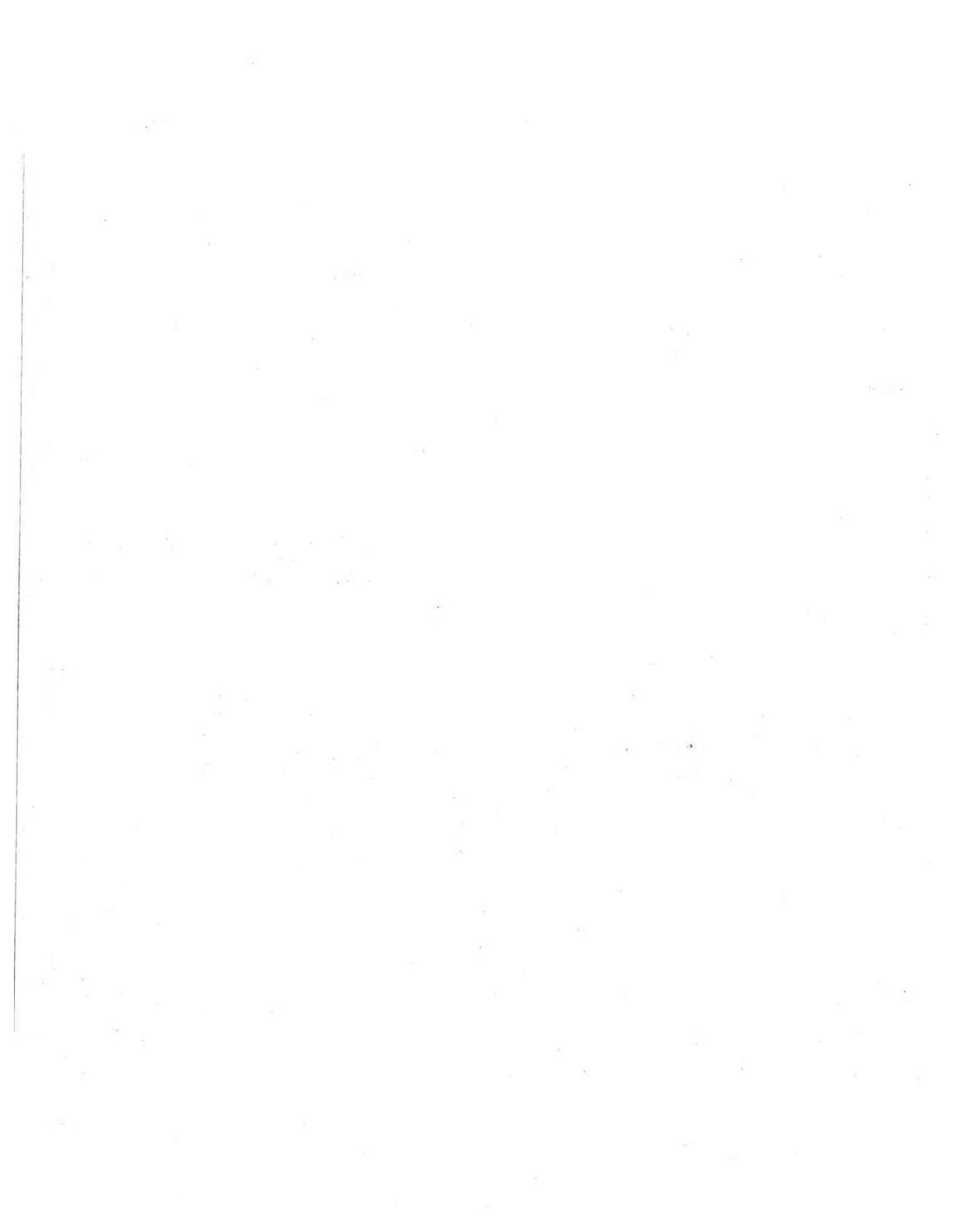
Analysis of historical trends in elemental carbon particle concentrations in the Los Angeles atmosphere suggests that outdoor ambient concentrations similar to those determined for 1982 also prevailed over most of the period from 1958 to the mid-1980s. Whereas a slight downward trend in elemental carbon particle concentrations was observed at the most urbanized sites, an upward trend was found at sites such as Azusa that experienced greatly increased urbanization over the period studied (1958 to mid-1980s). As mentioned when discussing the 1982 emission inventory, emission controls have been applied to heavy-duty diesel truck engines built in more recent years. Once the older truck fleet has been replaced by new vehicles, diesel-derived particulate matter concentrations in the atmosphere will be reduced substantially below the values shown in Table 2 of the present study.

ACKNOWLEDGMENTS

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Noncancer Effects of Diesel Emissions: Animal Studies

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INTRODUCTION

In the first part of this background paper we describe the noncancer effects that have been reported in animals exposed to diesel exhaust. We have limited our examination of animal studies to those that use inhalation as the mode of exposure to diesel exhaust. Also, because most of the animal studies have been done to evaluate the toxic effects of diesel exhaust exposure on the lungs, the emphasis is on the respiratory system. Most of the inhalation studies have used whole diesel exhaust diluted to specific particle concentrations. Exposure information is provided in either the text or the tables. With the exception of the studies conducted by the National Institute for Occupational Safety and Health (see Mentnech et al. 1984; Castranova et al. 1985; Fedan et al. 1985; Hahon et al. 1985; Lewis et al. 1986) and by Ishinishi and associates (1986), all the studies have used light-duty engines. Finally, the material presented is descriptive and is meant to summarize what has been found in animal studies. The implications of these findings are discussed elsewhere in this report (see background papers by Watts, and by Busby and Newberne, and Part I by Nauss and the Diesel Working Group).

In the second part of this paper we correlate the reported noncancer effects with different descriptors for dose. The primary focus is on studies using diesel exhaust. We do not attempt to summarize the available literature on nondiesel particles, for which there are several good sources (see Oberdörster and Ferin 1990; Mohr et al. 1994). When results from other studies using insoluble, nondiesel particles support a point in the discussion, these data are included. We also discuss some of the issues that should be considered when extrapolating a dose response observed in animals to one predicted in humans.

REVIEW OF FINDINGS

In this section we review the effects of diesel exposure on pulmonary function, nonspecific host defenses, immune responses, inflammation, proliferation of epithelial cells, metaplasia, alterations in connective tissue, and mortality. For some of the observed effects, details of the experimental protocols are provided in Tables 1 through 6. Because of the diversity in reporting and the absence of quantitative information, the effect of diesel exhaust on various outcomes is given using the referenced author's descriptions. For some studies, the terms "increased" or "no difference from controls" are used in the absence of statistical evaluation.

PULMONARY FUNCTION

Pulmonary function has been evaluated in a number of species exposed to diesel exhaust under different exposure protocols (details of experimental protocols and findings are summarized in Table 1). Most studies have been conducted in rats and hamsters, but limited information also is available from studies in cats, guinea pigs, and monkeys. In general, chronic exposures are necessary before significant effects are observed. Data from short-term studies (Pepelko 1982) or from early time points in chronic studies (Gross 1981; Mauderly et al. 1988) showed few effects on pulmonary function.

Many of the reported changes in pulmonary function suggest an increase in the stiffness of the lung parenchyma. Decreases in lung volumes (Vinegar et al. 1981; Moorman et al. 1985; Mauderly et al. 1988) and lung compliance (Heinrich et al. 1986; Mauderly et al. 1988) suggest a replacement of airspaces and elastic lung tissue by nonelastic fibrotic tissue. Alterations in pulmonary function, such as decreases in flow rates (Lewis et al. 1986) and increases in airway resistance (Heinrich et al. 1986), suggest the occurrence of obstructive disease. The nature and reversibility of this obstruction are not known. When airway resistance was measured in conjunction with acetylcholine challenge, exposure to diesel exhaust did not enhance the bronchoconstrictive response to the acetylcholine (Heinrich et al. 1986). Excised tracheal muscle from chronically exposed rats, however, was more responsive to acetylcholine than tissue from control rats (Fedan et al. 1985). Decreases in the diffusing capacity (Vinegar et al. 1981; Moorman et al. 1985; Mauderly et al. 1988) indicate inequalities in ventilation-perfusion relationships, which could be due to structural alterations in lung tissue.

Some of these findings in pulmonary function are supported by the histologic findings of fibrotic and emphysematous lesions described below. As discussed by Gross (1981) and Mauderly and coworkers (1988), however, the relationship of the changes in pulmonary function measurements to lung pathology is not always evident. Because of the patchy and focal nature of some of the histologic lesions, patterns of lung function impairment, such as restriction or obstruction, may not be apparent. In some cases, as in the study by Gross (1981), the functional findings may even be contradictory. Thus, one should be cautious in interpreting pulmonary function measurements from diesel exhaust exposure studies in the absence of other assays.

In summary, changes in pulmonary function have been reported in animals exposed chronically to diesel exhaust. Both restrictive and obstructive patterns of dysfunction

Table 1. Effects of Diesel Exhaust Exposure on Pulmonary Function^a

Parameters	Species	Exposure Conditions	Duration (months)	Particle Concentration (mg/m ³) ^b			Reference
				Effect ^c			
Decreases in lung volumes	Hamster	8 hours/day, 7 days/week	6	11.7	6.3		Vinegar et al. 1981
			6	*	*		
	Cat	8 hours/day, 7 days/week	12	11.7	6.3		Moorman et al. 1985
			27	(Year 2)	(Year 1)	NS	
	Rat	7 hours/day, 5 days/week	6	7.0	3.5	0.35	Mauderly et al. 1988
			12	NS	NS	NS	
			18	*	NA	NS	
			24	*	NA	NS	
Decreases in lung compliance	Rat	7 hours/day, 5 days/week	6	7.0	3.5	0.35	Mauderly et al. 1988
			12	NS	NS	NS	
			18	*	NA	NS	
			24	*	NA	NS	
	Rat	19 hours/day, 5 days/week	24	4.2			Heinrich et al. 1986
				*			
	Hamster	19 hours/day, 5 days/week	24	NS			Heinrich et al. 1986
Decreases in flow rates	Monkey	7 hours/day, 5 days/week	6	2.0			Lewis et al. 1986
			12	*			
			18	*			
			24	*			
Increases in resistance	Hamster	19 hours/day, 5 days/week	12	4.2			Heinrich et al. 1986
				*			
	Rat	19 hours/day, 5 days/week	12	*			Heinrich et al. 1986
			24	*			

^a Results are described relative to control animals.

^b Particle concentrations are in boldface, and resulting effect is given beneath rule in regular type.

^c * = Significantly different from value in control animals; NS = not significantly different from value in control animals; NA = data not available or significance values not given.

have been observed, and in some cases, pulmonary function findings were supported by the presence of histologic lesions.

NONSPECIFIC HOST DEFENSES

Some evidence suggests that exposure to diesel engine exhaust may compromise nonspecific host defenses. Assessment of mortality from and susceptibility to respiratory tract infection has been conducted in mice. Components of the host defense system (i.e., clearance and macrophage function) have been investigated primarily, but not exclusively, in rats.

Acute exposure (two hours and six hours) and subacute exposure (eight hours/day for 7, 15, or 16 days) of mice to diesel engine exhaust (6 to 7 mg/m³) caused an increase in mortality in response to aerosolized β -hemolytic group C *Streptococcus pyogenes* (Campbell et al. 1981); mortality in response to the A/PR8-34 influenza virus, however, was not affected by diesel exhaust exposure. Similarly, Hahon and associates (1985) found no effects on mortality and various parameters of viral infection after one month of exposure to diesel exhaust (2 mg/m³). After three and six months of exposure, however, lung consolidation and virus growth levels were greater in diesel-exposed animals; also, interferon and hemagglutinin-antibody levels were depressed. Earlier work by Hahon and colleagues (1982) had noted a depression of viral-induced interferon production when assayed in vitro.

Chan and coworkers (1981) observed normal mucociliary transport rates in rats acutely exposed (for less than one hour) to diesel exhaust (6 mg/m³). Battigelli and coworkers (1966) noted a transient depression in mucociliary clearance of excised rat tracheas after single or multiple exposures to high concentrations of diesel exhaust (8 or 17 mg/m³). Depression of mucociliary clearance was evident, which was reversible after exposed animals were allowed to recover in room air. After subjecting animals to chronic diesel exposure, Ishinishi and coworkers (1986) (rats, 1 or 2 mg/m³ light-duty engine exhaust, 2 or 4 mg/m³ heavy-duty engine exhaust for 16 hours/day, six days/week, for up to 30 months) and Heinrich and associates (1989) (hamsters, 3.7 mg/m³ for 19 hours/day, five days/week, for up to 18 months) reported damage to ciliated cells in the trachea and large airways of the animals. The effect of chronic exposure on mucociliary clearance rates is not known. Subchronic exposures, however, produced temporary changes in clearance rates in rats during the first few weeks of exposure; clearance rates returned to normal by 18 weeks of exposure (Wolff et al. 1981).

Alveolar clearance has been evaluated by several investigators (details of experimental protocols and findings are summarized in Table 2). In most studies diesel exhaust exposure decreased the alveolar clearance of indicator particles (Griffis et al. 1983; Chan et al. 1984; Heinrich et al. 1986; Mauderly et al. 1987, 1989, 1994; Wolff et al. 1987; Creutzenberg et al. 1990). In contrast, Lewis and coworkers (1986) found no impairment or a small acceleration in clearance of the indicator particle. The basis for this single observation of accelerated clearance is not known.

Studies on macrophage function produced findings that are probably related to differences in exposure levels and duration as well as methodologic differences in assay techniques and reporting (see discussion by Castranova et al. 1985). Viability and phagocytosis have been used to evaluate macrophage function. At low particle concentrations, macrophage viability was not impaired (Chen et al. 1980; Strom 1984; Castranova et al. 1985); at higher levels (3 to 6 mg/m³), a decrease in alveolar macrophage membrane integrity, an indicator of viability, was observed (Mauderly et al. 1982). Opinions differ on whether macrophages become more activated with prolonged diesel exhaust exposure. Chen and associates (1980) and Castranova and coworkers (1985) concluded from their data that macrophage phagocytic activity was depressed with exposure. Whereas these studies used indirect indicators of macrophage activity (cell appearance and chemiluminescence), Strom (1984) measured in vitro phagocytosis by lavaged cells. He found an increase in uptake of suspended particles with cells, including macrophages and polymorphonuclear leukocytes (PMNs)*, from animals exposed to diesel exhaust (1.5 mg/m³, 20 hours/day, 5.5 days/week, for 11 months). The impact on the relative uptake of particles by PMNs in overall phagocytosis, however, was not determined.

In summary, the depression of alveolar-macrophage-mediated clearance is the most consistent effect of diesel exhaust exposure on nonspecific host defenses. The effect of diesel exhaust on particular alveolar macrophage functions is less clear. Mucociliary transport rates appeared little affected; however, the functional impact of damaged ciliated cells in chronic-exposure studies is not known. Finally, although some evidence suggests that diesel exhaust has an effect on respiratory infection, its impact is insufficiently characterized to draw definitive conclusions.

IMMUNE RESPONSES

Studies evaluating immune competence in animals after exposure to diesel exhaust are limited. Increased numbers

* A list of abbreviations appears at the end of this paper.

Table 2. Effects of Diesel Exhaust Exposure on Long-Term Alveolar Clearance^a

Species	Exposure Conditions	Duration (months)	Particle Concentration (mg/m ³) ^b			Reference
			Effect ^c			
Rat	19 hours/day, 5 days/week	3	7.5	2.5	0.8	Creutzenberg et al. 1990
		12	↓	↓	↓	
		18	↓	↓	↓	
Rat	7 hours/day, 5 days/week	24	7.0	3.5	0.35	Wolff et al. 1987
			↓	↓	NS	
Rat	16 hours/day, 5 days/week	3	6.5	2.5		Mauderly et al. 1994
		18	↓	↓		
Rat	20 hours/day, 7 days/week	0.23 – 3.7	6.0	0.25		Chan et al. 1984
			↓	NS		
Rat	19 hours/day, 5 days/week	3	4.2			Heinrich et al. 1986
		8	↓			
		12	↓			
		19	↓			
Hamster	19 hours/day, 5 days/week	12	NS			Heinrich et al. 1986
Rat	7 hours/day, 5 days/week	4.5	4.1	0.94	0.15	Griffis et al. 1983
			↓	NS	NS	
Rat	7 hours/day, 5 days/week	6	3.5			Mauderly et al. 1987
			↓			
Rat	7 hours/day, 5 days/week	24	3.5			Mauderly et al. 1989
			↓			
Rat	7 hours/day, 5 days/week, heavy-duty engine	2	2.0			Lewis et al. 1986
			↑			

^a Results are described relative to control animals.

^b Particle concentrations are in boldface, and resulting effect is given beneath rule in regular type.

^c ↓ = decreased; NS = not significantly different from value in control animals; ↑ = increased.