PAPER

Mass, surface area and number metrics in diesel occupational exposure assessment

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Received 16th March 2005, Accepted 4th May 2005
First published as an Advance Article on the web 9th June 2005

While diesel aerosol exposure assessment has traditionally been based on the mass concentration metric, recent studies have suggested that particle number and surface area concentrations may be more health-relevant. In this study, we evaluated the exposures of three occupational groups—bus drivers, parking garage attendants, and bus mechanics—using the mass concentration of elemental carbon (EC) as well as surface area and number concentrations. These occupational groups are exposed to mixtures of diesel and gasoline exhaust on a regular basis in various ratios. The three groups had significantly different exposures to workshift TWA EC with the highest levels observed in the bus garage mechanics and the lowest levels in the parking ramp booth attendants. In terms of surface area, parking ramp attendants had significantly greater exposures than bus garage mechanics, who in turn had significantly greater exposures than bus drivers. In terms of number concentrations, the exposures of garage mechanics exceeded those of ramp booth attendants by a factor of 5–6. Depending on the exposure metric chosen, the three occupational groups had quite different exposure rankings. This illustrates the importance of the choice of exposure metric in epidemiological studies. If these three occupational groups were part of an epidemiological study, depending on the metric used, they may or may not be part of the same similarly exposed group (SEG). The exposure rankings (*e.g.*, low, medium, or high) of the three groups also changes with the metric used. If the incorrect metric is used, significant misclassification errors may occur.

1. Introduction

A number of studies worldwide have found an elevated risk of lung and ovarian cancer associated with occupational exposures to diesel engine emissions[1–5] in a variety of cohorts such as truck drivers, equipment operators, railroad workers, and bus workers. An important information gap that limits the use of these epidemiological data for quantitative risk assessment is the absence of quantitative exposure data (HEI[1]) from which to estimate the dose–response relationship. All of these studies have qualitatively estimated exposure from job titles, duration of employment and by other means. Mauderly[6] in his review of the epidemiological evidence for adverse health effects from diesel exposures underscores this point: "*The greatest single problem in these studies is the inaccuracy of the exposure assessment*...".

Animal studies indicate that the particulate matter component of diesel exhaust is responsible for lung tumor development, and further that the mutagenic compounds adsorbed on the particles are not as important as the carbonaceous core (HEI[1]). However, it is not clear which fraction of the particulate matter is responsible for the health effects. Nearly all of the mass emitted by engines is in the fine particle range and nearly all the number is in the nanoparticle range.[7] Several studies have suggested that at similar mass concentrations, nanometer size particles are more harmful than micron size particles.[8–24] One possible explanation for this might be that since the number of particles and particle surface area per unit mass increases with decreasing particle size and pulmonary deposition increases with decreasing particle size, dose by particle number or surface area will increase as size decreases. Lison *et al.*[17] and Tran *et al.*[21] have demonstrated a close association between aerosol surface area and inflammatory response when using a range of chemically inert materials with low solubility. Oxidative stress has been highlighted in a number of studies as being a significant mechanism underlying an indicated increase in toxicity within ultrafine and high specific surface area particles.[11,13,25]

Schwartz and Marcus[26] have shown a non-linear relationship between mortality and aerosol mass concentration at high concentrations, suggesting that mass may not be the most appropriate metric in all cases. Maynard and Maynard[27] have demonstrated that the Schwartz and Marcus data indicate a linear relationship between mortality rate and aerosol surface area, within the bounds of limiting assumptions. A recent study has demonstrated an association between aerosol surface area and decreased lung function among school children aged 7–10.[28] Particle size may also play a key role in particle behavior within the respiratory system, particularly in determining the likelihood of particles crossing cellular membranes. A number of studies have indicated that particles a few tens of nanometers in diameter may be capable of translocating from the lungs to the bloodstream,[29,30] or entering epithelial cells.[31,32]

Diesel particulate matter (DPM) is small in size and is composed of organic and elemental carbon, adsorbed and condensed hydrocarbons, and sulfate. In general, non-extractable elemental carbon accounts for a greater fraction of DPM mass than extractable organic compounds.[33] By number count, most diesel aerosol is found in the nuclei mode. The nuclei mode typically consists of particles in the 0.005 to 0.05 μm diameter range. This mode consists of volatile organic and sulfur compounds that form during exhaust dilution and cooling, along with solid carbon and metal compounds from the combustion process. The nuclei mode typically contains

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DOI: 10.1039/b503854e

1–20% of the particle mass and more than 90% of the particle number. However, most of the aerosol mass lies in the accumulation mode with particle size ranging from 50 nm to 1000 nm and a mass median diameter (MMD) lying between 100–200 nm.[7] This is where the carbonaceous agglomerates and associated adsorbed materials reside. The coarse mode contains 5–20% of the particle mass. It consists of accumulation mode particles that have been deposited on cylinder and exhaust system surfaces and later reentrained.

Roadway aerosol is described as either "fresh" or "aged". As an exhaust plume dilutes and cools, numerous events take place including nucleation, condensation, evaporation and coagulation. These processes occur rapidly, typically within 0.25 s while the plume is in the critical dilution regime of 5–50 : 1. Particle growth also occurs and mass shifts from the nuclei mode to the accumulation mode. In addition, the environment in which the aerosol is generated impacts the combustion aerosol both chemically and physically. As the aerosol continues to age, it is transformed by chemical and physical processes.[7]

EPA regulations limiting diesel exhaust emissions and air quality standards for particulate matter are all based upon mass measurements. DPM refers to the solid elemental carbon particles plus the adsorbed organic and inorganic chemicals. As discussed by McCawley,[34] reliance on measurements of total mass of DPM as the sole indicator of exposure may not accurately estimate the actual deposited dose of DPM in lung tissue, because the MMD of diesel aerosol is near the point of minimum deposition for the alveolar portion of the lung.[35] On a number basis, nanoparticle deposition efficiency is much greater than accumulation mode deposition efficiency, although on a mass basis it is less.

The specific surface area of diesel exhaust particles is typically in the range of 100 m^2 g^{-1}.[7] This corresponds to the specific surface area of a 0.03 μm carbon sphere. This suggests that nearly all of the surface area of the individual nuclei that comprise the agglomerates is available for adsorption of various atmospheric components that may undergo further reactions. Oberdörster[20] showed that for titanium dioxide particles surface area gives better correlation to respiratory response than either mass or number.

In view of the above, it is clear that future diesel epidemiological studies need to be based on exposure assessment methods with health-relevant exposure metrics. Since the most appropriate metric is still unclear at this point, the objective of this study was to provide a more careful evaluation of diesel exposure using different exposure metrics. We characterized the exposures of three groups of workers using exposure metrics based on aerosol mass, surface area, and number concentration. Personal samples were collected on bus drivers, parking garage attendants, and mechanics to obtain distributions of exposures for these exposed groups. Area samples were collected in buses, parking garages, and garage maintenance and repair facilities. Sampling focused on the Twin Cities and University of Minnesota transportation systems. These sampling locations represent environments where both diesel and gasoline powered vehicles operate on a regular basis in various ratios. Aerosol instruments capable of determining the number, volume, surface area and mass size distributions in near-real-time were combined with time-weighted average, personal exposure measurements of elemental carbon (EC) to assess exposure. It was thus possible to determine the aerosol footprints of the different locations using aerosol sampling methods that enabled the measurement of various aerosol characteristics in near real-time as well as determination of full-shift exposure. The relationship between different exposure metrics (based on mass, surface area, number) was studied and it was possible to identify differences in the exposures of the three occupational groups, as measured by these exposure metrics.

2. Methods

A. Instrumentation

The instrument suite used in this project enabled aerosol from <10 nm to 10 μm to be characterized and was uniquely capable of characterizing exposure.

i. Mass concentration (elemental carbon sampling). Elemental carbon (EC) accounts for a significant fraction of DPM emissions, and is readily detectable by thermal-optical analysis.[36] This analytical method is described in the NIOSH Manual of Analytical Methods.[37,38] The personal sampling train for EC samples consisted of a 10 mm MSA cyclone, 37 mm pre-fired ultra pure, quartz fiber, Pallflex filter held in a 3-piece 37 mm cassette, and a MSA ELF pump. Pumps were calibrated with a Gilibrator primary flow device (electronic bubble meter) and operated at 3.0 LPM so that the collected mass of EC was greater than the limit of detection for the method. At this flow rate, the cyclone had a 50% cut-point of 2.85 μm. The minimum sampling time was six hours. Diesel and spark-ignition aerosols are nearly all less than 1.0 μm in diameter, and thus the cyclone collected virtually the entire aerosol mass.

Quartz fiber filters are known to adsorb organic vapors during the sampling process. A correction factor was estimated for this adsorption by using dynamic blanks. A Teflon filter (Zefluor) was placed on top of the Pallflex filter in the three piece cassette and samples were collected as discussed above. The Teflon filter adsorbs little organic vapor but effectively removes particulate matter. The organic vapor passes through and adsorbs on the Pallflex filter, which is analyzed by the NIOSH 5040 method for EC. It is believed that the Pallflex filter reaches equilibrium with the adsorbed organic material thus allowing for a correction factor to be estimated. In addition to dynamic blanks, a limited number of field blanks were submitted for analysis.

ii. Surface area concentration (Diffusion Charger—DC). The diffusion charger measures the total active surface area of particulate matter. Positively charged ions are produced by a glow discharge, forming in the neighborhood of a very thin wire. These ions attach themselves to the sampled aerosol stream with a certain probability. The charged aerosol particles are then collected on a filter. The electric current flowing from the filter to ground potential is measured and is proportional to the number of ions attached to the particles. For particles in the free molecular range, the attachment is proportional to the surface area of the particles, but is independent of the composition of the particles.[39] Siegmann *et al.*[40] contend that the DC measures the so-called "active surface" in the size range from slightly above ten to a few hundred nm. The active surface is the effective surface area available for mass transfer in a kinetically limited situation and should be appropriate for describing the gas to particle mass transfer taking place in a diluting exhaust plume. However, for particles $\sim$1 μm, the instrument response scales as particle diameter, and thus the relationship with surface area is lost.[41]

A portable DC (EcoChem Analytics LQ1-DC) was used in this project. It was set to average data over a 10 s period, covering a range from 0 to 4000 fA with a resolution of 1 fA and a flow rate of 1.0 L min^{-1}.

iii. Surface area concentration (Photoelectric Aerosol Sensor—PAS). The PAS responds to photoemitting substances on the surface of aerosol particles. Ultraviolet irradiation of the sampled aerosol leads to the emission of photoelectrons from surface material that readily undergoes photoemission.[42] The remaining positively charged aerosol particles are sepa-

rated from the electrons and collected on a filter connected to an electrometer. The measured current is a function of the UV irradiation wavelength and intensity, the total available surface area and the photoemission properties of the surface materials. Commercially available instruments usually use a wavelength of 222 nm. Diesel accumulation mode particles strongly respond to the PAS.[43]

The PAS was originally promoted as a monitor for surface-bound polycyclic aromatic hydrocarbons (PAHs).[44,45] Surface bound PAHs have a high photoelectric (PE) yield, causing a high PAS response. DPM found in the accumulation mode consists primarily of EC, and has a significantly lower PE yield, which results in a more moderate PAS response.[46,47] For diesel accumulation mode particles, the PAS signal correlates with the accumulation mode surface area concentration. In mixed urban aerosols, on the other hand, where the PAH surface concentration (for example from spark ignition engines) may be much higher, the high PE yield of the PAH dominates the PAS response. Therefore, PAS signals can only be quantitatively interpreted in a certain context. Nevertheless, PAS signal observations are useful for monitoring of relative changes using the measured electrometer response (usually fA units). These values are corrected for lamp fluctuations, which enables good instrument-to-instrument comparability in commercially available instruments.

A portable PAS (EcoChem Analytics PAS 2000 CE) was used in this project. It was set to average data over a 10 s period, covering a range from 0 to 4000 fA with a resolution of 1 fA (estimated accuracy of ±2 fA). The PAS limit of detection is about 10 fA, and it has a flow rate of 1.0 L min^{-1}.

iv. Number concentration (Ultrafine Condensation Particle Counter—UCPC). The UCPC (Model 3025A, TSI Inc.) was used to obtain total particle number concentration. The UCPC counts particles in the range of 3–1000 nm, and operates by saturating the carrier air stream with a butyl alcohol vapor. The air stream is cooled which produces a supersaturation and causes vapor to condense onto the particles. The particles then rapidly grow to an optically detectable size (10–12 μm).

v. Size distribution (Scanning Mobility Particle Sizer—SMPS). The SMPS consists of a TSI 3071A Electrostatic Classifier and a TSI 3025A Ultrafine Condensation Particle Counter (UCPC). It was used to classify particles by an electrical mobility equivalent diameter. The SMPS was configured to cover the range of 8 to 300 nm in the high flow mode (10 L min^{-1} sheath air flow and 1.0 L min^{-1} aerosol flow). Data were collected using 60 s up scan and 30 s down scan times. Data were analyzed using version 3.2 of the TSI SMPS software. SMPS data presented here include the integrated total number concentration, surface area concentration, and geometric mean diameter. The SMPS active surface is calculated using expressions given by Pandis *et al.*,[48] Kasper *et al.*,[49] and Kasper *et al.*[50] assuming spherical particles and that the species charging the particles is a hydrated proton which has a mean free path of 14.5 nm.[51] This calculation should simulate the response of the DC although it does not include size dependent losses in either instrument.

B. Sampling strategy

i. Sampling locations and occupational categories. The Twin Cities Metropolitan and the University of Minnesota transit systems together offer an environment in which both diesel and gasoline powered vehicles operate on a regular basis in various mixtures from almost all gasoline vehicles to nearly all diesel-fueled buses. This provided a unique opportunity to measure the different exposure scenarios.

Area and personal samples were collected depending upon the specific location and situation. Personal samples were collected in or near the breathing zone of the worker over a full work-shift. The PAS, DC, SMPS and UCPC were used to collect area samples as near to the breathing zone of the worker as possible. These data were collected in near real-time and downloaded to a computer.

Three occupational categories were selected for monitoring: bus drivers (personal samples), parking garage attendants (personal and area samples), and bus mechanics (personal and area samples). These were selected because they provided a mix of exposure scenarios based on the mix of gasoline and diesel exhaust in each scenario as well as the age of the aerosol, and they are representative of workers employed in the transportation industry. Table 1 summarizes the number of different types of measurements and their sampling durations for the three occupational categories. Table 1 shows the number of workshifts. For each workshift, there will be a large number of measurements gathered depending on the sampling frequency of the real-time instruments, and a single workshift average is then calculated (shown in Table 2). For example, for DC, Table 1 shows that 6 workshift average measurements were obtained in bus drivers (3 + 2 + 1). In Table 2, we see the summary statistics for the workshift whose average sampling time is given. We also see that these 6 workshifts correspond to 5595 10-second average measurements.

ii. Bus drivers. It was not always possible to obtain personal exposure measurements during this study because of objections raised by either management or union personnel. This was the case with the bus driver sampling. Two members of the project team acted as surrogates for the bus drivers and rode the Metropolitan Transit buses for 6–8 h wearing personal samplers. It was assumed that their exposures would be similar to those of the bus drivers as they sat as close to the bus

Table 1 Summary data for number of workshifts monitored and sampling time periods using different instruments for each of the three occupational groups

	Bus route				Parking ramp		Bus garage	
	Route 16	Route 27	Route 75	Route 80	4th Street	Wash. Ave.	Camden	Cedar avenue
Average sampling duration ± standard deviation/min	327 ± 83	350 ± 62	412 ± 31	408 ± 55	650 ± 39	528 ± 106	434 ± 39	577 ± 95
EC[a]	9	8	11	11	11	23	19	15
PAS[b]	4	3	1	0	10	8	7	6
DC[b]	3	2	1	0	11	8	8	5
SMPS	0	0	0	0	0	10	7	6
UCPC[b]	0	0	0	0	0	10	5	5

[a] Each EC (elemental carbon) measurement is an average concentration measured for the entire work shift obtained using a quartz filter analyzed by NIOSH method 5040. [b] The PAS (photoelectric aerosol sensor) and the DC (diffusion charger) provided running 10-second averages and the UCPC (ultrafine condensation particle counter) provided 60-second averages over the entire work shift.

Table 2 Summary statistics for the different exposure metrics for the three occupational groups

	N	Sampling time (±SD)/ min	Mean (±SE)	S.D.	G.M.	G.S.D.	Range (5th–95th percentile)	*F*-value	*p*-value
Work shift average EC mass concentration/μg m^{-3}									
Bus drivers	39	378 ± 68	1.98 ± 0.21	1.33	1.43	3.28	BDL - 5.6		
Ramp attendants	34	577 ± 105	1.10 ± 0.11	0.63	1.06	1.75	BDL - 2.3	15	<0.001
Garage mechanics	35	496 ± 163	3.87 ± 0.60	3.52	3.20	1.71	BDL - 17.7		
Work shift average surface area concentration—Diffusion Charger/μm^2 cm^{-3}									
Bus drivers	6	281 ± 96	59 ± 12	28	46	2.62	6.7–88		
Ramp attendants	19	648 ± 235	156 ± 48	210	93	2.56	27–901	1.81	0.18
Garage mechanics	13	477 ± 180	90 ± 9	32	85	1.44	38–145		
10-second average surface area concentration—Diffusion Charger/μm^2 cm^{-3}									
Bus drivers	5595	281 ± 96	65 ± 0.6	46	48	2.55	5–144		
Ramp attendants	13,212	648 ± 235	148 ± 2.8	326	55	3.09	17–878	1063	<0.001
Garage mechanics	36,769	477 ± 180	91 ± 0.4	78	74	1.88	26–209		
Work shift average surface area concentration—Photoelectric Aerosol Sensor/ng PAH m^{-3}									
Bus drivers	8	277 ± 82	37 ± 10	28	29	2.03	9–58		
Ramp attendants	18	598 ± 271	12 ± 2.2	9.5	8.7	2.40	2.3–39	90	<0.001
Garage mechanics	13	503 ± 180	21 ± 2.2	7.9	19.4	1.66	5–28		
10-second average surface area concentration—Photoelectric Aerosol Sensor/ng PAH m^{-3}									
Bus drivers	5595	281 ± 96	25 ± 0.5	36	14	2.75	3–84		
Ramp attendants	13,212	648 ± 235	98 ± 2.7	304	13	5.11	2–752	57	>0.001
Garage mechanics	36,769	477 ± 180	22 ± 0.1	23	15	2.60	2–62		
Work shift average number concentration/particles cm^{-3}									
Ramp attendants	8	749 ± 293	3.06 ± 0.9 ($\times 10^4$)	2.54 ($\times 10^4$)	2.21 ($\times 10^4$)	2.37	0.8 – 8.0 ($\times 10^4$)	3.5	0.076
Garage mechanics	12	462 ± 239	6.59 ± 1.38 ($\times 10^4$)	4.76 ($\times 10^4$)	4.83 ($\times 10^4$)	2.55	0.5–1.46 ($\times 10^4$)		
1-minute average number concentration/particles cm^{-3}									
Ramp attendants	3535	749 ± 293	1.35 ± 0.02 ($\times 10^4$)	1.3 ($\times 10^4$)	0.97 ($\times 10^4$)	2.25	0.24–3.2 ($\times 10^4$)	12,138	>0.001
Garage mechanics	206,497	462 ± 239	7.6 ± 0.02 ($\times 10^4$)	7.7 ($\times 10^4$)	4.76 ($\times 10^4$)	2.86	0.7–21.7 ($\times 10^4$)		

driver as possible. The surrogates got off the bus at the end of each route and waited for the next bus to take them back to their point of origin. The same bus typically would not run the same route all day long. In fact, each bus route would have several bus drivers in different buses throughout the day. The amount of time spent on the buses was recorded daily. Table 1 shows the average sampling time duration and standard deviation for each bus route. Four bus routes (16, 27, 75 and 80) were selected, prior to sampling, based on their traffic patterns.

The personal air monitoring of the bus routes comprised 39 air samples for EC divided, roughly equally, among four different bus routes in the Minneapolis-St. Paul metropolitan area (shown in Table 1). Route 16 traveled between downtown Minneapolis to downtown St. Paul where the bulk of the traffic was a mixture of spark ignition commuter automobiles with some diesel truck traffic. Route 27 traveled between downtown Minneapolis to suburban Anoka approximately 20 miles away. Traffic comprised spark ignition autos and diesel trucks that followed this route to various industrial sites. Route 75 was also a suburban corridor to downtown Minneapolis but with somewhat lighter diesel truck traffic. Route 80 went from downtown Minneapolis to the Mall of America, Bloomington, MN and comprised mostly of freeway traffic along an interstate highway. The Mall has a semi-enclosed bus terminal with constant bus traffic. Much of this traffic consisted of buses that were idling while unloading, loading, and waiting for passengers.

A total of 39 personal EC samples were collected on the four routes as shown in Table 1. Only a single set of portable, battery powered, PAS and DC instruments was available for this study. When used on the buses, the instruments were placed in the laps of the surrogate bus drivers with a common sampling tube extending into the breathing zone next to the EC sampler. The instruments stored a running 10 s average of the surface area or PAH concentration in memory. Data were downloaded daily to a computer. The PAS was used on eight bus sampling days and the DC was used on six bus sampling days. On these days, project personnel maintained a log of heavy and light-duty traffic encountered on the bus routes. Traffic counts were recorded every minute.

iv. Parking ramp attendants. Parking ramp attendants at two ramps (the 4th Street ramp and the Washington Avenue ramp on the University of Minnesota campus) were monitored. They were exposed to a mixed aerosol, although the bulk of the parking ramp traffic was automobiles. The attendants were housed in booths with positive pressure ventilation and windows, but the intake vents for both ramps were located near potential sources of vehicle exhaust aerosol so workers may have been exposed to vehicular aerosol generated from sources that were not in the immediate vicinity of the parking ramp booth. The Washington Avenue ramp is one of the busiest campus parking facilities with constant in and out traffic. The 4th street ramp has periods with heavy commuter traffic in the morning and afternoon.

The EC samplers were placed near the breathing zone of the parking ramp attendants and close to the open window. There were several parking ramp attendants that worked in the booth throughout the day, to ensure that sufficient mass was collected for the chemical analysis of EC, it was decided to keep the cyclone near the breathing zone for several attendants rather than limit the sampling to one specific individual during a day. Typically, sampling began in the morning and ended in the late

evening (average sampling times and standard deviations are shown in Table 1). In addition to EC samples, we also used the portable PAS and DC instruments as shown in Table 1. At the Washington Avenue ramp the SMPS and UCPC were also used. Twelve of the 23 EC samples were taken concurrently with the real-time measurements.

v. Bus garage mechanics. The garage phase of this study was selected to provide an environment thought to be dominated by diesel aerosol. Although exposure was primarily from diesel aerosol, cigarette smoke and other submicron aerosol such as welding fume may also have been present. The selected locations were the Camden garage in Minneapolis and the Cedar Avenue garage in Richfield, MN. The primary activity at both garages was diesel engine maintenance.

Instrumentation included EC samplers, the UCPC, and the portable PAS and DC samplers as shown in Table 1. Nineteen EC samples were taken at the Camden garage at three different locations. Seven samples were collected simultaneously with the real-time instruments located in the main garage area where most of the engines were maintained. The other nine were split between a maintenance bay that was separated from the main garage area and used by maintenance workers and a loft location that was one story above the instruments and used by clerical workers. The Cedar Avenue garage was relatively new, and the same instrumentation was used. Fifteen EC samples were obtained at the garage, and six of these samples were collected simultaneously with the real-time instruments.

4. Results and discussion

This section is divided into three parts, each part describing the exposure assessment results based on a different exposure metric-mass concentration, surface area concentration, and number concentration. Table 2 presents summary statistics for the three exposure groups using the different exposure metrics. We used Analysis of Variance (ANOVA) for statistical comparisons using the S-Plus software package (Insightful Corporation, 2002).

A. Mass concentration measurements

Fig. 1 shows box plots of EC concentrations for all three occupational categories—bus drivers, parking ramp booth attendants, and garage mechanics. The specific locations at which measurements were made, *i.e.*, four bus routes, two parking ramps, and two garages with three locations each further divide these categories. The line inside each of the boxes is the median, the ends of the boxes are the 25th and 75th percentiles, and the ends of the lines are the 10th and the 90th percentiles of the measurements. The solid circles are the 5th and the 95th percentiles. Each measurement is the average EC concentration over a work shift (typically 6–7 hours). A number of measurements in the ramps and buses were close to or below the limit of detection ($\sim$1 μg m^{-3}). The three groups had statistically significant differences in exposures to EC as shown in Table 2 ($p < 0.001$). The least squares mean exposures and corresponding standard errors were 3.87 ± 0.60 μg m^{-3} for garage mechanics, 1.98 ± 0.21 μg m^{-3} for bus drivers, and 1.10 ± 0.11 μg m^{-3} for ramp attendants. The highest levels of EC were seen in the maintenance garages that were dominated by diesel exhaust and the lowest levels were observed in the parking ramp booths that were dominated by spark ignition (gasoline) exhaust aerosol. The four bus routes had a hybrid of diesel/spark ignition exposure, and had intermediate levels of EC. The EC levels ranged (5th to 95th percentiles) from the method detection limit (MDL = 1 μg m^{-3}) to 5.6 μg m^{-3} for the four bus routes, MDL to 2.30 μg m^{-3} in the ramps, and MDL to 17.7 μg m^{-3} in the garages.

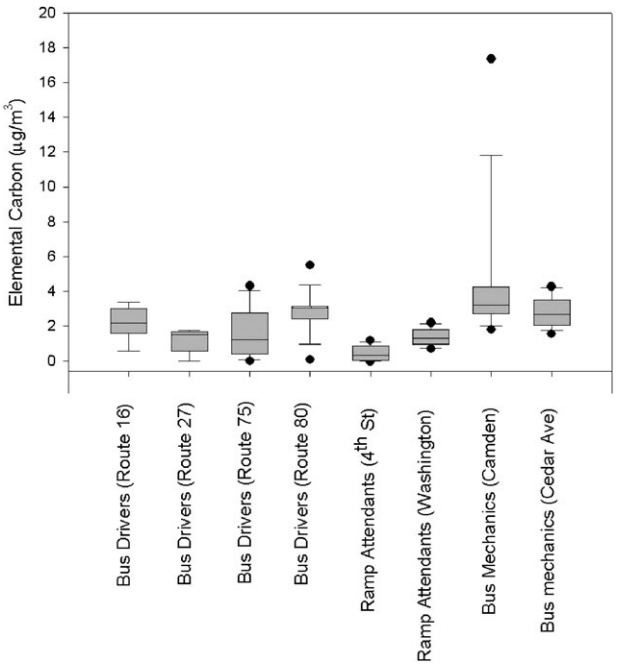

Fig. 1 Box plots of exposures to elemental carbon (EC) for the three occupational groups—bus drivers, parking ramp booth attendants, and bus garage mechanics. The groups are further divided into the different locations within each category where measurements were obtained. The line inside each of the boxes is the median, the ends of the boxes are the 25th and 75th percentiles, and the ends of the lines are the 10th and the 90th percentiles of the measurements.

Very low EC concentrations in the parking ramp booths are consistent with the facts that there was very little diesel traffic, that the booths were under positive pressure and the measurements were made inside the booth near the breathing zone of the attendants.

The Camden garage had statistically significant higher concentrations than the Cedar Avenue garage. The mean and standard errors of EC levels were 3.4 ± 0.5 μg m^{-3} for Camden, and 1.1 ± 0.5 μg m^{-3} for Cedar Avenue garage. Camden is an older garage with less ventilation. The Cedar Avenue garage is relatively new with better ventilation, which is reflected in the lower EC concentrations.

The results from the bus garages are consistent with a previous study conducted by NIOSH of trucking industry workers.[52] In that study the geometric mean EC exposure was 3.8 μg m^{-3} for highway truck drivers, 4.0 μg m^{-3} for local truck drivers, 12.1 μg m^{-3} for bus mechanics, and 27.2 μg m^{-3} for dockworkers using diesel-powered forklift trucks. In the same study, background levels measured in a residential area and near the highway ranged from 1–3 μg m^{-3}, similar to the levels we measured in the buses and parking ramps.

B. Surface area concentration measurements

As mentioned earlier, the diffusion charger (DC) measures the total surface area of the particles irrespective of their chemistry, while the photoelectric aerosol sensor (PAS) measures the surface adsorbed PAHs—a surrogate for the surface area of diesel exhaust aerosol specifically.

Fig. 2 shows a box plot comparison of the 10-second average DC measurements in buses, parking ramps, and bus garages. Table 2 shows that the arithmetic mean 10-second average surface area concentrations in parking ramps are significantly greater than those in bus garages, which in turn are significantly greater than those in buses. However, the much larger exposures in ramp attendants are due to a few large exposure occasions. This can be seen by comparing the GSDs of the exposure distributions for the three groups. The large standard

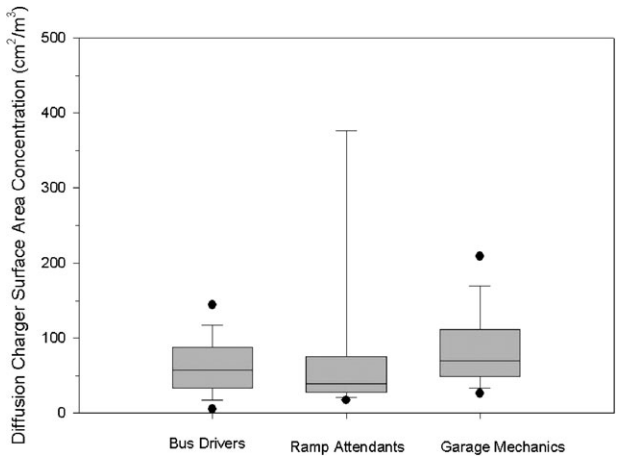

Fig. 2 Box plots of diffusion charger (DC) measurements in buses, parking ramps, and bus garages. A DC measurement was obtained every 10 seconds, and the box plots include all data from every sampling day for each worker category.

deviation for ramp attendants results from a few very high exposure conditions. Table 2 also shows that the work shift average surface area concentrations (arithmetic as well as geometric means) for the three occupational groups are not much different from the 10-second averages. However, the three groups are not significantly different for work shift average surface area concentrations. As expected, the range of values for work shift average values is narrower than for 10-second averages.

Fig. 3 shows a box plot comparison of the 10-second average PAS measurements in buses, parking ramps, and bus garages. Table 2 shows that using 10-second average PAS measurements, the ramp booths had the highest arithmetic mean exposures of 98 nanograms (ng) PAH m^{-3} compared with 25 and 22 ng PAH m^{-3} for bus drivers and garage mechanics. The three groups had statistically significant differences in PAS measurements as shown in Table 2 ($p < 0.001$). As Fig. 3 shows, the distribution for the ramp attendants is skewed so that even though the three groups have similar geometric means, the arithmetic means are very different. As in the case of the DC measurements, the much larger exposures in ramp attendants are due to a few large exposure occasions. Again, this can be seen by comparing the GSDs of the exposure distributions for the three groups. Interestingly, if work shift average PAS measurements are considered (arithmetic as well as geometric means), then the ramp attendants have the lowest exposures and bus drivers have the highest exposures. The differences are still significantly different. Thus, the sample averaging times have a significant effect on the exposure rankings.

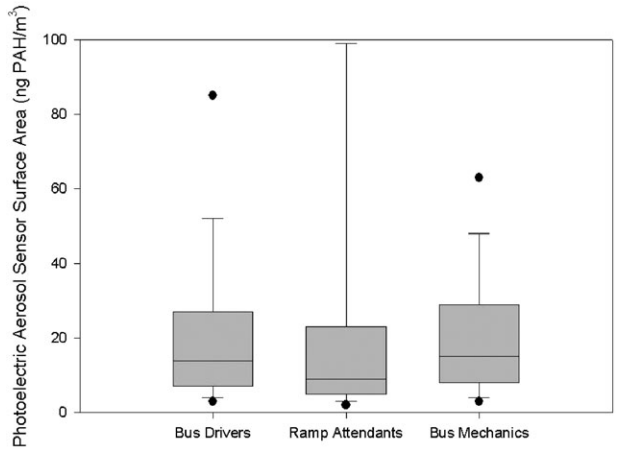

Fig. 3 Box plots of the photoelectric aerosol sensor (PAS) measurements in buses, parking ramps, and bus garages. A PAS measurement was obtained every 10 seconds, and the box plots include all data from every sampling day for each worker category.

C. Number concentration measurements

At selected sampling locations particle number concentrations were measured using the UCPC, that provided total counts, and the SMPS that provided size segregated particle counts.

An integrated number concentration is obtained from the SMPS size distribution by summing the number of particles counted in each scan channel. The UCPC data are averaged on a 1-minute time base to match the time base of the SMPS. The UCPC concentrations are consistently higher than the SMPS concentrations. The difference in total number concentrations from the SMPS and the UCPC is explained by the different measurement range of the instruments. The UCPC is designed to detect particles as small as 3 nm, while the lower sizing limit of the SMPS as configured in this study is nominally 8 nm. The difference in total and integrated number concentrations between the UCPC and the SMPS is partially due the concentration of particles ranging between 3 and 8 nm in diameter. In addition, differences in the total and integrated particle number concentrations are often attributed to diffusive particle loss inside of the SMPS column. With the SMPS configuration used here, such losses were significant for particles less than 50 nm.

Fig. 4 shows a box plot comparison of the 1-minute average aerosol number concentration (as measured by the UCPC) inside and outside the parking ramp booth and in the two garages. The concentrations inside the booth ranged between 1×10^4 to 2.5×10^4 particles cm^{-3}. As is to be expected, the number concentrations inside the booth (which is where the workers would be exposed) are much lower than outside. This is because the booth is under positive air pressure. The concentrations outside the booth are quite similar to the levels measured in the two garages, and ranged between 2.5×10^4 to 2.25×10^5 particles cm^{-3}. The levels in garages were significantly higher than the levels inside the booths. Table 2 shows that the arithmetic and geometric mean levels in garages are 5 to 6 times the levels in the booths. Thus the exposure distributions of the two corresponding cohorts (ramp booth attendants and garage mechanics) to 1-minute average particle number concentrations were significantly different ($p < 0.001$). The difference is only marginally significant for work shift averages ($p = 0.076$). No significant differences were noted between the levels in the two garages.

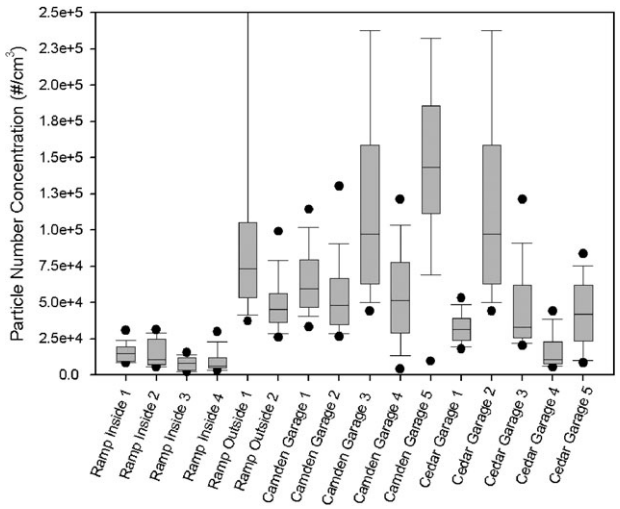

Fig. 4 Box plots of the 1-minute average aerosol number concentration measured by the UCPC inside and outside the Washington Avenue ramp booth and in the Camden and Cedar Avenue garages.

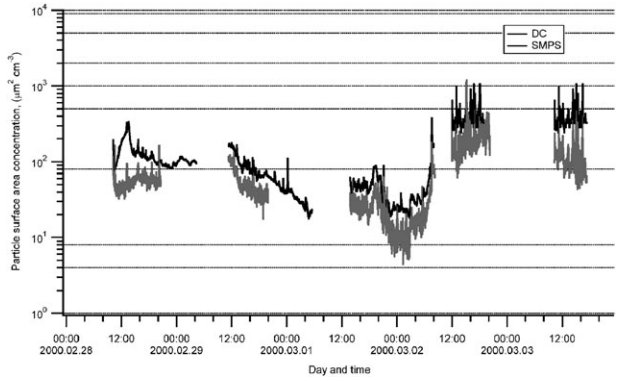

Fig. 5 Plot of the integrated SMPS surface area concentration and the corresponding 1-minute average diffusion charger (DC) reading at the parking ramp attendant booth.

Fig. 5 shows a plot of the integrated SMPS surface area concentration and the corresponding 1-minute average diffusion charger (DC) reading at the Washington ramp. The diffusion charger provides a direct measurement of surface area, while the SMPS provides the size distribution of the aerosol by particle number. The surface area of each size bin is calculated using the midpoint diameter of the bin range and the particle count in that bin. The total surface area is determined by adding up the surface areas of all bins. All days show a very close match between the measurements of the two instruments with the exception of the first half of February 28. This is most likely due to a sampling system malfunction on the first day of sampling.

Fig. 6 is a comparison between the SMPS calculated geometric mean aerosol number diameter, D_g, and data from the UCPC and DC. The D_g is determined from an SMPS particle size distribution using the following relationship:

$$D_g = \exp\left(\frac{\Sigma n_i \ln D_i}{N}\right) \quad (1)$$

where D_i and n_i is the particle diameter and number concentration of channel i respectively, and N is the total number concentration.

The total number count N and the total surface area S are used to determine the diameter of average surface, D_{as} as

$$D_{as} = \sqrt{\frac{S}{\pi N}} \quad (2)$$

where S is the total surface area ($\mu m^2\ cm^{-3}$) measured by the DC and N is the total number concentration ($\#\ cm^{-3}$) measured by the UCPC. Thus, not only do the DC and UCPC give real time concentrations, combined, they also give a meaningful representation of the particle size in real time.

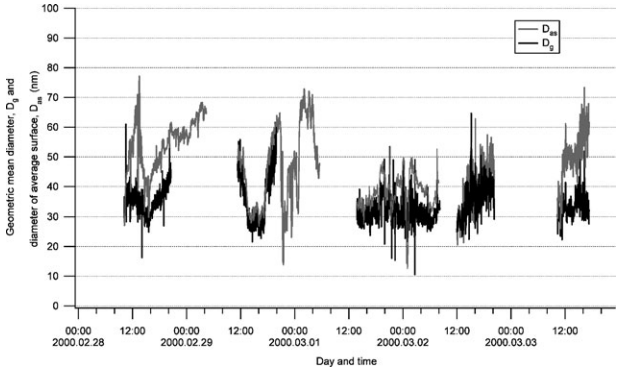

Fig. 6 Geometric mean diameter (D_g) calculated from scanning mobility particle sizer (SMPS) measurements and the diameter of average surface area (D_{as}) obtained from ultrafine condensation particle counter (UCPC) and diffusion charger (DC) measurements.

5. Conclusions

In this study, we evaluated the exposures of three occupational groups using the traditional mass concentration of elemental carbon, as well as with an array of instruments designed to measure the surface area and number concentration, in real time. The three groups had statistically significantly different exposures to work shift TWA EC with the highest levels observed in the bus garage mechanics (almost entirely diesel exhaust) and the lowest levels in the parking ramp booth attendants (dominated by spark ignition exhaust). In terms of surface area concentrations as measured by the DC, the arithmetic mean 10-second average exposures of parking ramp attendants are significantly greater than those of bus garage mechanics, which in turn are significantly greater than those of bus drivers. This is true for work shift average surface area exposures as well. In terms of the 10-second average PAS measurements, the ramp booth attendants had the highest mean exposures while the exposures for bus drivers and garage mechanics were comparable. The much larger exposures for ramp booth attendants are driven by a few large exposures. If work shift average PAS concentrations are considered instead of 10-second averages, then the ramp attendants have the lowest exposures and bus drivers have the highest exposures, emphasizing the importance of sampling time on the exposure metric. In terms of number concentrations, the exposures of garage mechanics exceeded those of ramp booth attendants by a factor of 5–6. Thus we see that depending on the exposure metric chosen, the three occupational groups have quite different exposure rankings. The exposure rankings (*e.g.*, low, medium, or high) of the three groups also change with the metric used. While at this point, it is still unclear as to which exposure metric is the most relevant to human health, it is clear that the choice of the exposure metric will affect the classification of workers into similarly or differently exposed groups in future epidemiological studies.

The measurements made by various instruments were consistent with each other, providing a useful validation of these methods. For instance, the surface area concentration obtained directly using the diffusion charger compared well with the surface area calculated using the detailed size distribution data from the SMPS. Since the DC is a much less expensive instrument than the SMPS, and is more rugged, these results suggest DC's might be more applicable in future epidemiological studies. Conversely, this could also point to the need for an inexpensive instrument for measuring aerosol size distributions in real time over the size ranges that an SMPS measures. We also found that the DC and UCPC together give both real time concentrations and a meaningful representation of the particle size in real time that are comparable to measurements made by the SMPS. A comparison of number concentrations measured using the UCPC and the SMPS showed generally higher concentrations with the UCPC. This is partially due to the difference in lower size cutoff of the two instruments, 3 and 8 nm for the UCPC and SMPS, respectively. In addition, diffusive particle losses are attributable to the observed difference.

Animal studies and previous occupational exposure studies have typically been at high exposure levels. Rodent bioassay exposures that cause lung tumors have been in the range of 1000 to 10,000 $\mu g\ m^{-3}$, while occupational exposures have ranged between 10–1000 $\mu g\ m^{-3}$.[1] Therefore, these studies are of limited use in estimating cancer risks due to ambient exposures. The three occupational groups in this study have exposures that are between 1–10 $\mu g\ m^{-3}$, *i.e.*, at the low end of occupational exposures and near the high end for ambient exposures. This demonstrates that near real-time instruments, such as the DC, UCPC and DC, are capable of accurately measuring low levels of exposure.

Acknowledgements

This project was funded by a grant from the Health Effects Institute.

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